

**HYDROGEN ISOTOPIC COMPOSITION OF WATER IN THE UNGROUPED CARBONACEOUS CHONDRITE TAGISH LAKE.** L. G. Vacher<sup>1</sup>, R. C. Ogliore<sup>1</sup> and N. Liu<sup>1</sup>. <sup>1</sup>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 <sup>15</sup>N organic globules, possibly similar to cometary (CHON) particles [6] and (ii) abundant <sup>13</sup>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 ( $\delta D$ , relative to SMOW) of its water is poorly constrained, but appears to be significantly depleted in D (inferred  $\delta D_{TL}$  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  $\delta D$  value of the water in Tagish Lake from *in-situ* Si/H and  $\delta D$  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 ( $\sim 7,700$  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 per-

formed with the Wash U NanoSIMS using  $\sim 10$  pA primary beam for meteoritic samples and  $\sim 2$  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 ( $15 \times 15 \mu\text{m}$ ,  $256 \times 256$  pixels) were collected simultaneously in multi-collection mode on EMs by combined peak switching (magnetic field #1: H, D<sup>-</sup> and magnetic field #2: <sup>18</sup>O, <sup>12</sup>C<sup>14</sup>N<sup>-</sup> and <sup>28</sup>Si<sup>-</sup>). An area of  $\sim 20 \times 20 \mu\text{m}$  was presputtered using a  $\sim 100$  pA beam before each measurement for  $\sim 1$ h to remove the C coat and residual adsorbed water from the surface of the samples. Measurements were collected over  $\sim 100$  cycles with integration times of  $1500 \mu\text{s}/\text{px}/\text{plane}$  for H and D and  $500 \mu\text{s}/\text{px}/\text{plane}$  for <sup>18</sup>O, <sup>12</sup>C<sup>14</sup>N and <sup>28</sup>Si (Figure 1). Hydrogen isotope ratios of unknowns were normalized to deposited kerogen from the Warrawoona Group ( $\delta D = -105\%$ ) and epoxy resin sitting within the cracks of the meteoritic samples (assumed to have a  $\delta D$  value of  $0\%$ ). The NanoSIMS image data were processed using L’image software (L. R. Nittler).

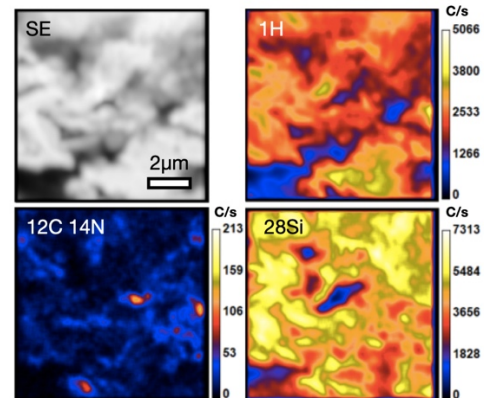


Figure 1: NanoSIMS ion images of SE, <sup>1</sup>H, <sup>12</sup>C<sup>14</sup>N and <sup>28</sup>Si of one phyllosilicates-rich matrix area of the CM Murchison.

**Results:** The  $\delta D$  values of Murchison and Maribo range between  $\sim -400$  and  $600 \pm 130\%$  ( $2\sigma$ ), and the phyllosilicates-rich matrix areas appear to be more depleted in D compared to the phyllosilicates-poor matrix. The  $\delta D$  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  $\delta D$  data suggest that this lithology is enriched in D compared to CM chondrites and range between  $\sim 600$  to  $1300 \pm 150\%$  ( $2\sigma$ ). These values are in good agreement with the  $\delta D$

values previously reported by [14] for Tagish Lake using a similar analytical condition. The  $\delta D$  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).

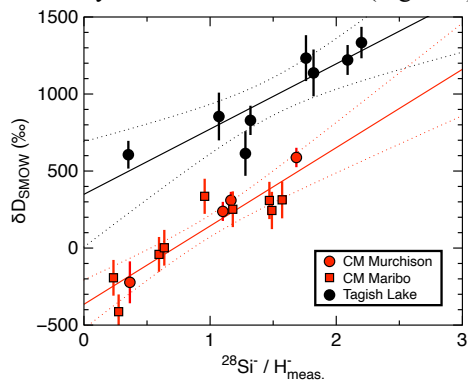


Figure 2:  $\delta D$  vs. Si/H (not corrected for different sensitivity factors between Si and H) plot of the hydrated matrix areas of CM chondrites (red) and Tagish Lake (black). Solid lines and dotted curves represent data regression and their 95% confidence intervals, respectively (errors are  $2\sigma$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

**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  $\delta D$  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  $\delta D$  value for water in Tagish Lake is significantly higher compared to that of the CM chondrites ( $\delta D_{CM} = -242 \pm 65\text{‰}$  vs.  $\delta D_{TL} = 335 \pm 335\text{‰}$ , vs.  $2\sigma$ ). Our estimate of  $\delta D$  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  $\sim 50\%$  of the H at low temperature ( $\sim 0^\circ\text{C}$ ) 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.

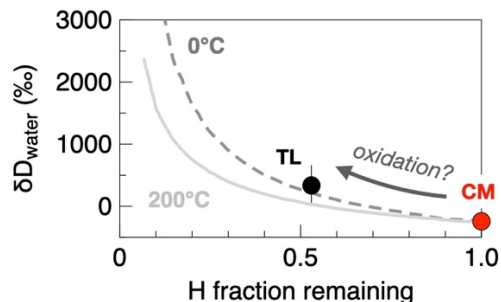


Figure 3:  $\delta D$  value of Tagish Lake (black) and CM chondrite (red) water vs. their bulk H concentrations relative to CM chondrites. The calculated  $\delta D$  values of the remaining water after loss of  $H_2$  from metal oxidation by Rayleigh fractionation at  $0^\circ\text{C}$  and  $200^\circ\text{C}$  is indicated by solid and dashed gray curves, respectively (adapted from [18], errors are  $2\sigma$ ).

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