

IN-SITU HEATING DECREASE KINETICS OF ALIPHATIC HYDROCARBONS IN TAGISH LAKE

METEORITE BY MICRO-FTIR. Y. Kebukawa¹, S. Nakashima^{1,2} and M.E. Zolensky³ ¹Tokyo Institute of Technology, Tokyo 152-8521, Japan (yoko.soleil@geo.titech.ac.jp), ²Osaka University, Osaka 560-0043, Japan, ³NASA Johnson Space Center, Houston TX 77058

Introduction: Carbonaceous chondrites are known to contain up to 3wt.% C, the major part of which corresponds to a macromolecular organic fraction [1]. Chondritic organic matter is based on small aromatic units, cross-linked by short aliphatic chains rather than large clusters of polyaromatic structures [2]. Two main characteristic features of those organics measured by FTIR are (1) an equivalent intensity of the asymmetric stretching mode absorptions for CH₃ (2960cm⁻¹) and CH₂ (2920cm⁻¹) and (2) a lack of aromatic CH-stretching mode (3040cm⁻¹) [3]. Tagish Lake is a new type of water- and carbon-rich type 2 carbonaceous chondrite [4, 5]. Its total carbon content is ~5 wt%, of which the organic carbon content reaches ~1.3 wt% [4]. Tagish Lake may have never experienced temperatures higher than 120°C after formation of organics based on the disappearance of infrared (IR) organic peaks in step heating experiments [6].

Here we report *in-situ* kinetic heating experiments of organics in Tagish Lake by micro-FTIR to characterize the nature of aliphatic hydrocarbons and their thermal stabilities.

Experimental Methods: Particles from the Tagish Lake matrix (~100µm in diameter) were pressed between two Al foils using an oil pressure pump. The Al-foils were opened and one side was set onto a heating stage (LINKAM FTIR 600) on the micro-FTIR (JASCO FT-IR-620+IRT30). Once an organic-enriched area was detected, the location was stored and transmission-reflection spectra in the range 4000-700cm⁻¹ were collected at room temperature with a 100x100µm or 70x70µm aperture. The samples were heated at 100°C/min from room temperature to 160, 180, 200, 230, 250 and 260°C, and then spectra from the same locations were collected every 50sec or 120sec for 3 hours at a constant temperature. Temporal changes of aliphatic C-H stretching peak heights (2960, 2930 cm⁻¹) were analyzed quantitatively.

Results and Discussion: Figure 1 shows typical FTIR absorption spectra collected before heating. All the IR spectra show clay mineral Al-OH stretching at 3685cm⁻¹, interlayer water O-H stretching around 3400cm⁻¹, aliphatic C-H stretching of CH₂+CH₃ at 2960, 2930, 2870cm⁻¹, H-O-H bending at 1630cm⁻¹, aliphatic C-H bending at 1460 and 1410cm⁻¹ and phyllosilicates lattice Si-O stretching at 1100cm⁻¹. Several

grains show a band around 1700 cm⁻¹ (C=O stretching) together with bands around 1300 and 1265 cm⁻¹ (C-O stretching)(Fig.1a). The other type of grains have a band around 1780 cm⁻¹ and a sharp peak around 1265 cm⁻¹. The presence of these C=O and C-O bands were previously interpreted as indicative of polyester-like compounds [7].

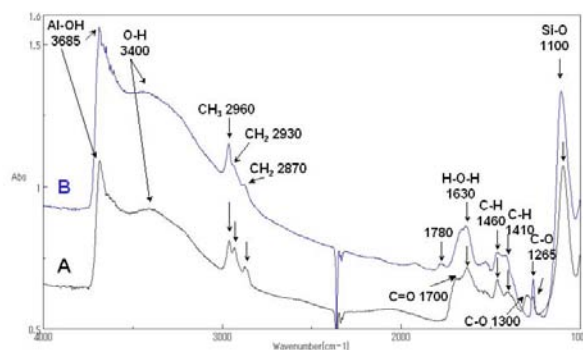


Fig.1: IR absorption spectra of the initial organic-rich portions in the Tagish Lake matrix fragments before heating experiments. A and B are from different parts of Tagish Lake.

Decrease of aliphatics upon heating: Figure 2 shows IR spectral change with time at 250°C in the 3400-2500cm⁻¹ range. Aliphatic C-H peaks decreased gradually with time. Peak heights of the 2960 and 2930 cm⁻¹ bands were determined with straight baselines at 3100-2800cm⁻¹ and their changes with time were plotted in Figure 3.

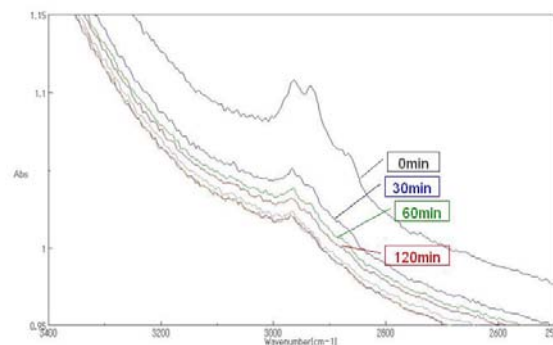


Fig.2: IR absorption spectra (3400-2500 cm⁻¹) of a Tagish Lake matrix fragment showing decrease of aliphatic C-H peaks while heating at 250°C from 0 min to 180 min.

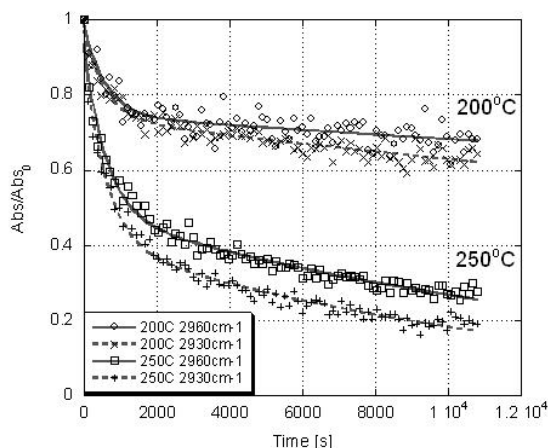


Fig.3: Changes of peak heights at 2960, 2930 cm^{-1} with a straight baseline (3100-2800 cm^{-1}) during heating at 200°C and 250°C of a Tagish Lake matrix fragment. The data were fitted by equation (1) to obtain first order rate constants k_1 and k_2 .

Kinetic analysis: The aliphatic C-H (2960, 2930 cm^{-1}) peak heights decreased rapidly for the first 1000 seconds and the decrease then became gentle for longer duration (Fig.3). These changes with time were found to be well fit by the following equation:

$$C = C_1 \exp(-k_1 t) + C_2 \exp(-k_2 t) \quad (1)$$

C_1 and C_2 are constants [Abs], k_1 and k_2 are the reaction rate constants [s^{-1}] and t is the time [s]. This equation corresponds to the sum of two first order reactions, indicating that the aliphatic C-H decrease includes the 'fast' and 'slow' reactions. The first order reaction rate constants k_1 and k_2 for aliphatic C-H decrease for each temperature were determined by fitting data sets with the above equation (Fig.3). These rate constants were plotted in an Arrhenius diagram (Fig.4). Activation energy E [kJ/mol] values were determined by fitting the data with the Arrhenius equation:

$$\ln k = \ln A - E / RT \quad (2)$$

A is the frequency factor [s^{-1}], R is the gas constant [J/K] and T is the absolute temperature [K]. Obtained activation energy E values of each reaction were 9 ± 8 kJ/mol for the fast reaction and 37 ± 11 kJ/mol for the slow reaction, respectively.

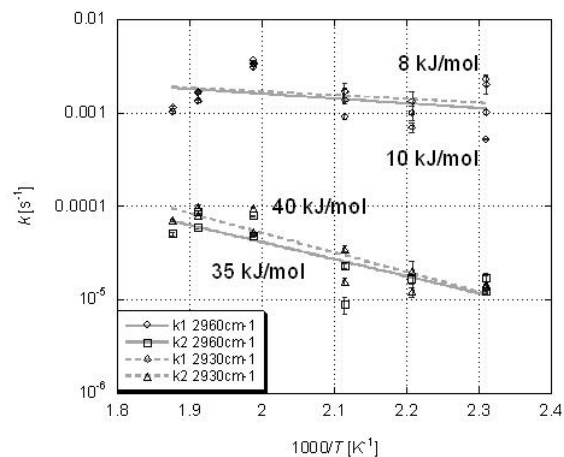


Fig.4: Arrhenius plots of aliphatic C-H (2960, 2930 cm^{-1}) decrease rate constants k_1 and k_2 for Tagish Lake matrix fragments. Activation energy E values of each reaction were 9 ± 8 and 37 ± 11 kJ/mol for the fast and slow reactions.

These kinetic data are now being compared with other carbonaceous chondrites. For example, the Orgueil (CI1 chondrite) showed similar decrease kinetics of aliphatics yielding the fast and slow reactions with similar rate constants. Aliphatic hydrocarbons in these carbonaceous chondrites are apparently mainly of two different groups, one being volatile and another being significantly more refractory.

Conclusions: Kinetic heating experiments of organic material in the Tagish Lake chondrite were conducted *in-situ* under a micro FTIR. Two types of aliphatic C-H groups were revealed by the kinetic analyses of their decrease with time: the fast and slow first order reactions with corresponding rate constants k_1 and k_2 . Activation energies for these aliphatic C-H decrease were 9 ± 8 and 37 ± 11 kJ/mol for the fast and slow reactions, respectively. Orgueil (CI1) has a similar aliphatic C-H nature. Aliphatic hydrocarbons in carbonaceous chondrites apparently consist of 2 different classes of compounds, one thermally fragile and the other being significantly more refractory.

References: [1] Hayes J. M. 1967 *Geochim. Cosmochim. Acta* 31 1395-440. [2] Gardinier A. *et al.* (2000) *Earth Planet. Sci. Lett.*, 184, 9-21. [3] Ehrenfreund P. *et al.* (2002) *Rep. Prog. Phys.*, 65, 1427-1487. [4] Brown P. G. *et al.* (2000) *Science*, 290, 320-325. [5] Zolensky M. E. *et al.* (2002) *Meteoritics Planet. Sci.*, 37, 737-761. [6] Nakamura K. *et al.* (2003) *LPSC*, XXXIV, 1432. [7] Nakamura K. *et al.* (2003) *Intl. J. Astrobiology*, 1, 179.