USING D/H RATIO OF WATER AND VOLATILE ORGANICS TO CONSTRAIN THERMOGENIC PROCESSES INSIDE ICE-ROCK BODIES. K. E. Miller[1], C. R. Glein[1], J. H. Waite[1], and S. J. Bolton[1], [1]Southwest Research Institute, San Antonio, TX 78238. Correspondence to kmiller@swri.edu.

Introduction: Cometary mission data indicate complex organic material is an abundant (almost 25 wt.%) component of primitive bodies in the outer solar system [1, 2], which suggests that such material may have been an important building block incorporated into bodies beyond the snowline [3]. Pyrolysis and volatilization of complex organics could occur [4] within the heated interiors of ocean worlds [5-7]. Recently, we showed that as much as 50% of Titan's atmospheric nitrogen may be derived from heating of primordial organics in the core [8].

Methane and other H-bearing organics are produced [9] in pyrolysis experiments on chondritic insoluble organic matter (IOM), which is considered an analog for complex primordial organics in the outer solar system [10]. One of the distinguishing characteristics of IOM is its high D/H ratio [11]. However, isotopic exchange between water and organics [12, 13] during outgassing should modify the observed D/H ratios of both. Here, we examine the implications of volatilization of D-rich IOM hydrogen on isotopic ratios for the Saturnian system, Kuiper Belt Objects, and Ceres.

The Saturnian System: *Titan and Enceladus.* If heating of organics in Titan's core is an important source of atmospheric volatiles [8], then a significant mass of organic-derived methane may have been similarly outgassed. We previously calculated that 8×10^{18} kg of methane may be released in this manner. Given this mass along with the measured D/H ratio of atmospheric methane (1.36×10^{-4}, [14]), an initial D/H ratio for IOM of 7.05×10^{-4} [15], and assumed equilibrium at 0 °C with 4×10^{22} kg of water, we calculated that Titan's primordial water may have had D/H similar to VSMOW. This ratio is very similar to findings using Cassini VIMS data to remotely constrain the D/H ratio for Saturn's B ring, as well as the surfaces of Hyperion, Iapetus, and Rhea [16]. These results suggest that the primordial D/H ratio of water ice in the Saturnian system may be VSMOW-like.

However, measurements of water in Enceladus' plume give a much higher D/H ratio of 2.9×10^{-4} [17]. If the primitive D/H ratio for the Saturnian system is indeed VSMOW-like, then the high D/H ratio measured in Enceladus' plume water can be explained by more vigorous hydrothermal alteration of organics compared to Titan. Assuming equilibration at 50 °C [18], thermogenic methane should have a D/H ratio of 2.33×10^{-4}. If the relative abundances of hydrogen derived from organics and water are similar at Enceladus, then the water D/H ratio is consistent with equilibration of between 36 and 96 % of volatilized organic hydrogen, much larger than at Titan.

The D/H Continuum. Based on the above comparison, we suggest that the D/H ratio of water can serve as a measure of internal equilibration and heating. Bodies in the Saturnian system span a spectrum of processing, from primitive materials in the B ring and at the surfaces of Rhea, Iapetus, and Hyperion to hydrothermally processed materials in the plume of Enceladus. We infer based on the D/H ratio of methane in Titan's atmosphere that the interior of Titan lies at an intermediate point along this spectrum.

Also potentially intermediate on this spectrum are Mimas and Dione, possible ocean worlds in the Saturnian system [19, 20]. Following assumptions in [8] and silicate fractions from [21] updated to reflect 40 to 50 wt.% organics with assumed density of 2200 kg/m^3 in the rock fraction, we calculate that 15% equilibration of volatilized organics yields a final D/H ratio for water of 1.61×10^{-4} for Mimas and 1.63×10^{-4} for Dione. However, the range in D/H for rock-poor bodies does not vary strongly with the extent of organic equilibration, with 100% organic equilibration yielding ratios of only 1.85×10^{-4} for Mimas and 2.01×10^{-4} for Dione.

Implications for the origins of Saturn's rings. The isotopic congruity between Saturn's rings and Enceladus, Rhea, Hyperion, and Iapetus [16] strongly suggest formation from a common water reservoir, consistent with our theoretical interpretation of Titan's D/H [8]. These results may provide important constraints on formation of the rings [22] and the mid-sized satellites [23]. Formation from a differentiated, Titan-like body may yield a water D/H ratio close to 1.8×10^{-4}, which is within error of the value determined by [16], but higher than the nominal VSMOW value. Future in situ data may help resolve the remaining uncertainty and provide a stronger test of this formation hypothesis. Current findings of a VSMOW-like ratio throughout the Saturnian system suggest formation of Titan, the mid-sized satellites, and the rings from a single isotopic reservoir ([24]; see [25] and references therein for discussion of possible formation scenarios).

Kuiper Belt Objects (KBOs): We performed similar calculations for Pluto and Triton (Fig.1). Following calculations in [26], but with the addition of 40 wt.% organics to the rocky fraction, we calculate a rock-to-water mass ratio of 2.5, which we use here for both KBOs. Thermal models of Pluto's interior suggest temperature in excess of 525 °C for a large fraction of

Pluto's core [27]; internal temperatures at Triton likely exceeded this value [28]. Here, we assume volatilization of 50% of H from refractory organics, consistent with a maximum temperature of ~550 °C [9] and use compositional data from the summer hemisphere of comet 67P/Churyumov-Gerasimenko (67P) [29]. Since geochemical conditions at Pluto and Triton remain poorly constrained, we varied two different parameters: (1) the extent of organic exchange, from 5 to 14% [Titan-like; (A) below] and from 45 to 100% [Enceladus-like; (B) below]; and (2) the initial D/H ratio of water, from VSMOW (1.56×10^{-4}) to 67P (5.3×10^{-4}, [30]). We assume hydrogen isotopic equilibration between water and organics, with the temperature of equilibration [31] shown by the color bar. Hypothesized regions for Pluto and Triton are indicated with red arrows and a "P" and "T" respectively based on suspected differences in the extent and temperature of internal equilibration [27, 28].

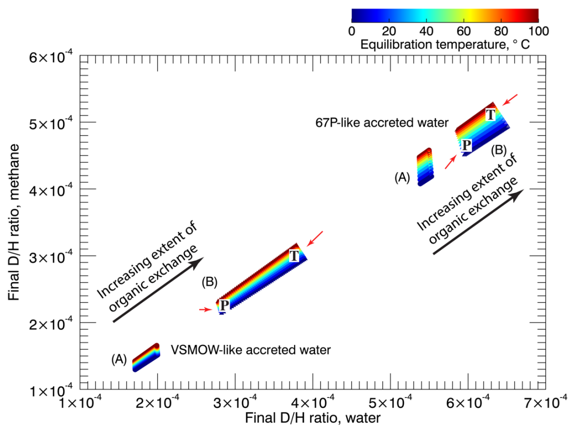

Fig. 1. *D/H ratios of interacting reservoirs of water and organics.*

Ceres: To predict the D/H ratios at Ceres, we assume that 5 to 40 wt.% of the rocky fraction is organic in nature. The lower limit is similar to CI chondrites (e.g. [15]). The upper bound comes from estimates by [32], who predict 20 wt.% carbon content in the regolith. In both cases, we assume that complex organics are 50 wt.% C. We also assume a rock:water ratio of 0.5 for the region of isotopic exchange [33]. Since Ceres shows evidence for extensive hydrothermal processing [34], we calculate the current ratios using 50% volatilization and 95% equilibration of organics. Assuming an initial VSMOW ratio for water, the predicted final D/H ratio of water is $(1.59\text{-}2.09)\times10^{-4}$, while that of organics equilibrated at 0 °C [35] is $(1.21\text{-}1.59)\times10^{-4}$. If Ceres had an initial 67P ratio for water due to formation at greater heliocentric distances [36], the predicted final D/H ratio of water is $(5.31\text{-}5.57)\times10^{-4}$, while that of organics is $(4.04\text{-}4.24)\times10^{-4}$.

Conclusions: The D/H ratios of water and organic material at mid-sized ice-rock bodies may be an indicator of the extent of heating in the interior. Mixing of relatively D-poor water with D-rich organics derived from volatilization of accreted insoluble organic matter leads to a spectrum of D/H ratios in processed materials. In the Saturnian system, this processing may suggest a common origin for Saturn's B ring, mid-sized moons, and Titan. We also predict isotopic ratios at Pluto, Triton, and Ceres given reasonable assumptions on the water and organic fractions and initial isotopic ratios at these bodies. These results highlight the value of data on D/H ratios, and especially the importance of measuring D/H for volatile organic compounds in addition to water. Our results provide testable hypotheses for future missions to Titan, Pluto, and Ceres, and highlight the importance of measuring methane D/H at Enceladus and Europa.

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