Determination of Water D/H in Hydrated Chondrites Using NanoSIMS Imaging

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Introduction: Hydrogen isotopic compositions (expressed as D/H or δD) in chondrites are a powerful tool for deciphering the source of water delivered to terrestrial planets [1, 2]. CM chondrites are traditionally related to hydrous C-complex asteroids and contain up to ~10 wt.% H_2O, retained as OH in phyllosilicates [3, 4]. The D/H ratio of phyllosilicates (a direct proxy for water) in chondrites cannot be determined directly using whole rock measurements, because their matrices also accreted D-rich organics which are mixed with D-poor phyllosilicates at the sub-micrometer scale [1, 5]. To address this issue, water D/H 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, 6]. However, SIMS measurements of water D/H using this method can be compromised by *(i)* contamination and/or *(ii)* limited dispersion of the phyllosilicates/organics ratio measured with a large primary beam. 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.

Methods: We addressed both issues using the Wash U NanoSIMS 50 which allows us to obtain coordinated isotopic and elemental data with high-spatial resolution. H^-, D^- with $^{12}C^-$, $^{12}C^{14}N^-$, $^{12}C^{15}N^-$, $^{28}Si^-$ are collected using magnetic-field peak-jumping in "Combined Analysis" mode. Centering of the secondary ions beam in Cy and P2/P3 planes of the secondary column changes between the low and high masses, resulting in misaligned ion images. Thus, we used AutoHotkey scripts to send a different Cy voltage for every B-field set up through the virtual keyboard of the NanoSIMS. To separate phyllosilicate-rich 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 all measured species. The true phyllosilicate composition [C, N, Si, H] is estimated from the data and is then used to estimate the water D/H composition from the linear regression model. NanoSIMS isotopic analyses were carried out in a matrix area of the CM Maribo and our analytical conditions were the same as outlined in [7].

Results and discussion: First, we calculated a δD value of -178 ± 46‰ (2σ) for the phyllosilicates in Maribo using the D/H vs. C/H correlation from the resized pixels. This value is higher than previous measurements using SIMS ($\delta D \approx -420$ to -270‰, [8, 9]), demonstrating that D/H ratio of phyllosilicate cannot be simply determined using the D/H vs. C/H line in this matrix area.

Second, we calculated the δD value of the phyllosilicates in Maribo using all the measured species and the linear regression model described above. We found that the phyllosilicate D/H 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). 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. We calculated a δD value of −286 +/- 60‰ for the phyllosilicate endmember of Maribo. This value is consistent with those previously determined by SIMS, demonstrating that our method can be used to precisely determine the water D/H on very small areas, such as returned samples from C-complex asteroids Ryugu (JAXA) and Bennu (OSIRIS-REx), which require efficient analyses of a small amount of material.

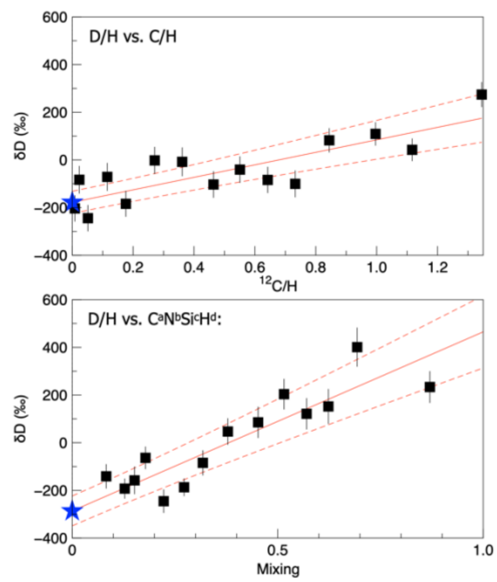

Fig. 1 - (top) δD vs. ^{12}C/H plot and (bottom) δD vs. mixing (C, N, Si and H) plot showing the calculated H-isotopic composition of the phyllosilicate endmember in Maribo (blue star) using two different linear regression models (see text for details).

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] Vacher et al. (2020) *GCA, 3*:53–66. [5] Le Guillou et al. (2014) *GCA, 131*:368–392. [6] Piani L. et al. (2018) *Nature Astrononomy*, 2:317–323. [7] Vacher L.G. and Ogliore R.C. (2022) *The 53rd LPSC*, Abstract #2653. [8] van Kooten E. M.M.E. et al. (2018) *GCA, 237*:79–102. [9] Piani L. et al. (2021) *EPSL, 567*:117008.