HYDROGEN ISOTOPIC COMPOSITION OF WATER IN THE UNGROUPED CARBONACEOUS CHONDRITE TAGISH LAKE.

L. G. Vacher[1], R. C. Ogliore[1] and N. Liu[1]. [1]Department of Physics, Washington University in St. Louis, St. Louis, MO 63130, USA (lvacher@wustl.edu).

Introduction: D-type asteroids are believed to be among the most pristine objects in the Solar System and contain primordial water and organic compounds [1, 2]. D-type asteroids are observed to locate at the outer edge of the main belt today [3], but several studies suggest that they originated in the outer part of the protoplanetary disk and possibly accreted cometary ice before their inward migration to the main belt [4]. D-type meteoritic analogs are not well established, but the ungrouped (C2) Tagish Lake (TL) carbonaceous chondrite − a highly porous and aqueously altered carbonaceous chondrite with a similar reflectance spectrum as D asteroids − may be our best representative sample of this type of asteroids [5]. Tagish Lake chondrite exhibit several unique features, including *(i)* highly anomalous D and ^{15}N organic globules, possibly similar to cometary (CHON) particles [6] and *(ii)* abundant ^{13}C-rich carbonates [7]. Together, these characteristics suggest that the parent-body of Tagish Lake may have formed in the cold outer Solar System and potentially incorporated a significant amount of ice [8].

Tagish Lake has experienced aqueous alteration on its parent-body, as demonstrated by the presence of abundant phyllosilicates, magnetite and carbonates [9]. The H isotopic composition (δD, relative to SMOW) of its water is poorly constrained, but appears to be significantly depleted in D (inferred δD_{TL} for water ranging between −900‰ and −270‰) when compared to cometary water [10]. However, this result is based on mass-balance calculations between whole rock and primordial CR-like insoluble organic matter (IOM), assuming that the chondrite groups accreted a common CR-like D-rich IOM precursor [11]. Alternatively, it has been proposed that chondrite groups may have accreted more D-poor IOM of different origins [12], which consequently could result in an inaccurate estimate of the H isotopic composition of water in Tagish Lake. Here we evaluate the δD value of the water in Tagish Lake from *in-situ* Si/H and δD measurements of its hydrated fine-grained matrix by using the Cameca NanoSIMS 50 microprobe at Washington University in St. Louis.

Methodology: Secondary electron microscope (SEM) observations were performed using a Tescan Mira3 FEG-SEM. We acquired high-resolution BSE mosaics (~7,700 images) on carbon-coated polished sections of Tagish Lake [13] and the two CM chondrites Murchison and Maribo. Both phyllosilicates-rich and phyllosilicate-poor areas were flagged for isotopic analysis. Hydrogen isotopes of the matrix were performed with the Wash U NanoSIMS using ~10 pA primary beam for meteoritic samples and ~2 pA for standard measurements. Prior to isotopic analyses, samples were stored in the carousel chamber for 1−2 weeks to remove adsorbed water. Then, negative secondary ion images (15x15 μm, 256 x 256 pixels) were collected simultaneously in multi-collection mode on EMs by combined peak switching (magnetic field #1: H$^-$, D$^-$ and magnetic field #2: ^{18}O$^-$, ^{12}C^{14}N$^-$ and ^{28}Si$^-$). An area of ~20×20 μm was presputtered using a ~100 pA beam before each measurement for ~1h to remove the C coat and residual adsorbed water from the surface of the samples. Measurements were collected over ~100 cycles with integration times of 1500 μs/px/plane for H and D and 500 μs/px/plane for ^{18}O, ^{12}C^{14}N and ^{28}Si (Figure 1). Hydrogen isotope ratios of unknowns were normalized to deposited kerogen from the Warrawoona Group (δD = −105‰) and epoxy resin sitting within the cracks of the meteoritic samples (assumed to have a δD value of 0‰). The NanoSIMS image data were processed using L'image software (L. R. Nittler).
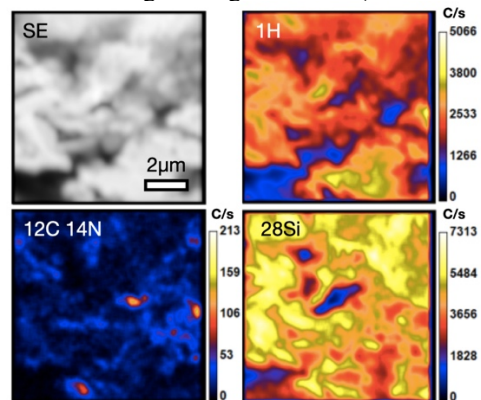

Figure 1: NanoSIMS ion images of SE, ^{1}H, ^{12}C^{14}N and ^{28}Si of one phyllosilicates-rich matrix area of the CM Murchison.

Results: The δD values of Murchison and Maribo range between ~ −400 and 600 ± 130‰ (2σ), and the phyllosilicates-rich matrix areas appear to be more depleted in D compared to the phyllosilicates-poor matrix. The δD values of all the data of the two CM chondrites are linearly correlated (R^2 = 0.85) with the Si/H ratios. An SEM survey of our polished of Tagish Lake reveals that the overall petrography of our sample is consistent with the dominant carbonate-poor lithology previously described by [9]. Our δD data suggest that this lithology is enriched in D compared to CM chondrites and range between ~600 to 1300 ± 150‰ (2σ). These values are in good agreement with the δD

values previously reported by [14] for Tagish Lake using a similar analytical condition. The δD values and Si/H ratios of the matrix of Tagish Lake are linearly correlated ($R^2 = 0.76$) and display a slope similar to that defined by the two CM chondrites (Figure 2).
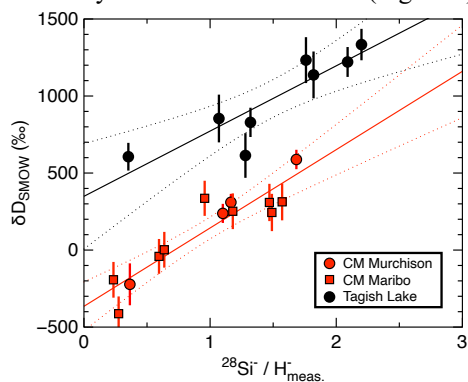

Figure 2: δD *vs.* Si/H (not corrected for different sensitivity factors between Si$^-$ and H$^-$) plot of the hydrated matrix areas of CM chondrites (red) and Tagish Lake (black). Solid lines and dotted curves represent data regression and their 95% confidence intervals, respectively (errors are 2σ).

Discussion: The D/H ratios measured for the two CM chondrites and Tagish Lake are correlated with the elemental Si/H ratio − a proxy for the level of matrix hydration [15]. Our observed positive correlations between δD and Si/H likely reflect mixing between D-poor phyllosilicates (represented by low Si/H ratios) and a D-rich organic reservoir (represented by high Si/H ratios) [16]. If correct, then the resulting intercept should approximate the H isotopic composition of the alteration fluid. Using these D/H *vs.* Si/H correlations, Our extracted δD value for water in Tagish Lake is significantly higher compared to that of the CM chondrites ($\delta D_{CM} = -242 \pm 65$‰ *vs.* $\delta D_{TL} = 335 \pm 335$‰, *vs.* 2σ). Our estimate of δD in CM water is consistent with the results of previous studies within uncertainties [17, 18].

The presence of D-rich water in the chondrite Tagish Lake may reflect either *(i)* the accretion of D-rich water from the outer part of the Solar System [5] or *(ii)* the loss of volatile H$_2$ by Rayleigh-type distillation, resulting in the oxidation of metal to magnetite [19]. Magnetite is very abundant in the matrix of Tagish Lake [9], indicating that Fe oxidation played an important role in determining its secondary mineralogy. As Tagish Lake is not so mineralogically and isotopically different from CI and CM chondrites, a plausible scenario that may explain its particular D-rich water is that the Tagish Lake's parent-body lost some fraction of its H during the conversion of metal to magnetite by aqueous alteration. In order to test this hypothesis, we compared the H isotopic composition of the Tagish Lake water and its total H concentration

previously reported for this sample (H = 0.43 wt. %) relative to CM Murchison and Maribo (H = 0.84 wt. %) [20]. Assuming that the Tagish Lake parent-body accreted a similar amount of D-poor water ice as the CM parent-body, a loss of ~50% of the H at low temperature (~0°C) by Rayleigh fractionation is able to reproduce the H budget of Tagish Lake (Figure 2). The work present here suggests that the D-rich composition of Tagish Lake's water may reflect only secondary processes on its parent-body and argue against the accretion of cometary-like ice in D-type asteroids.
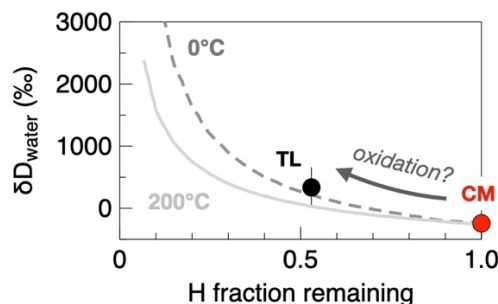

Figure 3: δD value of Tagish Lake (black) and CM chondrite (red) water *vs.* their bulk H concentrations relative to CM chondrites. The calculated δD values of the remaining water after loss of H$_2$ from metal oxidation by Rayleigh fractionation at 0°C and 200°C is indicated by solid and dashed gray curves, respectively (adapted from [18], errors are 2σ).

References: [1] Kanno M. A. et al. (2003) *Geophys. Res. Lett., 30(17),* 1909. [2] Barucci M. A. et al. (2018) *MNRAS, 476,* 4481–4487. [3] DeMeo F. E. et al. (2014) *Nature, 505,* 629–634. [4] Levison H. F. et al. (2009) *Nature, 460,* 364–366. [5] Hiroi T. et al. (2001) *Science, 293,* 2234–2236. [6] Nakamura-Messenger K. et al., (2006) *Science, 314,* 1439–1442. [7] Brown T. et al. (2000) *Science, 290,* 320–325. [8] Fujiya W. et al. (2019) *Nat. Astro., 3,* 910–915. [9] Zolensky M. E. et al. (2002) *MAPS, 37,* 737–761. [10] Alexander C. M. O'D. et al. (2012) *Science, 337,* 721–723. [11] Alexander C. M. O'D. et al. (2013) *GCA, 123,* 244–260. [12] Orthous-Daunay F. R. et al. (2013) *Icarus, 223,* 534–543. [13] https://presolar.physics.wustl.edu/meteorite−deep−zoom/tagish−lake. [14] Patzek M. et al. (2020) *GCA, 272,* 177–197. [15] van Kooten E. M.M.E. et al. (2019) *GCA, 237,* 79–102. [16] Piani L. et al. (2015) *EPSL, 415,* 154–164. [17] Piani L. et al. (2018) *Nat. Astron., 2,* 317–323. [18] Piani L. and Marrocchi Y. al. (2018) *EPSL, 504,* 64–71. [19] Sutton S. et al. (2017) *GCA, 211,* 115–132. [20] Vacher et al. (2020) *GCA, 3,* 53–66.