PHYLLOSILICATE-LIKE SPECIES IN TAGISH LAKE METEORITE AS SEEN BY RAMAN SPECTROSCOPY. Alian Wang and Bradley Jolliff, Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University in St. Louis Rudolph Hall, One Brookings Drive, St. Louis, MO, 63130, USA. (alianw@levee.wustl.edu)

Tagish Lake Meteorite: The Tagish Lake meteorite (TL) is a fresh fall meteorite, observed on January 18, 2000, over the Northwest and Yukon territories and British Columbia, parts of which fell into the ice of frozen Tagish Lake. The collected samples were maintained in frozen state under unprecedentedly clean conditions [1]. TL is among the five meteorites with known pre-entry orbits. The calculated entry orbit of TL extends to the outer region of the asteroid belt where C, P, and D type asteroids predominate [1]. Its optical reflectance spectrum has a good match with the D-type asteroids [2], known to have hydrated silicates and suspected to be rich in carbon compounds.

Petrologic classification assigned the TL meteorite to be type 2, i.e., showing a moderate degree of low temperature alteration in the presence of water [3]. Oxygen isotopic studies suggested that it is close to primitive CI chondrites [4]. Geochemical data show that its closest match is CM chondrites for the elements that condense above 1340 K; but that it lies between CI and CM chondrites for the elements condensed below 1080 K [5]. In addition, TL contains far more carbon than either CI or CM chondrites, and far more nano-diamonds than any other meteorites. This characteristic suggests a formation farther out in the solar nebula than other meteorites [6]. In general, TL is recognized to be one of the most primitive meteorites.

We report a Raman spectroscopic and Raman imaging study of TL sample 10a, focusing on its *phyllosilicate-like* species. We also report the characterization of all molecular species. Our goal is two-fold: (1) determine the structural form of *phyllosilicate-like* species in the most primitive extra-terrestrial materials; and (2) application of Raman spectroscopy in missions to Mars, Moon, and asteroids, including Phobos and Deimos.

***Phyllosilicate-like* species in TL revealed by previous TEM and XRD studies:** Mg-rich serpentine, clinochlore, and saponite were first inferred from compositional data and TEM images in an investigation of mineralogy and petrology [3]. TEM images show the flakes assigned to *phyllosilicates* as having a small size of 0.3-0.4 μm and extremely thin (< 200 Å), e.g., < 20 stacked layers with a constant interlayer spacing of 14 Å. Another comparative TEM study [7] on *phyllosilicate-rich* meteorites (Tagish Lake, F96CI024, Y98M03IB15, M240U066, EURO020, and SAYAMA) shows the development of *phyllosilicate-like* structure (the length and thickness of stacked layers with a constant interlayer spacing) in TL is poorest among the six examined meteorites. Finally, the structural investigation of *phyllosilicate-like* species in TL using high quality XRD data [8] defined these species as "*poorly crystalline, fine-grained inter-layered saponite-serpentine*", on the basis of very broad saponite-serpentine XRD lines that suggest a high degree of structural disorder.

Characterization of phyllosilicates using Raman spectroscopy: As a non-destructive molecular characterization technique, Raman spectroscopy is very sensitive to the degree of polymerization of silicates. The distinction among ortho-, chain-, ring-, phyllo-, and tecto-silicates can be made by direct inspection of Raman spectral patterns [9]. For example, the existence of a Raman peak near 650-750 cm^{-1} is a straightforward indication of $Si\text{-}O_{bridging}\text{-}Si$ bond that exists in chain-, ring-, and phyllo-silicates. On the other hand, the existence of a Raman peak near 900-1100 cm^{-1} is a straightforward indication of an $Si\text{-}O_{non\text{-}bridging}$ bond that has a strong presence in the ortho- and chain-silicates, but very weak in others. Our recent paper [9] shows that each type of phyllosilicate has a fingerprint Raman spectrum. Furthermore, Raman spectral features are sensitive to the state of structural disorder. A totally amorphous structure would maintain the approximate major Raman peaks of a crystalline polymorph, but having much enlarged peak widths and weak peak intensities. Examples include the quenched silicate melts with polymerized Si_xO_y units similar to those in ortho-, chain-, ring-, phyllo-, and tecto-silicates [10]. For this reason, Raman peak width has been used to evaluate the crystallinity of a mineral phase. The above criteria are used in this Raman study of *phyllosilicate-like* species in TL.

Sample and Experiments: The TL meteorite sample 10A (TL-10a) was kindly provided by Dr. Chris Herd. It contains several aggregates, extremely porous, with light-toned chondrules embedded in dark matrix (Fig. 1). In the 1st set of Raman measurements, a few hundred Raman point-measurements were made on each of three aggregates, using a HoloLab5000 Raman system (Kaiser Optical System Inc.) with a cw green laser (532 nm) for excitation. This system has a very simi-

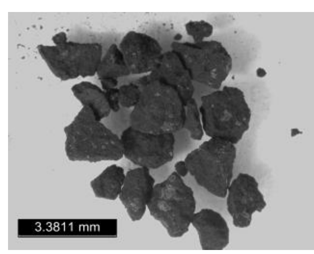
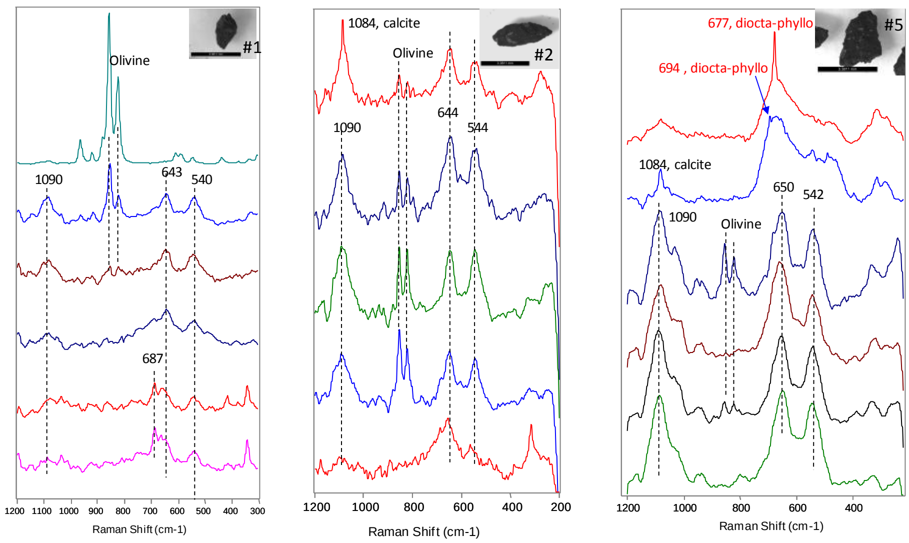


Figure 2. Typical Raman spectra of "phyllosilicate-like" species in three aggregates of TLM 10a



lar optical efficiency (F/2) to CIRS (Compact Integrated Raman System), developed under the MatISSE program. The main results are reported here. The 2nd set of Raman imaging measurements using an InVia Raman imager (Renishaw) will be reported at the conference.

Raman spectral features of *phyllosilicate-like* species in TL-10a and their structural meaning: Figure 2 shows typical Raman spectra that can be assigned to *phyllosilicate-like* species, obtained from three aggregates of TL-10A. These species were much more frequently encountered in TL-10a than in Murchison and Allende meteorites [11], which suggests a much higher abundance of *phyllosilicate-like* species in TL. In TL-10a, these species are mostly detected in chondrules, less often in the dark matrix.

Overall, we found the following Raman spectral features and their structural interpretations. (1) Besides the narrow peaks of olivine and calcite, two sets of strong Raman peaks occur near 1100 cm^{-1} and in the 540-700 cm^{-1} region, which indicates the existence of $Si\text{-}O_{non\text{-}bridging}$ and $Si\text{-}O_{bridging}\text{-}Si$ bonds in the structures of these species. The existence of $Si\text{-}O_{non\text{-}bridging}$ bonds means the lowest polymerization degree of the *phyllosilicate-like* species is similar to a chain-silicate. (2) The peak intensity ratios in the spectra, $Int_{900\text{-}1100cm^{-1}}/Int_{600\text{-}700cm^{-1}}$, are highly variable among those from different aggregates, or those from the same aggregate. In some spectra, the peak near 900-1100 cm^{-1} appears non-existent. This variation suggests that the degree of polymerization is highly variable, from chain-silicate-like to phyllosilicate-like; (3) Comparing with the narrow peak widths of olivine and calcite, those peaks assigned to *phyllosilicate-like* species all have broad peak widths, indicating low-crystallinity (in agreement with previous XRD studies); (4) a few spectra (top two spectra of aggregate #5) show a narrow Raman peaks at <700 cm^{-1} without a peak near 900-1100 cm^{-1} at comparable peak intensity. This type of spectral pattern matches with that of crystalline dioctahedral phyllosilicates (in agreement with previous TEM studies). However, the lack of peaks near 370-380 and 230 cm^{-1} for *serpentine*, 354 and 187 cm^{-1} for *saponite*, 544 and 354 cm^{-1} for *chlorite* (based on [9]), does not support their existence in grain #5 where the two Raman spectra were obtained. (5) The presence of a peak near 540 cm^{-1} in many spectra poses a question that needs further high spatial resolution Raman imaging investigation (the planned 2nd set of Raman measurements).

Other mineral phases in TL-10a: Carbon formed at different temperatures, nanodiamonds, olivine of different Fo values, orthopyroxene, two types of phosphates, calcite, dolomite, gypsum, goethite, titano-magnetite with low crystallinity, and sharp Raman peaks from organics were detected and characterized in TL-10a. Some of these molecular species were NOT detected previously by XRD, TEM and EMPA.

Fluorescence character of TL-10a: Under 532 nm excitation, the only fluorescence emission from a few spots appeared to have sharp peaks in the 660-690 nm region that are from electronic transitions of rare earth elements (REE), which did not obscure the Raman peaks.

Conclusions: Most of the *phyllosilicate-like* species in TL-10a, the most primitive meteorite known, has low-crystallinity and retain a polymerization degree similar to that of chain-silicates. Crystalline dioctahedral phyllosilicates only rarely occur.

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References: [1] Brown et al., (2000) *Science, 290,* 320; [2] Hiroi et al. (2001) *Science, 293,* 2234; [3] Zolensky et al., (2002) *MPS, 37,* 373; [4] Friedrich et al., (2002) *MPS, 37,* 677; [5] Mittlefehldt et al., (2002), *MPS, 37,* 703; [6] Grady et al., (2002) *MPS, 37,* p713; [7]Noguchi et al., (2002) *EPSL, 202,* 229; [8] Izawa et al., (2010) *MPS, 45,* 675; [9] Wang et al., (2014) *JRS, under revision;* [10] McMillan (1984) *Am. Mineral., 69,* 622; [11] Kong & Wang (2009) 41st LPSC, abs *#2730*.