

Deuterated water ice on the satellites of Saturn

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ABSTRACT

The deuterium to hydrogen ratio in water ice in a planetary body carries important information on the history of water processing and delivery in the protostellar nebula. For a giant planet satellite, the D/H ratio is also affected by the processes and temperatures of the circumplanetary or circumstellar environment in which the satellites formed. Here we present robust JWST spectroscopic detections of the 4.14 μm O-D stretch absorption line (analogous to the 3 μm water O-H stretch) on the mid-sized Saturnian satellites and use these detections to infer a D/H ratio on each satellite. Within the limitations of the technique, we find that all of the satellites are consistent with having a D/H ratio of about $1.5\times$ Vienna Standard Mean Ocean Water (VSMOW), which is about an order of magnitude higher than the value of the atmosphere of Saturn. A much higher previously reported D/H ratio for Phoebe is ruled out at the 10σ level, and a 3σ upper limit of $2.3 \times \text{VSMOW}$ is obtained. The elevated D/H ratios demonstrate that the solid planetesimals and pebbles that built the satellites never sublimed and re-equilibrated with the gaseous circumplanetary disk. The similarity of the D/H measurements across all satellites suggest that the D/H ratio of water ice in the vicinity of Saturn at the time of satellite formation was also approximately $1.5 \times \text{VSMOW}$.

1. INTRODUCTION

Deuterated water is a powerful tracer of the processing of interstellar ice in planetary systems, providing a window into how interstellar ices, organics, and dust are incorporated into the disks (Cleeves et al. 2014; Yang et al. 2013; Albertsson et al. 2014). In our own protoplanetary nebula, dust grains delivered from cold molecular clouds could have carried water ice with a D/H ratio enriched by orders of magnitude above the bulk solar system value of about 2.1×10^{-5} (Geiss & Gloeckler 1998). In warmer regions of the disk, sublimation of

these ices into the gas phase would cause quick equilibration of the D/H ratio with the bulk H_2 (Lécluse & Robert 1994), leading to water with solar D/H values. In the outer regions of the disk, direct incorporation of this ice into growing bodies or sublimation of the ice in regions too cold to re-equilibrate with H_2 , would preserve the elevated D/H values (Yang et al. 2013). The values of D/H across the solar system thus tell the story of transport, sublimation, and temperature in the disk.

In the inner solar system, all water ice grains would have completely sublimated, so D/H values should be expected to be solar. Nonetheless, the inner solar system is enriched by about a factor of ~ 7 compared to the solar value,

with a value of about 1.5×10^{-4} , as measured on Earth, Mars, Vesta, and C- and S- type asteroids (Hallis 2017). Such elevated values already show that some material from interstellar ices is eventually transported as solids into the terrestrial region, though the precise mechanisms are debated (Alexander 2017). In the colder outer portions of the disk, interstellar ices should be able to be more directly incorporated into icy bodies like comets, Kuiper belt objects, or icy satellites. Models for outer solar system water ice D/H ratios predict values ranging from a factor of several enriched over the terrestrial value (Yang et al. 2013; Furuya et al. 2017) to a factor of 100 over terrestrial (Albertsson et al. 2014) depending on differences in stellar outflow, ice transport and incorporation, and disk temperatures.

Comets are the best studied messengers from the outer solar system, and they have been found to have D/H ranging from the terrestrial value to enrichments by about a factor of 4 (i.e., Bockelée-Morvan et al. 2015; Lis et al. 2019; Müller et al. 2022). The sublimation and jetting processes active on these rapidly heating comets could lead to fractionation effects that could change D/H measured in the gaseous coma (Brown et al. 2012), making interpretation more difficult, but it appears plausible that comets may have formed over a variety of distances and temperatures in the nebula and that some increase in D/H with distance is present.

The D/H ratios of the satellites of the giant planets should hold additional information on the D/H values in the middle-solar system and on the processing of ices within the circumplanetary environments. Based on our understanding of isotopic exchange in circumstellar environments (Yang et al. 2013; Albertsson et al. 2014), satellite formation in a hot circumplanetary environment should lead to complete re-equilibration of the D/H ratio to the value of the dominant H_2 gas, which, for Jupiter and Saturn

is approximately the solar value (Pierel et al. 2017). Temperature gradients across the formation region could be revealed by systematic D/H gradients. Little is known of these D/H ratios, but using spectra from the Visual and Infrared Mapping Spectrograph (VIMS) onboard the Cassini spacecraft, Clark et al. (2019, hereafter C19) demonstrated that the fundamental O-D stretch absorption feature – analogous to the $3 \mu m$ O-H stretch feature in water ice – is detectable in the rings and icy satellites of Saturn at approximately $4.14 \mu m$. While the absorption features were near the limit of detection for the VIMS data, new JWST observations have robustly shown the $4.14 \mu m$ feature in the rings of Saturn (Hedman et al. 2024). Here we present JWST reflectance spectra of the $4.14 \mu m$ region of the icy Saturnian satellites at higher signal-to-noise and spectral resolution than obtained for the VIMS observations. We then discuss the implications of these detections of deuterated water on the surfaces of these satellites for both the formation of the solar system and the Saturnian system.

2. OBSERVATIONS AND ANALYSIS

JWST observations of the Saturnian satellites were obtained between 16-Oct-2023 and 25-Jul-2024. The observations and data reduction are fully described in Brown et al. (2025), so are only briefly summarized here. Spectra of the leading and trailing hemispheres of the inner medium-sized satellites of Saturn – Mimas, Tethys, Dione, and Rhea – and of the outer co-rotating satellite – Iapetus – as well as single observations of the non-corotating Hyperion and Phoebe were taken using the G235H and G395M grisms, covering the wavelength range from 1.7 to $5.2 \mu m$, with a gap between 2.38 and $2.48 \mu m$ in the G235H setting. Critically, the G395M grating does not have the 4.08 - $4.26 \mu m$ gap that the higher resolution G395H grating does. The O-D $4.14 \mu m$ line would fall within the gap for higher resolution data. The

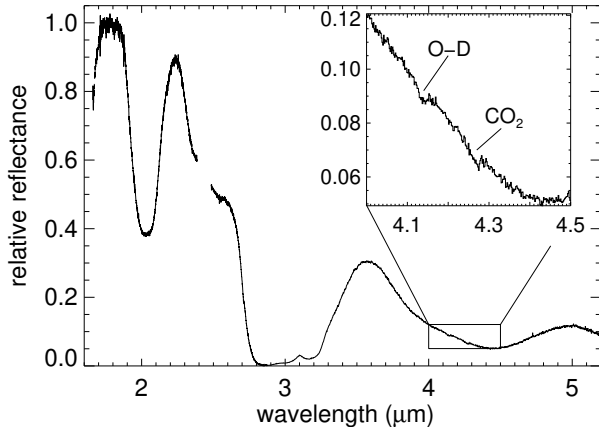


Figure 1. JWST spectrum of the leading hemisphere of Dione with an inset highlighting the 4.14 μm O-D stretch absorption and the 4.26 μm CO_2 absorption.

full spectrum of each satellite can be seen in [Brown et al. \(2025\)](#).

Fig. 1 shows the JWST spectrum of the leading hemisphere of Dione, which is dominated by the usual 2, 3 and 4.5 μm absorption features of water ice. The inset shows two small absorption features between 4.1 and 4.3 μm . These features are the 4.14 μm O-D stretch absorption and the 4.26 μm CO_2 absorption discussed in [Brown et al. \(2025\)](#).

The absorption due to the O-D stretch is seen on nearly all of the satellites. To better visualize each of the regions around the O-D stretch, we divide each spectrum by a continuum, which we construct by fitting the spectrum from 4.0 to 4.2 μm to a second order polynomial while excluding the region from 4.10 to 4.17 μm . Each of the continuum-divided spectra is shown in Fig. 2. In addition, we show a least-squares gaussian fit to the continuum-divided spectrum, where we fix the width of the gaussian to be 0.0124 μm – a value found from first allowing this parameter to be free and then taking the average of the results. For our least-squares fit, we derive uncertainties in the original spectrum by calculating the root-mean-square devi-

ation from the spread after our continuum division. The fractional absorption, which we define as the depth of the absorption compared to the continuum-divided spectrum, using our fixed gaussian width, is shown in Table 1.

3. THE D/H RATIO

While the measurements of the 4.14 μm absorption feature confirms the detection of deuterated water on these objects, converting this detection into a D/H ratio is more complicated. The detected O-D stretch feature is analogous to the 3 μm O-H stretch for non-deuterated water. The O-H stretch feature is saturated in all of the spectra, so a simple ratio of the 4.14 to the 3 μm depth will not yield meaningful results.

C19 use a reflectance spectrum radiative transfer model to understand the spectral effects of incorporation of deuterated water into a spectrum. For objects with significant non-water ice components, they use this method for their final derived D/H values. For clean water ice, they showed from their modeling that for grain sizes between about 5 and 100 μ – which brackets the range of grain sizes on these satellites – the ratio of the 4.14 μm HDO absorption to that of the 2 μm H_2O combination band stays approximately constant and can be used to estimate the D/H ratio. They calibrated their modeling approach with three laboratory spectra of water ice with D/H values of 1, 3.2, and 16 times that of Vienna Standard Mean Ocean Water (VSMOW) – which has a D/H value of 1.56×10^{-4} ([Hagemann et al. 1970](#)) – to which they fit a third-order polynomial and suggest an accuracy of $\sim 10\%$ for clean water ice. As will be shown below, the D/H ratios derived for the inner icy satellites using this method match that found from the *in situ* measurements of the Enceladus plume within the uncertainties ([Waite Jr et al. 2009](#)), increasing confidence in the technique.

Table 1. Measured and derived spectral parameters

satellite	longitude	O-D	2 μm	4.14-to-2 μm	D/H
		absorption	absorption	ratio	
	(deg)	(%)	(%)		($\times$ VSMOW)
Mimas (leading)	52	4.5 ± 0.3	67	0.066 ± 0.005	1.6 ± 0.1
Mimas (trailing)	262	3.6 ± 0.3	60	0.060 ± 0.005	1.4 ± 0.1
Tethys (leading)	78	3.9 ± 0.3	66	0.059 ± 0.005	1.4 ± 0.1
Tethys (trailing)	271	3.2 ± 0.3	63	0.051 ± 0.004	1.2 ± 0.1
Dione (leading)	98	5.1 ± 0.4	60	0.085 ± 0.006	2.1 ± 0.2
Dione (trailing)	274	3.1 ± 0.3	45	0.068 ± 0.007	1.6 ± 0.2
Rhea (leading)	76	4.0 ± 0.2	65	0.061 ± 0.004	1.4 ± 0.1
Rhea (trailing)	261	3.2 ± 0.3	56	0.058 ± 0.006	1.3 ± 0.1
Hyperion	-	3.1 ± 0.5	54	0.057 ± 0.009	1.3 ± 0.2
Iapetus (leading)	80	0.8 ± 0.2	18	0.045 ± 0.009	1.0 ± 0.2
Iapetus (trailing)	267	2.5 ± 0.3	69	0.036 ± 0.005	0.8 ± 0.1
Phoebe ^a	65	1.3 ± 0.8	15	—	1.7 ± 1.1

NOTE— Longitude is the sub-observer longitude at the time of observation. Hyperion has no defined longitude system. The D/H ratio is given relative to VSMOW.

^aThe D/H value for Phoebe is derived by comparison to radiative transfer models of C19, rather than the ratio method used for the other satellites.

This band ratio approach has important benefits and important limitations. The most important benefit is that the method is straightforward, directly related to the observations, and easily reproducible. In addition, the method is insensitive to grain size over the range relevant for the Saturnian satellites, and the ratio of the depth of the 2 to 4.13 μm absorption lines is preserved if the water ice is linearly mixed with a spectrally neutral material, which is possibly relevant on the darker satellites. This band ratio is *not* preserved if water ice is intimately-mixed with a spectrally neutrally material. In this case, the band ratio can either rise, if the material is darker than the water ice at all wavelengths, or it can fall, if the material is brighter than the water ice. Phoebe, which is optically dark and has more muted water signatures than the other mid-sized satellites (Clark et al.

2005), likely is effected by these issues. Other potential uncertainties can arise owing to the different possible states of the water ice (crystalline vs. amorphous vs. a mixture) and their possibly different effects on both the 2 μm and 4.14 μm features, which could affect all measurements.

With the caveats noted above in mind, we adopt the C19 ratio method for converting the spectra to values of D/H for this initial analysis for all satellites except for Phoebe (discussed below). We calculate the depth of the 2 μm absorption by fitting a linear continuum to the median of the spectrum between 1.79 and 1.871 μm and the median between 2.23 and 2.26 μm , dividing the full spectrum by this continuum, and measuring the maximum fractional depth in the region between 1.79 and 2.24 μm . The depth of the 4.14 μm line is taken from the gaussian fits

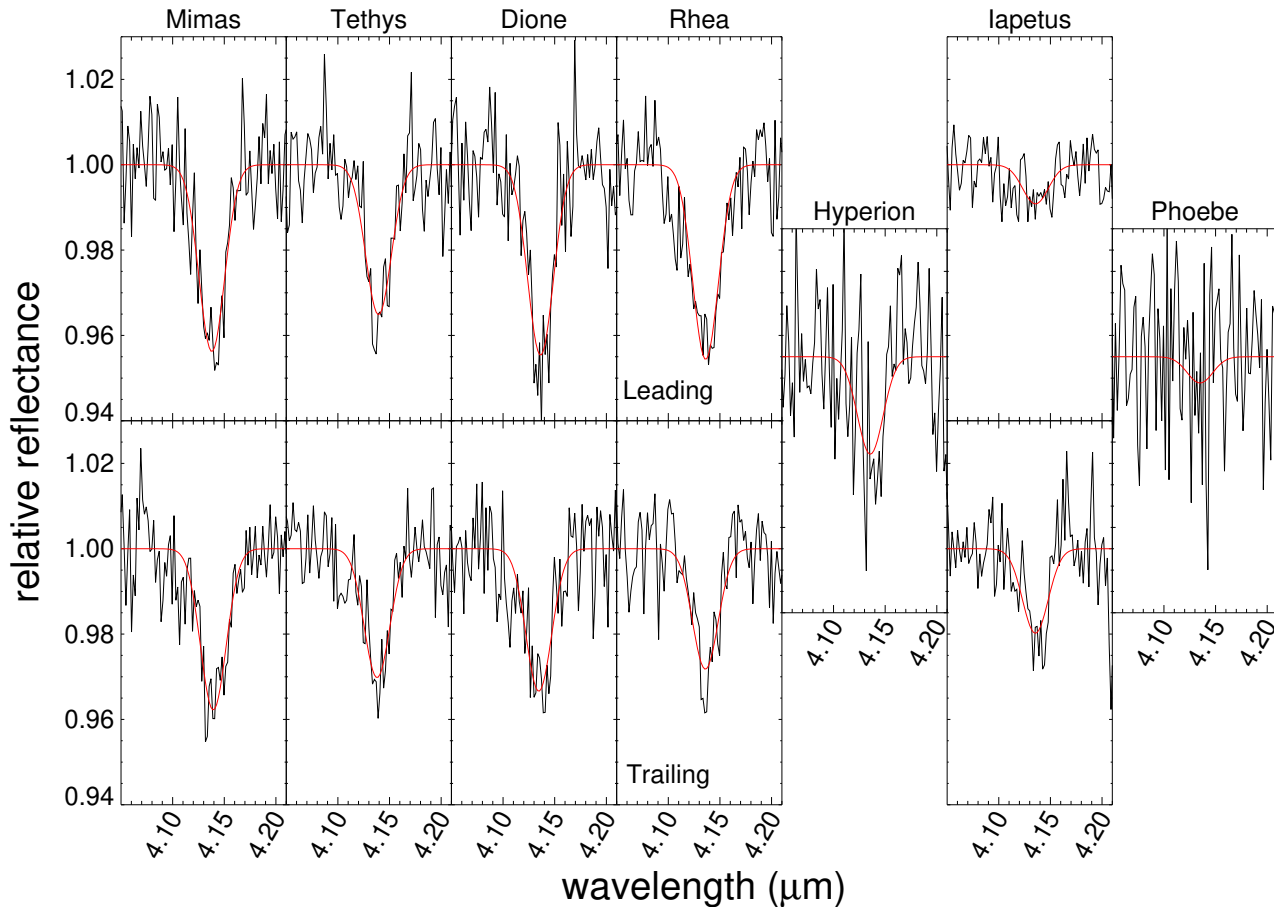


Figure 2. The continuum-divided spectra of the Saturnian satellites, in the region of the O-D absorption. The red line shows a gaussian fit to the data using a fixed width. Most satellites have separate measurements for the leading and trailing hemispheres, but Hyperion and Phoebe, which are not synchronously rotating, only have single measurements. The O-D absorption is robustly detected at nearly every satellite.

in Figure 2. Table 1 lists these values for each of the satellites as well as the uncertainties for the $4.14 \mu\text{m}$ depth. No uncertainty is given for the $2 \mu\text{m}$ depth as our ratio uncertainties are dominated by the $4.14 \mu\text{m}$ depth uncertainty. Note that the band area ratio would make a better observational measurement, as this ratio is unaffected by the spectral resolution of the measurements, but here we use band depth to remain consistent with C19. The bands here are fully resolved, so the area and depth ratios will be the same. The D/H values derived from these ratios are also given in Table 1, while Fig-

ure 3 shows both the ratio and the derived D/H for each satellite.

3.1. The inner satellites

The D/H values derived for the inner icy satellites are consistent with the value derived in C19 for Rhea, $(1.2 \pm 0.2 \times \text{VSMOW})$ and within the uncertainties of the Cassini Ion and Neutral Mass Spectrometer (INMS) measurement of D/H in the plume of Enceladus, which found a value of $1.85^{+.95}_{-.45}$ compared to VSMOW (Waite Jr et al. 2009). For most satellites, we found consistent values for the leading and trailing hemispheres.

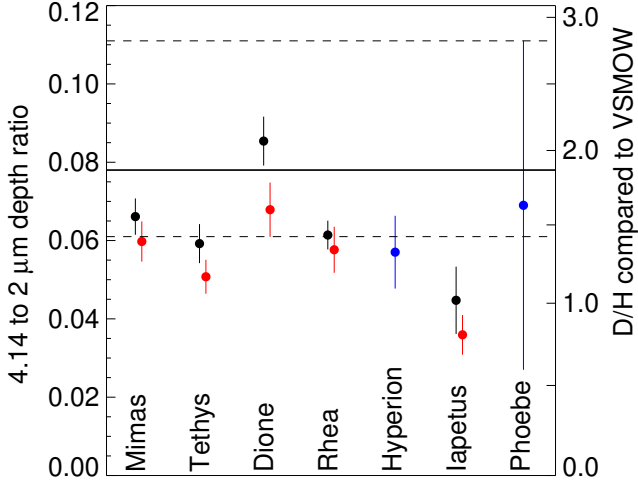


Figure 3. The ratio of the depth of the 4.14 μm absorption to 2 μm absorption for each of the satellites. The leading hemispheres are shown as black points while the trailing hemispheres are red. Hyperion and Phoebe, which are non-synchronously rotating, are shown in blue. The D/H value derived using the C19 calibration is shown on the right. The value measured for Enceladus is shown as the bold horizontal line, while the 1σ upper and lower limits are shown as thinner dashed lines. The D/H value shown for Phoebe is derived from calibration to a radiative transfer model, rather than from the 4.14 to 2 μm depth ratio.

Two exceptions to this general trend are seen. Dione has a derived D/H value elevated above the other inner satellites, and its leading hemisphere has a significantly higher value than its trailing hemisphere. The implied $\sim 30\%$ variation between the leading and trailing hemispheres of Dione is difficult to explain with a native source for deuterated water. The leading hemisphere of Dione receives significantly more mass influx from the E-ring than the trailing hemisphere (Kempf et al. 2018), which could plausibly bring enhanced amounts of deuterated water, but we would then expect Mimas, which receives a higher E-ring flux on the trailing hemisphere, to have the opposite asymmetry, which is not observed. The most conser-

vative interpretation is that all of the D/H values of these inner icy satellites are identical and that the spread seen in derived D/H values reflects the limitations of converting the 4.14 to 2 μm absorption ratio to a D/H value, though it should be noted that in almost all cases the leading and trailing hemisphere measurements are identical within the uncertainties. In this interpretation, the deuterated water detected could either be native to each satellite or could still be brought in from the E-ring if all surfaces are at least covered enough to be optically thick, as suggested by radar measurements (Le Gall et al. 2019).

3.2. Hyperion and Iapetus

Hyperion, which receives little Enceladus material but does contain patches of what is likely Phoebe-ring dark material, has a derived D/H ratio consistent with those of the inner satellites. If the dark material on Hyperion is primarily a coating and thus spatially segregated, the 4.14 to 2 μm ratio should accurately estimate D/H. If, on the other hand, the surface ice of Hyperion is more intimately mixed with Phoebe-like dark material, this material will suppress the 2 μm feature (where Hyperion is bright) more than the 4.14 μm feature (where Hyperion is dark), leading to an elevated 4.14 to 2 μm ratio and a higher inferred value of D/H. We thus take the derived value for Hyperion to be an upper limit to the true value. More detailed modeling will be required to accurately determine the value of D/H for Hyperion.

The derived values for the leading and trailing hemispheres of Iapetus are consistent in spite of the nearly factor-of-four difference in the 2 μm band depth and factor of 2 difference in reflectance around 4.5 μm seen by these observations (Brown et al. 2025). This consistency suggests that the band ratio method is adequately accounting for these differences, though, like for Hyperion, we consider the measurement for the dark leading hemisphere of Iapetus to be a up-

per limit. Formally, the values derived for Iapetus are $\sim 40\%$ lower than those on the inner icy satellites, but we again conservatively interpret this spread as being with the range of uncertainty of our approximation. As with Hyperion, detailed modeling of the spectrum of Iapetus could help to obtain more accurate results.

3.3. *Phoebe*

C19 suggest an elevated value of D/H of $8 \pm 2 \times$ VSMOW for Phoebe using VIMS data and a radiative transfer spectral model. The details of the model are difficult to reproduce for comparison, so we instead chose to use a simple spectral comparison to evaluate the claim of elevated D/H on Phoebe. In Figure 4 we show the JWST spectrum of Phoebe, the VIMS disk-average spectrum of Phoebe, and the averaged spectra of the other satellites. As can be seen from the Figure, the C19 VIMS spectrum appears to have a strong $\sim 4.15 \mu\text{m}$ absorption with an average depth of 4.5% from 4.124 to $4.158 \mu\text{m}$ – slightly longer wavelengths than the D/H features seen on the other satellites by JWST. The JWST Phoebe spectrum rules out such a line at about the 10σ level.

While we cannot reproduce the model of C19, if we take their modeling as a calibration point and assume the $\sim 6\%$ depth of the feature seen by VIMS indeed corresponds to a D/H ratio of $8 \times$ VSMOW, we would infer that the $1.3 \pm 0.8\%$ value measured for the $4.14 \mu\text{m}$ depth at Phoebe corresponds to a value of $1.7 \pm 1.1 \times$ VSMOW, or, more appropriately, a 1σ upper limit of $2.8 \times$ VSMOW. Interestingly, this value is not dissimilar to the value of $2.1^{+1.6}_{-1.4}$ that would be derived from using the simple ratio method, lending support to our use of that method for Hyperion and Iapetus.

4. THE ORIGINS OF THE SATELLITES

The D/H ratios of the satellites of Saturn are enhanced by at least an order of magnitude compared to the atmosphere of Saturn,

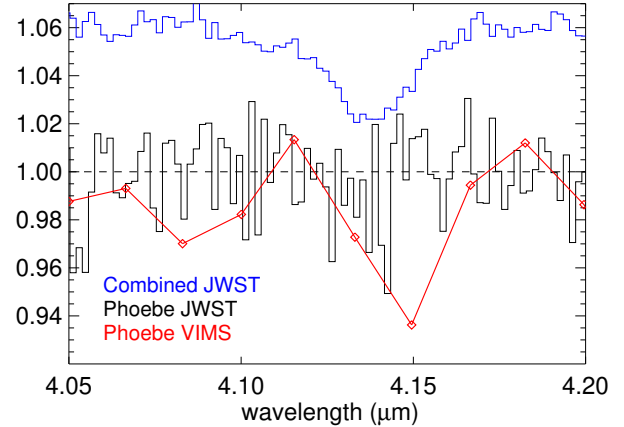


Figure 4. A comparison of the continuum-divided JWST spectrum of Phoebe and the VIMS spectrum of Phoebe from C19. Also shown is the average spectrum of all of the Saturnian satellites with robust $4.14 \mu\text{m}$ absorption detections. The JWST data rule out an absorption with the position and depth of that seen by VIMS at the 10σ level.

which has a D/H similar to the solar value (Blake et al. 2021). The strong implication of this simple fact – even with the uncertainties in the D/H calibration – is that the satellites did not form out of material that condensed out of a hot planetary sub-nebula, as initially explored by Pollack & Consolmagno (1984). In such a case the deuterated water would have re-equilibrated with the much more abundant H_2 and the D/H value would be quickly diluted to the Saturnian value. Multiple other lines of evidence have shown that satellite formation in a hot circumplanetary nebula is implausible, however, and no modern formation model posits such a formation pathway.

Current models for the formation of the Saturnian satellites suggest either slow formation in a gas-starved disk (i.e. Canup & Ward 2006; Batygin & Morbidelli 2020) or formation from reaccreted ring material, where the ring can be the result of a larger satellite disruption (Canup 2010) or the result of the tidal disruption of a large passing icy body (Dones 1991;

Hyodo et al. 2017). All of these scenarios can be made consistent with the approximately constant D/H value across the Saturnian system under the assumption that the planetesimals and pebbles which form the satellites all came from regions with elevated D/H.

In the hybrid scenario suggested by Blanc et al. (2025) and informed by recent ideas of faster migration for the Saturnian satellites, large satellites form at some distance from Saturn and migrate inward where some are perhaps lost. The penultimate satellite is tidally disrupted and forms the rings – which eventually spawns the icy mid-sized satellites – while the proto-Titan survives inward migration and, upon dissipation of the disk, tidally migrates outward. Hyperion and Iapetus presumably also form out of this initial disk, though no satisfactory explanation of their formation pathway has been presented (Castillo-Rogez et al. 2018). In this scenario, the original satellites would have to have formed from icy planetesimals and pebbles which did not equilibrate with the gas disk. The lack of a rise in the D/H ratio beyond Titan would then suggest that no strong temperature gradient existed across the satellite formation region and that the D/H value of the satellites largely reflects that of the planetesimals and pebbles entering the system at the distance of Saturn. The similarity of the D/H ratio of the icy mid-sized satellites is a natural consequence of their origin from a single body.

The inferred upper limit for the D/H ratio of Phoebe is consistent with that derived for the other satellites. Phoebe appears to have a D/H ratio broadly consistent with the range seen in comets, suggesting a pre-capture origin in the outer solar system.

5. CONCLUSIONS

Deuterated water is detected on all of the observed mid-sized icy satellites and on Hyperion and Iapetus. The D/H ratio on these satellites

is approximately an order of magnitude higher than in the atmosphere of Saturn, demonstrating that the ices incorporated into these satellites never sublimated and equilibrated with the gaseous circumplanetary nebula. Only upper limits can be placed on Phoebe, but it cannot have a significantly higher D/H ratio than the other satellites in the system.

The similarity in D/H ratio of all of the satellites suggests that this ratio is representative of the D/H ratio of the planetesimals and pebbles in the vicinity of Saturn at the time of satellite formation. The inferred value of $\sim 1.5 \times$ VS-MOW is enriched compared to the inner solar system, but does not appear to be as high as some of the cometary values seen.

This moderate enhancement in D/H at the distance of Saturn suggests perhaps a mild increase in D/H as a function of heliocentric distance in the solar system, similar to that seen in the laminar models of (Albertsson et al. 2014) that do not have transport, which seems unrealistic. Models tracking D/H ratios incorporating modern ideas of disk structure, pebble transport and accretion, and satellite formation have yet to be constructed, but will be critical for interpreting D/H ratios measured in planetary environments.

One interesting prediction from these values of D/H in the ices in the vicinity of the forming Saturn is that the ices at Uranus should be similar. Indeed, the presence of the disk gap at Jupiter suggests that most solid material would be flowing into the Saturnian system from beyond Saturn. Uranus, which makes no such gap, would then likely be bathed in the same solid material. The D/H ratio at Uranus is depleted compared to VSMOW by a factor of 3.5 (Feuchtgruber et al. 2013), a value from than 5 times lower than that we have inferred for the Saturnian satellites. Uranus is expected – though not confirmed – to have fully mixed its atmosphere and interior in its

past, and thus the D/H ratio is expected to reflect the bulk average of the nebular H_2 and the ices that initially formed the planet. Using this expectation, [Feuchtgruber et al. \(2013\)](#) derive a D/H ratio for the ices that formed Uranus of a value of $\sim 0.4 \times \text{VSMOW}$, a value more than 3.5 times lower than that we derive for the ices that formed the Saturnian satellites. [Feuchtgruber et al. \(2013\)](#) themselves are uncomfortable with this conclusion and suggest multiple possible solutions, including the possibility that the interior is not mixed and that the interior is significantly more rocky than current assumed. The high values of D/H for the Saturnian satellites highlight this continued discrepancy.

Using the $4.14 \mu\text{m}$ O-D stretch feature to infer a D/H ratio via reflectance spectroscopy is a powerful technique, particularly with the advent of JWST coverage in this wavelength region. We caution, however, that significant laboratory and modeling work is still needed to understand the robustness of this technique and its application across the solar system. While the nearly-pure water ice surfaces of the inner mid-

sized satellites of Saturn present perhaps the ideal test case for this technique, understanding how to reliably apply the technique to more complicated surfaces remains work in progress.

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Facilities: JWST/NIRSpec

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