

# DETERMINATION OF WATER D/H IN HYDRATED CHONDRITES USING NANOSIMS IMAGING.

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**Introduction:** Hydrogen isotopic compositions (expressed as D/H or  $\delta D = [(D/H_{\text{sample}}/D/H_{\text{VSMOW}}) - 1] \times 1000$ ) in chondrites are a powerful tool for deciphering the source of water delivered to terrestrial planets [1, 2]. CM-type carbonaceous chondrites are traditionally related to hydrous C-complex asteroids and likely originated relatively far from the Sun [3, 4]. These chondrites are dominated by hydrated minerals (~70–90 vol.%) and contain up to ~10 wt.% H<sub>2</sub>O, mainly in the form of hydroxyl (OH) in phyllosilicates [5, 6]. The H-isotopic composition of phyllosilicates (a direct proxy for water) in chondrites cannot be determined directly using whole rock measurements [1], because their matrices also accreted D-rich organics which are intimately mixed with D-poor phyllosilicates at the sub-micrometer scale [7].

To address this issue, the  $\delta D$  value of water has been estimated by in-situ measurements of both D/H and C/H in hydrated chondrites, which define a mixing line in a D/H vs. C/H plot. The intercept gives the isotopic composition of the phyllosilicate alone [1, 8]. However, SIMS measurements of water D/H using this method can be compromised by 1) contamination and 2) limited dispersion of the phyllosilicates/organics ratio measured with a relatively large primary beam (**Fig. 1**). Contamination from C and H can compromise the precision, and more importantly, the accuracy, of the intercept value and thus the derived water D/H value. All measurements like this are contaminated by terrestrial H to some degree. If a large range of phyllosilicates/organics (i.e., C/H) is not sampled by the measurements, a linear fit to the D/H vs. C/H data will have poor precision (accuracy would not be compromised).

**Methods:** We addressed both of these issues using the Wash U NanoSIMS 50 and novel data acquisition and analysis techniques. The NanoSIMS allows us to obtain coordinated isotopic and elemental data with high-spatial resolution (~100nm). However, scanning ion images of all species must be precisely aligned in order to take advantage of the small primary beam spot size. Secondary ions of H<sup>-</sup>, D<sup>-</sup> with <sup>12</sup>C<sup>-</sup>, <sup>12</sup>C<sup>14</sup>N<sup>-</sup>, <sup>12</sup>C<sup>15</sup>N<sup>-</sup> and <sup>28</sup>Si<sup>-</sup> are collected using magnetic-field peak-jumping in “Combined Analysis” mode. Centering of the secondary ions beam in the horizontal (Cy) and vertical (P2/P3) planes of the secondary column changes between the low and high masses, resulting in misaligned scanning ion images.

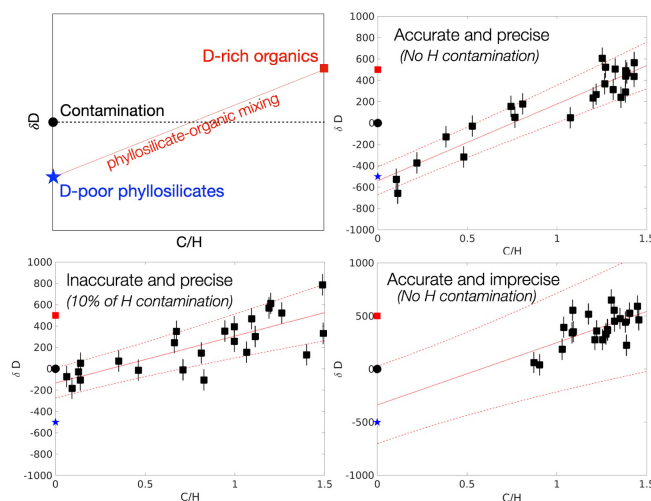
The NanoSIMS software does not allow for changing most secondary beam alignment parameters for different B-fields during acquisition. To overcome this problem, we used AutoHotkey scripts to send a different Cy voltage for every B-field set up through the virtual keyboard of the NanoSIMS. This technique can be used for other applications to make Combined Analysis mode on the NanoSIMS more robust. Our code is available on the WashU lab’s Github page.

To separate phyllosilicate-rich pixels in the scanning ion image from organic-rich pixels, we assume that D/H is not simply a linear function of C/H, but in general D/H is approximated by a function using

$$D/H = C^a N^b Si^c H^d$$

all measured species:

Taking the logarithm of both sides, a linear regression model is created using Matlab’s stepwiselm function. This function adds or removes terms by stepwise regression. The true phyllosilicate “endmember” composition [C, N, Si, H] is estimated from the data or standards, and is then used to estimate the water D/H composition (and uncertainties) from the linear regression model. Badly contaminated or otherwise compromised measurements have very large or small a, b, c, d values compared to high-fidelity measurements. We verified the accuracy and precision of this analysis technique using randomized, simulated data.



**Fig. 1:** Simulated  $\delta D$  vs. C/H plots showing the effects of terrestrial H contamination and the low degree of isotopic mixing between D-poor phyllosilicates and D-rich organics on the determination of the H-isotopic composition of phyllosilicates in hydrated chondrites.

**Analyses:** Isotopic analyses were carried out in a phyllosilicate-rich matrix area of the CM Maribo (provided by Martin Bizzarro from the Natural History Museum of Denmark in Copenhagen) using these new techniques. We used a  $\sim 1$  pA  $\text{Cs}^+$  primary beam focused to  $\sim 100$  nm. Prior to isotopic analyses, the sample was stored in the carousel chamber for more than 2 weeks to minimize the contribution from adsorbed water. Negative secondary ion images ( $10 \times 10$   $\mu\text{m}$ ,  $256 \times 256$  px) were collected simultaneously in multi-collection mode on EMs by combined peak switching (B-field #1:  $\text{H}^-$ ,  $\text{D}^-$  and B-field #2:  $^{12}\text{C}^-$ ,  $^{12}\text{C}^{14}\text{N}^-$ ,  $^{12}\text{C}^{15}\text{N}^-$  and  $^{28}\text{Si}^-$ ). An area of  $\sim 15 \times 15$   $\mu\text{m}$  was presputtered using a  $\sim 75$  pA beam before each measurement for  $\sim 3,000$  s to remove the C coat and residual adsorbed water from the surface of the samples. Measurements were collected over  $\sim 50$  cycles with integration times of 2000  $\mu\text{s}/\text{px}/\text{plane}$  for B-field #1 and 500  $\mu\text{s}/\text{px}/\text{plane}$  for B-field #2. Mass resolution power (MRP) was set to  $\sim 6,000$  to resolve  $^{13}\text{C}^{14}\text{N}^-$  contribution from  $^{12}\text{C}^{15}\text{N}^-$ . D/H of unknowns were standardized to a kerogen standard from the Warrawoona Group ( $\delta\text{D} = -105\text{‰}$ ) pressed into gold foil. The reproducibility of the kerogen was  $\sim 30\text{‰}$  for  $\delta\text{D}$  ( $1\sigma$ ,  $n = 11$ ). NanoSIMS image data was processed using Matlab.

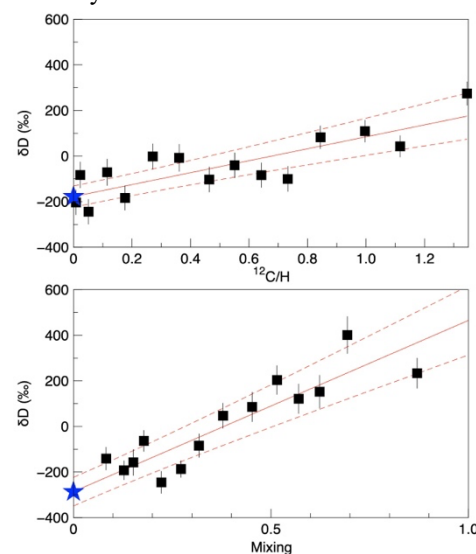
**Results:**  $\text{H}^-$ ,  $^{12}\text{C}^-$  and  $^{12}\text{C}^-/\text{H}^-$  images from the matrix area of Maribo are well aligned, indicating that the secondary ion beams were successfully centered for both B-fields. This allows us to analyze coordinated small areas for the different species. We resized the images so that the pixel size was larger than the beam size. Results from our data processing are shown in Fig. 2 and discussed below.

**D/H vs C/H:** First, we determined the D/H ratio of phyllosilicates in Maribo using the zero-intercept of the D/H vs. C/H linear correlation from the resized pixels. Using this method, we calculated a  $\delta\text{D}$  value of  $-178 \pm 46\text{‰}$  ( $2\sigma$ ) for the phyllosilicates endmember. This value is higher than previous measurements [9, 10] using SIMS ( $\delta\text{D} \approx -420$  to  $-270\text{‰}$ ). Our result shows that the H-isotopic composition of the phyllosilicate endmember cannot be simply determined in this matrix area using the D/H vs. C/H line, probably because of contamination from C and/or H.

**D/H vs  $\text{C}^a\text{N}^b\text{Si}^c\text{H}^d$ :** Second, we calculated the D/H ratio of phyllosilicates in Maribo using all the measured species and the linear regression model described in this abstract. We found that the H-isotopic composition of the phyllosilicate endmember is best correlated for dominant contributions of N, Si and H ( $b = 0.14$ ,  $c = 0.58$  and  $d = -0.86$ ) and minor contributions of C ( $a = 0.06$ ). We note that the C parameter ( $a$ ) is small compared to those from the other species. This suggests that C could be contaminated due to incomplete removal of C coating

from the analysis area and/or the presence of C-bearing phase, as expected from the D/H vs. C/H correlation. From these parameters, we calculated a  $\delta\text{D}$  value of  $-286 \pm 60\text{‰}$  for the phyllosilicate endmember of Maribo. This value is consistent with those previously determined by SIMS, and the precision is similar. However, our NanoSIMS measurements are from a single  $100 \mu\text{m}^2$  area which is  $\sim 50$  times less area than the SIMS estimates [e.g., 9].

**Conclusion:** Our new NanoSIMS acquisition and analysis techniques allow us to precisely and accurately determine the H-isotopic characterization of water on very small areas. Our method can be used to study small-scale D/H variability in matrix, and small hydrated inclusions in meteorites. In addition, our technique can be used for the isotopic characterization of returned samples from C-complex asteroids Ryugu (JAXA) and Bennu (OSIRIS-REx), which require efficient analyses of a small amount of material.



**Fig. 2:** (top)  $\delta\text{D}$  vs.  $^{12}\text{C}/\text{H}$  plot and (bottom)  $\delta\text{D}$  vs. mixing (C,N,Si and H) plot showing the calculated H-isotopic composition of the phyllosilicate endmember in Maribo (blue star) using two different linear regression models (see text for details).

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**References:** [1] Alexander C. M. O'D. et al. (2012) *Science*, 337, 721–723. [2] Piani L. et al. (2020) *Science*, 369, 1110–1113. [3] Hiroi T. et al. (1996) *MAPS*, 31, 321–327. [4] Desch S. J. (2018) *APJS*, 238, 11. [5] Howard et al. (2015) *GCA*, 149, 206–222. [6] Vacher et al. (2020) *GCA*, 3, 53–66. [7] Le Guillou et al. (2014) *GCA*, 131, 368–392. [8] Piani L. et al. (2018) *Nat. Astron.*, 2, 317–323. [9] van Kooten E. M.M.E. et al. (2018) *GCA*, 237, 79–102. [10] Piani L. et al. (2021) *EPSL*, 567, 117008.