IN SITU HEATING BEHAVIOR BY INFRARED MICROSPECTROSCOPY OF ORGANIC COMPONENTS IN TAGISH LAKE METEORITE.

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Introduction: The Tagish Lake meteorite is a new type of water- and carbon-rich carbonaceous chondrite [1,2]. Its total carbon content is ~ 5 wt% and the organic carbon content reaches ~1.3 wt% [1]. We reported from the Tagish Lake sample#TL3B6 the first *in situ* observation of the hollow organic globules (Fig.1) [3]. TL3B6 is generally enriched in the organic globules that consist of aliphatic and oxygenated functionality similar to the material produced by the laboratory simulation of UV photolysis of interstellar ice analogs[4] suggesting that the organic globules in Tagish Lake may be extremely primitive organic material that formed before or during the formation of the solar system.

Here we report the micro-sampling FTIR analysis of the TL3B6 and the *in situ* step heating experiments: which can allow us to place 1) significant constraints on the organic functionality in Tagish Lake; 2) the thermal stability of the organics; and 3) thermal history of the meteorite and its parent body. For comparison, the membranous films formed from hydrothermal reaction of an OH-bearing amino acid (theronine: Thr) and silica mixture [5] were examined.

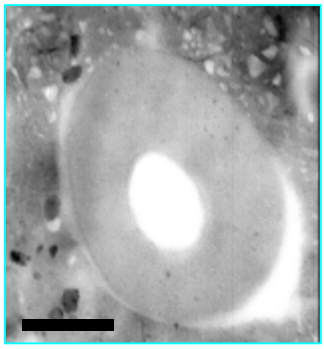

Fig.1: An organic globule in TL3B6 matrix, surrounded by fine-grained crystals of saponite with entangled ribbon-like structure. The dark grains dispersed in the matrix are sulfides. Scale bar equals 200nm.

Sample Preparation and Experimental Technique: Several fragments (100μm in size) from TL3B6 matrix were embedded in elemental sulfur and ultramicrotome thin sections were prepared for TEM investigation. The remainder of the sample in the sulfur was recovered and softly pressed into KBr plates for μFT-IR measurements by JASCO MFT-2000 and JASCO IRTRON. For the step heating experiments, multiple particle (~1mm in size) from TL3B6 matrix were softly pressed between two Al-foils. The Al-foils were opened and one side was set onto a well calibrated LINKAM 600 heating stage on the FT-IR microscopes. Once an organic-enriched area was detected, the location was stored and transmission-reflection spectra in the range 4000 – 700 cm^{-1} were collected at room temperature with a 100x100 μm aperture. The sample was then heated at 10 °C/min and spectra from the same location were collected at every 10 °C step. The film-like products formed on the Thr + Si solution surface heated ~160°C for two days [5] were prepared and measured in the same manner.

Results and Discussion: Figure 2 shows FTIR spectra collected from the initial sample (before heating) TL3B6 rich in organic compounds. The IR spectra show absorption features from phyllosilicates (Si-O) lattice vibration at 750 ~ 1110 cm^{-1} and interlayer water around 3400 cm^{-1}. However the structural hydroxyl at 3650 cm^{-1} was not resolved. The spectra show strong CH_2+CH_3 stretching vibrations due to aliphatic hydrocarbon at 2860, 2920 and 2950 cm^{-1} and C-H bending vibrations at ~1380 – 1460 cm^{-1}. Oxygenated functionality are also recognized at 1740 and 1710cm^{-1} (C=O) and at 1280 cm^{-1} (C-O) suggesting the presence of ester (RCOOR'). We believe that these organic features are delivered from the hollow organic globules observed by TEM (Fig.1).

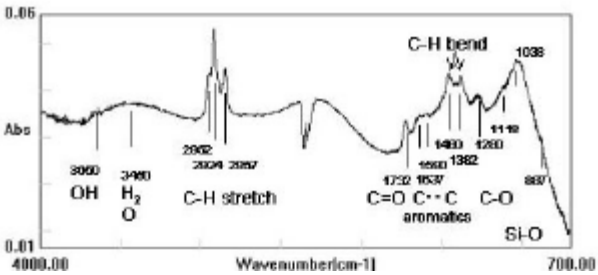

Fig.2: IR absorption spectrum of an initial organic–rich portion in a TL3B6 matrix fragment before the *in-situ* heating experiment.

Step Heating Experiments: After detecting organic-rich regions with the FTIR microscope (e.g. Fig.2), the samples were step-heated and the spectral changes were monitored up to 500°C:

Aliphatic C-H: Absorption bands at 2952, 2925 and 2854 cm^{-1} are due to C-H stretching vibrations of CH_3 and CH_2 groups (aliphatic hydrocarbons) (Fig.3). The intensity of these bands begin to decrease at 160 °C and disappear at 320°C (Fig.4).

C=O and C-O: Two absorption features are identified in the carbonyl (C=O) functional region at 1742 and 1712 cm^{-1}(Fig. 5). The 1712 cm^{-1} band might be due to

ketone and/or aldehyde and it disappears at 120°C. The 1742 cm^{-1} band might correspond to esters. It decreases from 240 °C and disappears at 320 °C (Fig.6). C-O stretching features in the 1160 to 1380 cm^{-1} behave in the same manner as the 1742 cm^{-1} band during heating, supporting the decomposition of esters.

Si-O and others: The Si-O stretching vibration near 980 cm^{-1} is stable until 500 °C. Compared to spectra from bulk Tagish Lake matrix [6], the present samples enriched in the hollow globules demonstrate a distinct enrichment in organics such as aliphatic hydrocarbons and esters. Note that the spectra from almost all other area in TL3B6 are dominated by strong features from phyllosilicates with structural hydroxyl at 3670 cm^{-1}, which is not recognized in the present organic-rich portions.

Thr+Si film product: The organic signatures of the membrane-like (polyester) products formed from hydrothermal reaction of Thr+Si [5] show strong similarities to the Tagish Lake sample (Fig.7. See also [7]). The hydrothermal reaction in [5] is consistent with the alteration conditions of Tagish Lake matrix, suggesting the possibility of membrane formation from organic-phyllosilicate mixtures. In the heating experiment of the polyester-like film product, the C-H stretching and C-H bending features disappear at 320 °C, although 1700-1750 cm^{-1} features possibly due to amide (CO-NH) bonds [7] remain until around 440 °C.

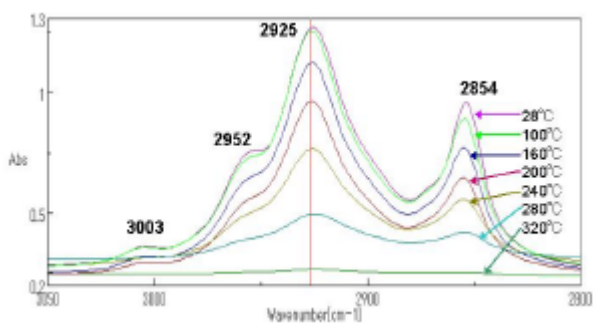

Fig.3: IR absorption spectra (3050-2800 cm^{-1}) of a TL3B6 matrix fragment showing C-H stretching vibration features before (28 °C) and during heating (100 to 320 °C).

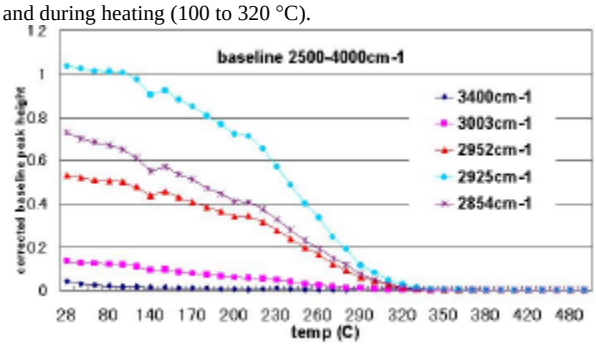

Fig.4: Changes of peak heights in the 3400-2800 cm^{-1} range after the baseline correction (4000-2500 cm^{-1}) during the step heating.

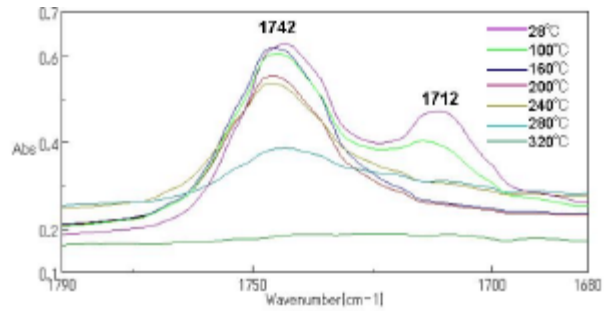

Fig.5: IR absorption spectra (1800-1680 cm^{-1}) of a TL3B6 matrix fragment showing two C=O functional features before (28 °C) and during heating (100 to 320 °C).

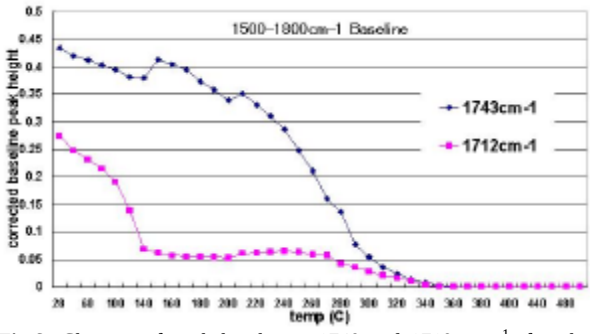

Fig.6: Changes of peak heights at 1740 and 1710 cm^{-1} after the baseline correction (1800-1500 cm^{-1}) during the step heating.

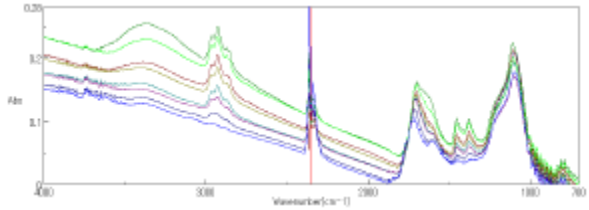

Fig.7: IR absorption spectra (4000-700 cm^{-1}) of the film products formed from hydrothermal reaction of Thr+Si during the step heating (28 °C: green, 120 °C: red, 320 °C: blue)

Conclusions: The organic rich portions of Tagish Lake show IR features of aliphatic C-H and C=O and C-O, similar to those of the film-like products formed from hydrothermal reaction of Thr and Si with polyester-like components, which are thermally stable up to 320 °C. The disappearance of the 1712 cm^{-1} band by the step heating experiments suggests that Tagish Lake may have never experienced temperature higher than 120 °C after the formation of membrane-like hollow organic globules.

References: [1] Brown P.G. et al., *Science*, 290, 320 (2000) [2] Zolensky M.E. et al. (2002) Meteoritcs Planet. Sci. 37, 737-761 [3] Nakamura K. et al. (2002) *Intl. J. Astrobio. 1*, 179-189. [4] Dworkin J.P. et al. (2001) *PNAS* 98, 815-819. [5] Shiota, D. & Nakashima, S. (2001) In: *Geochemistry & the Origin of Life*, p71-84. [6] Keller L.P.& Flynn G.J (2001) *LPSC* XXXIII, 1639. [7] Nakashima, S. & Shiota, D. (2001) In: *Geochemistry & the Origin of Life*, p135-177.