

Rapid contamination during storage of carbonaceous chondrites prepared for micro FTIR measurements

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Abstract

The carbonaceous chondrites Tagish Lake and Murchison, which contain abundant hydrous minerals, when pressed on aluminum plates and analyzed by micro FTIR, were found to have been contaminated during brief (24 hours) storage. This contamination occurred when the samples were stored within containers which included silicone rubber, silicone grease or adhesive tape. Long-path gas cell FTIR measurements for silicone rubber revealed the presence of contaminant volatile molecules having 2970 cm^{-1} (CH_3) and 1265 cm^{-1} (Si-CH_3) peaks. These organic contaminants are found to be desorbed by in-situ heating infrared measurements from room temperature to 200–300 °C. Careful preparation and storage are therefore needed for precious astronomical samples such as meteorites, IDPs and mission returned samples from comets, asteroids and Mars, if useful for FTIR measurements are to be made.

INTRODUCTION

Organic Components of Extraterrestrial Materials

Asteroids and comets could have provided the early Earth with life's precursor molecules, and studies of carbonaceous chondrite meteorites (presumably derived from primitive asteroids) provide a record of organic prebiotic chemistry in the early solar system (Pizzarello et al. 2006). Carbonaceous chondrites are known to contain up to a few wt.% of indigenous organic matter. The largest fraction (70–99%) of this is present as complex insoluble organic matter (IOM) (e.g., Pizzarello et al. 2006). In carbonaceous chondrites, the classes of soluble organic compounds that have familiar biochemical counterparts include amino acids, fatty acids, purines, pyrimidines and sugars (Botta and Bada 2002; Sephton 2002; Pizzarello et al. 2006). In addition, alcohols, aldehydes, amides, amines, mono- and di-carboxylic acids, aliphatic and aromatic hydrocarbons, heterocyclic aromatics, hydroxyl acids, ketones, phosphonic and sulfonic acids, sulfides as well as fullerenes have been reported (Botta and Bada 2002; Sephton 2002; Pizzarello et al. 2006).

IOM in chondrites is studied by numerous methods including solid state ^{13}C and ^{15}N nuclear magnetic resonance (NMR) (Cronin et al. 1987; Gardinier et al. 2000; Pizzarello et al. 2001; Cody et al. 2002; Cody and Alexander 2005; Remusat et al. 2005a; Yabuta et al. 2005), X-ray absorption near-edge structure (XANES) (Cody et al. 1999; Flynn et al. 1999; Derenne et al. 2002), electron paramagnetic resonance (EPR) (Duchesne et al. 1964; Schulz and Elofson 1965; Binet et al. 2002, 2004a, b; Gourier et al. 2004), chemical degradation (Bitz and Nagy 1966; Hayatsu et al. 1977, 1980; Remusat et al. 2005b), pyrolytic release studies (Studier et al. 1972; Levy et al. 1973; Bandurski and Nagy 1976; Komiya et al. 1993; Komiya and Shimoyama 1996; Sephton et al. 1999, 2000, 2004, 2005; Remusat et al. 2005a; Oba and Naraoka 2006; Yabuta et al. 2007), isotope studies (Naraoka et al. 1997; Alexander et al. 1998; Sephton et al. 1998, 2000, 2003; Becker et al. 1999; Sephton and Gilmour 2000; Wang et al. 2005; Oba and Naraoka 2006; Remusat et al. 2006; Alexander et al. 2007; Huang et al. 2007), Raman spectroscopy (Busemann et al. 2007) and Fourier transform infrared (FTIR)

spectroscopy (Hayatsu et al. 1977; Wdowiak et al. 1988; Ehrenfreund et al. 1991, 1992; Murae 1994; Kissin 2003).

There are also organic studies of both hydrous and anhydrous chondritic interplanetary dust particles (IDPs) (Sandford and Walker 1985; Bradley et al. 1992; Clemett et al. 1993; Flynn et al. 1998, 2002, 2003, 2004; Aléon et al. 2001, 2003; Matrajt et al. 2003, 2005, 2006; Keller et al. 2004; Quirico et al. 2005) as well coma dust grains from comet 81P/Wild 2 recently returned to Earth by the Stardust Spacecraft (Sandford et al. 2006; Keller et al. 2006; Cody et al., 2007).

Contamination Problems for Extraterrestrial Samples

A number of possible terrestrial contamination sources have already been suggested. Volatile organic compounds may be adsorbed onto the surface of a meteorite in the terrestrial environment (Murae 1995). The long chain *n*-alkanes that occurred in some meteorites extract were shown to be terrestrial contaminants by isotope analyses (Sephton et al. 2001). The long chain fatty acids (C₁₅ to C₁₈) in pyrolysate from some meteorites were suggested to be of biological origin, possibly from bacterial contaminants (Remusat et al. 2005a; Yabuta et al. 2007). Isoprenoid hydrocarbons reported in the Murchison meteorite were found to be terrestrial origin by means of isotopic analyses (Krishnamurthy et al. 1992). Sulfonic acid esters were reported to be identified by infrared spectra of solvent extracts of the Orgueil meteorite (Studier et al. 1965), but were subsequently suggested to be misidentified silicon oil contamination (Burlingame and Schnoes 1966). Phthalate esters and diisopropylnaphthalenes reported in Orgueil are known to be common laboratory contaminants (Watson et al. 2003).

Possible sources of terrestrial contaminants have been discussed by a number of authors. Studier et al. (1968) proposed automobile exhaust products as a source of contamination of aromatic compounds in meteorites. Plows et al. (2003) suggested that much of the atmospheric PAH pollution emitted from sources such as internal

combustion engines contains a large proportion of alkylated PAHs (Kawamura et al. 1994; Gingrich et al. 2001). Cronin and Pizzarello (1990) proposed possible airborne source of terrestrial contamination including petroleum distillates such as vacuum pump oils, lubricating fluids for rock saws for cutting meteorites, and plasticizers. The sesquiterpenoid derivatives detected in the Orgueil meteorite are essentially plant oil-derived terrestrial contaminants (Watson et al. 2003). The $\delta^{13}\text{C}$ values for the *n*-alkanes from carbonaceous chondrites are identical to those of petroleum-based products and other mixtures of fossil hydrocarbons (Sephton et al. 2001). The compounds pristane and phytane, found in some chondrites, are thought to be biological contaminants partly due to their structural specificity which is unlikely to be produced by abiotic processes (Cronin and Pizzarello 1990). Han et al. (1969) concluded that the Allende meteorite picked up a significant quantity of terrestrial biological contamination between its fall on February 8, 1969 and its collection on February 15, 1969, despite its falling into an arid environment in northern Mexico. Carbonaceous chondrites which have long terrestrial ages, such as Orgueil, can provide valuable evidence of the effects of long term exposure to potential terrestrial contaminants (Watson et al. 2003).

Despite these contamination problems, majority of chondritic organic matter can be assumed indigenous due to some evidences such as isotopic composition.

Infrared Spectroscopic Measurements

Fourier transform infrared (FTIR) spectroscopy is a non-destructive technique for organic components and minerals, and has been successfully applied to chondritic organic matter (Hayatsu et al. 1977; Wdowiak et al. 1988; Ehrenfreund et al. 1991, 1992; Salisbury et al. 1991; Murae 1994; Raynal et al. 2000; Flynn et al. 2001; Keller and Flynn 2001; Nakamura et al. 2002, 2003a; Kissin 2003; Matrajt et al. 2004) and hydrous and anhydrous chondritic IDPs (Sandford and Walker 1985; Bradley et al. 1992; Clemett et al. 1993; Flynn et al. 1998, 2002, 2003, 2004; Keller et al. 2004;

Matrajt et al. 2005), mainly based on aliphatic stretching features in the region 3000–2800 cm^{-1} .

Thermal stabilities of organic matter of carbonaceous chondrites also have been studied by FTIR spectroscopy. Nakamura et al. (2003a) conducted preliminary in-situ FTIR heating experiments of organic matter in the Tagish Lake meteorite and found varying thermal stabilities of different organic functional groups. Flynn et al. (2001) reported that the 3000–2800 cm^{-1} region of the infrared spectrum of Tagish Lake is similar to Orgueil and Murchison but that Tagish Lake contains an organic component that is lost on heating to 100 °C for 1/2 hour. Wdowiak et al. (1988) reported infrared spectra of an acid insoluble residue of Orgueil heated in vacuum up to 500°C which showed an increase of aromatic features at higher temperatures and a simultaneous decrease for aliphatic features.

The organic features of both bulk chondrites and IOM observed by FTIR have typically been considered to be of indigenous origin, since terrestrial contaminants are likely to be found in the free fraction (which is relatively susceptible to contamination) but not within the organic macromolecular component (which is less prone to contamination) (Watson et al. 2003), and the majority of organic matter (over 70 wt.%) in carbonaceous chondrites consists of IOM (e.g., Pizzarello et al. 2006). Furthermore, infrared spectra show similarities between interstellar carbonaceous grains and IOM, an equivalent intensity of the aliphatic C–H stretching absorptions for CH_3 (2960 cm^{-1}) and CH_2 (2920 cm^{-1}), and a lack of aromatic C–H stretching absorption (3040 cm^{-1}) (Ehrenfreund et al. 2002).

However, the C–H bands of infrared spectra taken from the surfaces of meteorites may arise at least in part from pollution of the laboratory environment with vacuum pump oils (Salisbury et al. 1991). Raynal et al. (2000) and Flynn et al. (2003, 2004) discuss the possibility of contamination of C–H stretching bands of IDPs due to the silicone oil which is used to capture IDPs. Infrared spectra of recently-investigated

comet Wild 2 coma grains showed organic features at $\sim 2900\text{ cm}^{-1}$ due to aliphatic C–H and 1706 cm^{-1} due to C=O, however aliphatic C–H features contain some contributions from the aerogel capture media (Sandford et al. 2006).

Here, we report a new type of rapid contamination (occurring within one day) due to volatile organic compounds from some laboratory materials commonly used for sample preparation and storage.

SAMPLES AND EXPERIMENTAL METHODS

Sample Preparation for Micro FTIR Spectroscopy

For the present Fourier transform infrared (FTIR) spectroscopic measurements, the sample powders were pressed between two aluminum plates (0.08 mm thick) using an oil pressure pump at about 100 kgw/cm^2 to make the sample flat and fixed on the aluminum plate. The two aluminum plates were then separated and the resultant flattened grains on an aluminum plate were used for infrared spectroscopy. In addition, sample powders were pressed between a KBr plate ($\sim 1\text{ mm}$ thick) and a platinum plate using an oil pressure pump at about 100 kgw/cm^2 , after which the platinum plate was removed. The samples fixed on the KBr plates were then used for infrared spectroscopy.

Infrared Microspectroscopy

A ceramic infrared light source, a Mercury-Cadmium-Telluride (MCT) detector and a $\times 16$ Cassegrain mirror were used for the FTIR spectroscopy (JASCO FT-IR-620+IRT30). The background spectra were collected on the aluminum plate or the KBr plate.

Transmission-reflection spectra (transmission spectra in the case of samples on KBr plates) were collected at room temperature in the range $4000\text{--}700\text{ cm}^{-1}$, with a $100 \times 100\text{ }\mu\text{m}^2$ aperture. Infrared incident light was first transmitted through the sample, which was typically a few tens of micrometers thick, then reflected off from the surface

of aluminum plate, and again transmitted through the sample. In the case of the samples fixed on the KBr plate transmission spectra were collected with infrared incident light passing through KBr and then the samples. In this instance the background spectra were collected on the sample-free area of the same KBr plate.

Contamination Characterization Experimental Procedures

Samples

The following samples were pressed on aluminum plates and stored in polystyrene trays with silicone rubber mats.

Carbonaceous chondrites: (1) Tagish Lake (ungrouped type 2 chondrite) fell in January of 2000 onto a frozen lake in Canada. Its matrix consists mainly of saponite, serpentine, Fe-Ni sulfides, carbonates, olivine and magnetite (Brown et al. 2000; Zolensky et al. 2002; Nakamura et al. 2003b). (2) Murchison (CM2) fell in 1969 in Australia. Its matrix consists mainly of serpentine, tochilinite, Fe-Ni sulfides, carbonates, olivine and Fe-Ni metal (Zolensky and McSween 1988; Zolensky et al. 1993). (3) Moss (CO3) fell in 2006 in Norway, and consists mainly of olivine, troilite and kamacite (Bischoff and Schmale 2007; Greenwood et al. 2007). Moss has an unusually low matrix-to-chondrule ratio (Greenwood et al. 2007).

Natural and synthetic minerals used were as follows. (1) Fine-grained antigorite ($(\text{Mg,Fe}^{2+})_3\text{Si}_2\text{O}_5(\text{OH})_4$) monoclinic, Nichika Corp., No. #14-4-12-1 from Nakanochaya, Miyatsu, Kyoto, Japan. (2) Muscovite ($\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$) from Ishikawa, Fukushima, Japan. Several small muscovite fragments were crushed to a fine powder using an alumina mortar and pestle. (3) Synthetic montmorillonite powder (pure (99%) sodium montmorillonite $\text{Na}_{0.33}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$), called Kunipia F ®, obtained from Kunimine Industries Co., Ltd.

Chemical reagents were as follows. (1) Silica gel, Wakosil C-300, 40–64 µm (spherical) from Wako Pure Chemical Industries, Ltd. (2) Silicon dioxide (SiO_2) from

Wako Pure Chemical Industries, Ltd. (3) Potassium bromide (KBr), from JASCO International Co., Ltd. A cubic crystal of KBr (~5 mm) was crushed to a fine powder using an alumina mortar and pestle.

Infrared spectra were collected immediately after sample preparation and then stored in a polystyrene tray with a silicone rubber mat for 14–30 hours in a desiccator. After this storage, infrared spectra of the same sample positions were measured again.

Contamination experiments with the silica gel

The silica gel samples were pressed on (1) an aluminum plate and (2) a KBr plate by the above methods. Infrared spectra were collected immediately after the sample preparation then stored in polystyrene trays with silicone rubber mats for 24–26 hours in a desiccator. After this storage, infrared spectra of the same sample positions were measured again.

In order to verify the contamination from storage containers, the silica gel samples pressed on aluminum plates were stored in the following five different ways: (1) in a glass petri dish wrapped in aluminum foil, (2) in an antistatic polystyrene case, (3) fixed with adhesive tape in a glass petri dish, which were then wrapped in aluminum foil, (4) fixed with silicone grease in glass petri dishes, which were then wrapped in aluminum foil, (5) in a polystyrene tray with a silicone rubber mat. All these sample storage containers were stored in a desiccator. After 16–26 hours of storage, infrared spectra of the same sample positions were measured.

Step Heating Experiments

Tagish Lake and antigorite on aluminum plates were set onto a heating stage (LINKAM FTIR 600) and placed into the micro FTIR. After measuring the sample spectra at room temperature, the samples were heated at 10 °C/min from room temperature up to 500°C using the heating stage. During the heating, sample spectra

were collected from the same location at every 10°C step. The temperature was kept constant during the collection of the sample spectra.

Microscopic ATR-IR and Gas Cell FTIR Analyses

Microscopic infrared attenuated total reflection (ATR-IR) analyses were performed using a JASCO MFT 2000 spectrometer using a microscopic ATR system (Jasco ×20 Micro ATR-VZ) equipped with an ATR crystal of ZnSe. Reflection spectra were obtained at a resolution of 4 cm⁻¹ with 100 scans for 240 × 240 μm regions. A silicone rubber mat and adhesive tape, which seemed to be contamination sources, were directly touched to the ATR crystal and then analyzed.

A long path gas cell (Infrared Analysis Inc., 10-PA) was used to measure infrared spectra of volatile compounds emitted from the silicone rubber mat. The infrared light pass length was 10m by 40-fold reflection and the volume was 2.3 L. The gas cell was attached to an FTIR spectrometer (Bomem MB154). Infrared spectra were measured at room temperature with an infrared light source, a MCT detector, and a CsI beam splitter (Ishikawa et al. 2007). The silicone rubber mat (10 × 10 cm) was placed into the gas cell. Then infrared spectra of the volatiles from the silicone rubber mat in the atmosphere (air) at room temperature were collected. Infrared spectra were first collected immediately after placing the silicone rubber mat in the gas cell, then every 10 minutes for a total of 26 hours. 128 scans were stacked at 1 cm⁻¹ resolution in the 7000–500 cm⁻¹ range.

RESULTS

Organic Contamination of Various Materials Stored in the Polystyrene Tray with a Silicone Rubber Mat

Samples pressed on aluminum plates stored in the polystyrene tray with the silicone

rubber mat were (1) Tagish Lake, (2) Murchison, (3) Moss, (4) antigorite, (5) muscovite, (6) montmorillonite, (7) silica gel, (8) silicon dioxide and (9) KBr.

Tagish Lake and Murchison samples show weak infrared absorption bands around 2900 and 1260 cm^{-1} . The height of these absorption bands increased after 24–30 hours of storage in the polystyrene tray with the silicone rubber mat (Figs. 1a, b and 2a, b). The organic features observed in the spectra and their possible interpretations are summarized in Table 1. The bands around 2963, 2940 and 2875 cm^{-1} are considered to be due to aliphatic C–H groups. The 2963 and 2875 cm^{-1} peaks are due to asymmetric and symmetric stretching vibrations of CH_3 , respectively, while the 2940 cm^{-1} peak is due to CH_2 vibrations. The 1262 cm^{-1} band can be assigned to C–O and/or Si– CH_3 bending vibrations. These organic features appeared to have increased for Tagish Lake and Murchison after storage. On the other hand, no organic features are detected on the Moss meteorite even after 24 hours of storage (Figs. 1c and 2c).

The infrared absorption spectra of Tagish Lake show a shoulder around 3650 cm^{-1} due to structural hydroxyl (O–H) (Fig. 1a). A broad O–H stretching band around 3400 cm^{-1} and an H–O–H bending band around 1630 cm^{-1} (Figs. 1a and 2a) are probably due to water molecules loosely adsorbed to minerals (Murae 1994) and as interlayer molecular water in phyllosilicates (Keller and Flynn 2001). Serpentine and saponite present in the matrix of Tagish Lake (Zolensky et al. 2002; Nakamura et al. 2003b), and 3650 and 3400 cm^{-1} bands correspond to these minerals. The absorption feature at 1450 cm^{-1} can be due to carbonates. The 1450 cm^{-1} band shows a slight increase after storage. This band might include contributions from aliphatic C–H bending vibration modes.

The infrared absorption spectra of Murchison show a broad O–H stretching band around 3400 cm^{-1} and an H–O–H bending band around 1640 cm^{-1} due to water molecules (Figs. 1b and 2b). The 1530 and 1460 cm^{-1} band appeared after storage. The 1530 cm^{-1} band is plausibly due to overtone or combination of Si–O stretching and bending vibrations. The 1460 cm^{-1} band is probably due to aliphatic C–H bending.

The infrared absorption spectra of Moss do not show particular bands at 4000–2500 cm^{-1} and 1800–1200 cm^{-1} region (Figs.1c and 2c). Noise at 4000–3500 cm^{-1} and 1800–1500 cm^{-1} were due to atmospheric water vapor. No significant spectral changes were observed following storage for 24 hours.

Some organic features appeared in the spectra of antigorite, muscovite, montmorillonite after 14–25 hours of storage (Figs. 1d, e, f and 2d, e, f) and silica gel, pressed on aluminum plates and stored in a polystyrene tray with silicone rubber (Figs. 1g and 2g). No organic features appeared in the spectra of silicon dioxide and KBr (Figs. 1h and 2h).

The infrared absorption spectra of antigorite show features at 3670 and 3570 cm^{-1} due to structural O–H. A broad O–H stretching band around 3440 cm^{-1} and an H–O–H bending band around 1640 cm^{-1} is due to adsorbed water molecules (Figs.1d and 2d). Infrared spectra of antigorite after 14 hours of storage show some organic absorption features. The 2963 and 2878 cm^{-1} peaks are due to asymmetric and symmetric stretching absorptions of CH_3 , respectively. The 2938 cm^{-1} peak is due to CH_2 groups. The 1260 cm^{-1} band is due to C–O and/or Si– CH_3 . A band around 1540 cm^{-1} might be due to overtone or combination of Si–O stretching and bending vibrations. The 1405 cm^{-1} band is probably due to Si– CH_3 and/or O–H. The 1470 cm^{-1} and 1370 cm^{-1} bands are probably due to aliphatic C–H bending.

The infrared absorption spectra of muscovite show features at 3640 cm^{-1} due to structural O–H. A broad O–H stretching band around 3400 cm^{-1} and an H–O–H bending band around 1640 cm^{-1} is due to adsorbed water molecules (Figs.1e and 2e). The 1260 cm^{-1} band can be due to C–O and/or Si– CH_3 which might represent contamination before our present sample preparation, because the muscovite sample was natural and not cleaned. Infrared spectra for muscovite after 25 hours of storage show some organic absorption features. The 2963 and 2873 cm^{-1} peaks are due to asymmetric and symmetric stretching absorptions of CH_3 , respectively. The 2938 cm^{-1} peak is due to

CH₂ groups. The 1545 cm⁻¹ band might be due to overtone or combination of Si–O stretching and bending vibrations. The 1400 cm⁻¹ band is probably due to Si–CH₃ and/or O–H. The 1465 cm⁻¹ band is probably due to aliphatic C–H bending.

The infrared absorption spectra of montmorillonite show features at 3630 cm⁻¹ due to structural O–H. A broad O–H stretching band around 3430 cm⁻¹ and an H–O–H bending band around 1650 cm⁻¹ due to interlayer water molecules (Figs.1f and 2f). Infrared spectra for montmorillonite after 25 hours of storage showed some organic absorption features. The 2965 and 2875 cm⁻¹ peaks are due to asymmetric and symmetric stretching absorptions of CH₃, respectively. The 2938 cm⁻¹ peak is due to CH₂ groups. The 1525 cm⁻¹ band might be due to overtone or combination of Si–O stretching and bending vibrations. The 1375cm⁻¹ band is probably due to aliphatic C–H bending.

The infrared absorption spectra of silica gel show a broad O–H stretching band around 3400 cm⁻¹ and an H–O–H bending band around 1630 cm⁻¹ due to adsorbed water (Figs.1g and 2g). Infrared spectra for silica gel after 26 hours of storage show some organic absorption features. The 2963 and 2880 cm⁻¹ peaks are due to asymmetric and symmetric stretching absorptions of CH₃, respectively. The 2940 cm⁻¹ peak is due to CH₂ groups. The 1465 and 1385 cm⁻¹ bands are probably due to aliphatic C–H bending. The 1700 cm⁻¹ bands is probably due to C=O. The 1520 cm⁻¹ band might be due to overtone or combination of Si–O stretching and bending vibrations. The 1410 cm⁻¹ band is probably due to Si–CH₃ and/or O–H. The 1262 cm⁻¹ band is due to C–O and/or Si–CH₃.

The infrared absorption spectra of silicon dioxide show bands at 2000–1000 cm⁻¹ region due to Si–O stretching absorption within silicates. A broad O–H stretching band around 3400 cm⁻¹ was due to adsorbed water molecules (Figs.1g and 2g). No significant spectral change was observed after storage for 25 hours.

The infrared absorption spectra of KBr show only interference fringes except a

broad O–H stretching band around 3450 cm^{-1} due to water molecules (Figs. 1h and 2h). No significant spectral change was observed after 25 hours of storage.

The spectra of Tagish Lake, Murchison, antigorite, muscovite, montmorillonite and silica gel showed organic features after storage while Moss, silicon dioxide and KBr did not. Table 1 shows the organic features observed in the spectra and their possible interpretations.

Contamination experiments with silica gel

Silica gel pressed on a KBr plate was stored in a polystyrene tray with a silicone rubber mat for 24 hours and on an aluminum plate for 26 hours. After storage some organic absorption features appeared for both of these silica gel samples (Figs. 1g, 2g and 3).

The infrared absorption spectra of silica gel pressed on KBr plate show a broad O–H stretching band around 3400 cm^{-1} and an H–O–H bending band around 1630 cm^{-1} due to adsorbed water molecules (Fig. 3). After 26 hours of storage on the aluminum plate the silica gel sample showed some organic absorption features. The 2965 and 2880 cm^{-1} peaks are due to asymmetric and symmetric stretching absorptions of CH_3 , respectively. The 2940 cm^{-1} peak is due to CH_2 groups. The 1705 cm^{-1} band is probably due to $\text{C}=\text{O}$. The 1530 cm^{-1} band might be due to overtone or combination of Si–O stretching and bending vibrations. The 1470 cm^{-1} band is probably due to aliphatic C–H bending. The 1410 cm^{-1} band is probably due to Si– CH_3 and/or O–H. The organic bands observed in the spectra and their possible assignments are listed in Table 1.

No organic features appeared on the spectra of silica gel pressed on aluminum plates stored in (1) a glass petri dish for 26 hours (Figs. 4a and 5a), or (2) an antistatic polystyrene case for 25 hours (Figs. 4b and 5b). The spectra of (3) the silica gel sample pressed on the aluminum plate, which was fixed with adhesive tape in a glass petri dish and stored for 25 hours show some organic absorption features (Figs. 4c and 5c). The

2957 and 2870 cm^{-1} peaks are due to asymmetric and symmetric stretching absorptions of CH_3 , respectively. The 1480, 1470, 1455, 1395 and 1367 cm^{-1} bands are probably due to aliphatic C–H bending (Table 1). The spectra of (4) the silica gel sample pressed on the aluminum plate, which was fixed with silicone grease in a glass petri dish and stored for 16 hours show some organic absorption features (Figs. 4d and 5d). The 2967 cm^{-1} peak is due to stretching absorptions of CH_3 . The 1410 cm^{-1} band is probably due to Si– CH_3 and/or O–H. The 1266 cm^{-1} band is due to C–O and/or Si– CH_3 (Table 1).

Changes with Time of the Organic Features of Silica Gel Samples

Fig. 6 shows changes with time of aliphatic C–H stretching peaks at 2965 cm^{-1} with 3000–2890 cm^{-1} baseline of silica gel stored in the polystyrene tray with a silicone rubber mat. The peak intensities for one sample position steadily increased during 50 hours of storage, and the other increased up to 28 hours, then leveled off. These results indicate the distinct possibility of saturation of organic adhesion within a few days.

Step Heating Experiments

In order to analyze quantitatively infrared spectral changes upon heating of Tagish Lake contaminated by silicone rubber, the following peak heights were determined with corresponding baselines; 2963 cm^{-1} peak with 3000–2950 cm^{-1} baseline and 1265 cm^{-1} peak with 1280–1255 cm^{-1} baseline. Changes in these organic peak heights during heating are presented in Fig. 7a, b (thick curves).

The aliphatic C–H absorption bands at 2963 cm^{-1} decreased rapidly from 100 to 300°C, and finally disappeared at 310–320°C. The 1265 cm^{-1} peak (Si– CH_3 and/or C–O) decreased gradually from 25°C up to approximately 200°C.

The following peak heights of contaminated antigorite were determined with corresponding baselines; 2963 cm^{-1} peaks with 3000–2950 cm^{-1} baseline and 1262 cm^{-1} peak with 1275–1255 cm^{-1} baseline. The aliphatic C–H absorption bands at 2963 cm^{-1}

decreased from 50 to approximately 300°C, and finally disappeared at 330–340°C. The 1262 cm⁻¹ peak (Si-CH₃ and/or C-O) decreased gradually from 40°C up to approximately 300°C (Fig. 7c, d; thin curves).

The ATR-IR and the Gas Cell FTIR Measurements

The ATR-IR spectra of the silicone rubber mat show asymmetric and symmetric stretching absorptions of CH₃ bands at 2962 and 2905 cm⁻¹, respectively (Fig. 8). The 1415 cm⁻¹ band is due to Si-CH₃. The 1257 cm⁻¹ band is due to Si-CH₃. 1060 and 1007 cm⁻¹ bands are due to Si-O. 864 and 785 cm⁻¹ bands are due to Si-C. The 2360 cm⁻¹ band is due to atmospheric CO₂.

The ATR-IR spectra of the adhesive tape show asymmetric and symmetric stretching absorptions of CH₃ bands at 2958 and 2872 cm⁻¹, respectively (Fig. 9). The 2931 cm⁻¹ band is due to stretching of CH₂. The 1455, 1395 and 1376 cm⁻¹ bands are probably due to aliphatic C-H bending. The 1729 cm⁻¹ band is due to C=O. The 1237, 1157, 1117, 1063, 1023, 940, 840 and 758 cm⁻¹ bands are due to C-O. The 2360 cm⁻¹ band is due to atmospheric CO₂.

The volatiles from the silicone rubber mat were measured by the gas cell FTIR. Infrared spectra were first collected immediately after placing the silicone rubber mat in the gas cell, then every 10 minutes for 26 hours. Fig. 10 shows a spectrum for volatiles from a silicone rubber mat in the atmosphere (air) of the gas cell after 3 hours. The 3250 cm⁻¹ band is due to O-H stretching of water molecules. The 2970 and 2905 cm⁻¹ bands are due to asymmetric and symmetric stretching absorptions of CH₃, respectively. The 1265 cm⁻¹ band is due to Si-CH₃. The 1080 cm⁻¹ band is due to Si-O. The 900, 850 and 810 cm⁻¹ bands are due to Si-C. Absorption intensities of these organic features rapidly increased within approximately one hour then increased slowly (Figs. 11 and 12).

DISCUSSION

Contamination from silicone rubber mat and adhesive tape

The hydrated carbonaceous chondrites Tagish Lake and Murchison were found to adsorb volatile organic compounds during storage with a silicon rubber mat after approximately one day. Organic contamination was also recognized on antigorite, muscovite, montmorillonite and silica gel following storage with a silicone rubber mat, silicone grease or adhesive tape. These samples were never directly in contact with a silicone rubber mat, silicone grease or adhesive tape. Therefore, organic volatile molecules from these latter materials must have been adsorbed on the samples. Only hydrated carbonaceous chondrites and hydrous minerals showed organic adsorption, suggesting the importance of surface OH groups of minerals for this process. The Moss meteorite, for example, which is completely anhydrous and thermally metamorphosed - Bischoff and Schmale (2007); Greenwood et al. (2007), showed no such contamination. One result of metamorphism is that Moss has distinctly lower porosity and permeability than the unmetamorphosed chondrites Murchison, Tagish Lake and Orgueil. These results are consistent with our micro FTIR mapping which showed that organic rich areas were included in the mineral OH rich areas of Tagish Lake (Kebukawa et al. 2007). Since the samples pressed on both aluminum and KBr plates were contaminated, the transmission-reflection measurement on aluminum plates is not the origin of the contamination.

The gas cell FTIR absorption bands of the volatile from the silicone rubber (Fig. 10) are similar to those in the ATR-IR spectrum of silicone rubber (Fig. 8), with some differences in peak positions. Degradation products of silicone rubber are reported to be primarily cyclic oligomers (Deshpande and Rezac 2001), particularly methylsiloxane oligomers which are decomposed and vaporized from polydimethylsiloxane, which is the major constituent of silicone rubber. Therefore, the infrared absorption bands at $1410\text{-}1400\text{ cm}^{-1}$ and $\sim 1260\text{ cm}^{-1}$ for the contaminated chondrites and mineral samples are considered to be due to Si-CH₃.

The spectral features of the volatile compounds from the silicone rubber (~ 2965 and $\sim 1260\text{ cm}^{-1}$ from Si-CH₃ groups) are similar to the contamination organics from the silicone rubber mat and silicone grease, except for the absence of a $\sim 1260\text{ cm}^{-1}$ band for montmorillonite (Fig. 2f). However, the $1545\text{--}1520\text{ cm}^{-1}$ band found on the samples stored with the silicone rubber mat was not found in either the gas cell spectrum or in the ATR-IR spectrum of the silicone rubber. Therefore these might be due to overtone or combination of Si-O stretching and bending vibrations which appears after adsorption of methylsiloxane, or another unknown organic contamination.

The organic contamination for the samples stored with adhesive tape can be explained primarily by the volatiles from the adhesive tape.

Volatile materials were detected immediately (within a few tens of minutes) after the placement of the silicone rubber mat in the gas cell (Fig. 11), indicating rapid release of significant amounts of volatiles from the silicone rubber. They were subsequently rapidly adsorbed on samples with hydrous minerals within a few hours (Fig. 6). The sample-containing polystyrene tray can be rapidly filled with volatile materials such as siloxane oligomers, which contaminate the samples during storage.

Heating Behavior of Contaminated Tagish Lake Meteorite and Antigorite

The IR observation of step heating behavior of Tagish Lake and antigorite samples (Fig. 7) should be evaluated by considering their contamination by volatile organic compounds from the silicone rubber. The 2963 cm^{-1} (CH₃) and $\sim 1265\text{ cm}^{-1}$ (Si-CH₃) peak heights of antigorite (Fig. 7c, d) showed a similar behavior - decreasing from room temperature to about 300°C . These results can be understood as arising from desorption of methylsiloxane-like contaminants. The departure of these contaminants up to 300°C is in agreement with the suggestion of Sephton et al. (2003) that the first release peak at 300°C of hydrous pyrolysis products of IOM is probably due to isotopically light terrestrial contamination. Nakamura et al. (2003a) reported that peaks at 2952 , 2925 and

2854 cm^{-1} due to aliphatic C–H bands began to decrease upon heating to 160°C, and disappeared at 320°C. The aliphatic C–H stretch at 2940 cm^{-1} of the acid insoluble residue of Orgueil remained after heating at 300°C in vacuum, but did not appear after heating at 415°C (Wdowiak et al. 1988). Therefore it is difficult to distinguish whether aliphatic features are indigenous or not.

The Si-CH₃ band at ~1265 cm^{-1} of Tagish Lake (Fig. 7b) and antigorite (Fig. 7d) showed a similar behavior - rapidly decreasing upon heating from room temperature. However, the disappearance of this band occurred at approximately 200°C for Tagish Lake and 300°C for antigorite. Since Tagish Lake contains clay minerals such as saponite in addition to serpentine minerals (Zolensky et al. 2002), this difference can be due to adsorption of methylsiloxane-like contaminants by the different clay mineral assemblage.

The CH₃ band at 2963 cm^{-1} of Tagish Lake (Fig. 7a) showed a different thermal behavior than the above results due to methylsiloxane-like contaminants. This band was more thermally stable than the contaminants, especially from room temperature to around 100°C. These results suggest the presence of other contaminants and/or indigenous organic compounds in the Tagish Lake meteorite, in accord with previous analyses (Pizzarello et al. 2001).

CONCLUSIONS

We examined organic contamination by micro FTIR measurements of carbonaceous chondrite samples, reaching the following critical conclusions.

1. The carbonaceous chondrites containing hydrous minerals (Tagish Lake and Murchison) pressed on aluminum plates and measured by transmission-reflection micro FTIR measurements were found to be contaminated during storage after only one day, as revealed by an increase of ~2965 cm^{-1} and ~1260 cm^{-1} peaks. The Moss meteorite which contains no

hydrous minerals, did not show an increase of these peaks, indicating no organic contamination. This difference is probably related to the differing mineralogy and physical properties (including porosity and permeability) of these chondrites.

2. Hydrous minerals such as antigorite, muscovite, montmorillonite and silica gel showed organic contamination by the same infrared measurements, while anhydrous materials such as SiO₂ and KBr showed no contamination. These results indicate importance of surface OH groups for the organic contamination.
3. This contamination occurred when the samples were stored within containers which included silicone rubber, silicone grease or adhesive tape.
4. Long path gas cell FTIR measurements for silicone rubber revealed the presence of volatile molecules having 2970 and 2905 cm⁻¹ (CH₃), 1265 cm⁻¹ (Si-CH₃), 1080 cm⁻¹ (Si-O) and 900, 850 and 800 cm⁻¹ (Si-C) peaks. These are considered to be methylsiloxane oligomers released from the silicone rubber.
5. In-situ heating infrared measurements on the contaminated antigorite showed a similar decrease of the 1262 cm⁻¹ (Si-CH₃) and 2963 cm⁻¹ (CH₃) peaks from room temperature to 300°C indicating desorption of volatile contaminants. On the other hand, the 2963 cm⁻¹ (CH₃) peak of the contaminated Tagish Lake meteorite showed more thermal stability (300°C) than the 1265 cm⁻¹ (Si-CH₃) peak from room temperature to 200°C. This result suggests the possibility of other contamination and/or indigenous organic compounds in the Tagish Lake meteorite.

These results indicate that careful preparation and storage are essential if one is to make FTIR measurements for precious astromaterial samples such as meteorites, IDPs and samples returned from comets, asteroids and Mars. Every possible contamination

source should be evaluated before anything is done to these samples. Very short exposure times are all that are needed to compromise valuable, and often irreplaceable samples.

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REFERENCES

- Aléon M., Engrand C., Robert F., and Chaussidon M. 2001. Clues to the origin of interplanetary dust particles from the isotopic study of their hydrogenbearing phases. *Geochimica et Cosmochimica Acta* 65:4399–4412.
- Aléon J., Robert F., Chaussidon M., and Marty B. 2003. Nitrogen isotopic composition of macromolecular organic matter in interplanetary dust particles. *Geochimica et Cosmochimica Acta* 67:3773–3783.
- Alexander C. M. O’D., Russell S. S., Arden J. W., Ash R. D., Grady M. M., and Pillinger C. T. 1998. The origin of chondritic macromolecular organic matter: A carbon and nitrogen isotope study. *Meteoritics & Planetary Science* 33:603–622.
- Alexander C. M. O’D., Fogel M., Yabuta H., and Cody G. D. 2007. The origin and evolution of chondrites recorded in the elemental and isotopic compositions of their macromolecular organic matter. *Geochimica et Cosmochimica Acta* 71:4380–4403.

- Bandurski E. L. and Nagy B. 1976. The polymer-like organic material in the Orgueil meteorite. *Geochimica et Cosmochimica Acta* 40:1397–1406.
- Becker L., Popp B., Rust T., and Bada J. 1999. The origin of organic matter in the Martian meteorite ALH84001. *Earth and Planetary Science Letters* 167:71–79.
- Binet L., Gourier D., Derenne S., and Robert F. 2002. Heterogeneous distribution of paramagnetic radicals in insoluble organic matter from the Orgueil and Murchison meteorites. *Geochimica et Cosmochimica Acta* 66:4177–4186.
- Binet L., Gourier D., Derenne S., Pizzarello S., and Becker L. 2004a. Diradicaloids in the insoluble organic matter from the Tagish Lake meteorite: Comparison with the Orgueil and Murchison meteorites. *Meteoritics & Planetary Science* 39:1649–1654.
- Binet L., Gourier D., Derenne S., Robert F., and Ciofini I. 2004b. Occurrence of abundant diradicaloid moieties in the insoluble organic matter from the Orgueil and Murchison meteorites: A fingerprint of its extraterrestrial origin? *Geochimica et Cosmochimica Acta* 68:881–891.
- Bischoff A. and Schmale K. 2007. Ca,Al-rich inclusions within the Moss CO3 chondrite - Indications for severe secondary alteration (abstract #1561). 38th Lunar and Planetary Science Conference. CD-ROM.
- Bitz M. C. and Nagy B. 1966. Ozonolysis of polymer-type material in coal kerogen and in Orgueil meteorite - a preliminary report. *Proceedings of the National Academy of Sciences of the United States of America* 56:1383–1390.
- Botta O. and Bada J. L. 2002. Extraterrestrial organic compounds in meteorites. *Surveys in Geophysics* 23:411–467.
- Bradley J. P., Humecki H. J., and Germani M. S. 1992. Combined infrared and analytical electron-microscope studies of interplanetary dust particles. *Astrophysical Journal* 394:643–651.
- Brown P. G., Hildebrand A. R., Zolensky M. E., Grady M., Clayton R. N., Mayeda T. K., Tagliaferri E., Spalding R., MacRae N. D., Hoffman E. L., Mittlefehldt D. W.,

- Wacker J. F., Bird J. A., Campbell M. D., Carpenter R., Gingerich H., Glatiotis M., Greiner E., Mazur M. J., McCausland P. J. A., Plotkin H., and Mazur T. R. 2000. The fall, recovery, orbit, and composition of the Tagish Lake meteorite: A new type of carbonaceous chondrite. *Science* 290:320–325.
- Burlingame A. L. and Schnoes H. K. 1966. Organic matter in carbonaceous chondrites. *Science* 152:104–106.
- Busemann H., Alexander C. M. O'D., and Nittler L. R. 2007. Characterization of insoluble organic matter in primitive meteorites by microRaman spectroscopy. *Meteoritics & Planetary Science* 42:1387–1416.
- Clemett S. J., Maechling C.R., Zare R. N., Swan P. D., and Walker R. M. 1993. Identification of complex aromatic-molecules in individual interplanetary dust particles. 1993. *Science* 262:721–725.
- Cody G. D. and Alexander C. M. O'D. 2005. NMR studies of chemical structural variation of insoluble organic matter from different carbonaceous chondrite groups. *Geochimica et Cosmochimica Acta* 69:1085–1097.
- Cody G. D., Alexander C. M. O'D., and Tera F. 1999. New insights into the chemistry of the Murchison macromolecule (abstract). *Meteoritics & Planetary Science* 34 (Suppl.):A25–A26.
- Cody G. D., Alexander C. M. O'D., and Tera F. 2002. Solid-state (^1H and ^{13}C) nuclear magnetic resonance spectroscopy of insoluble organic residue in the Murchison meteorite: A self-consistent quantitative analysis. *Geochimica et Cosmochimica Acta* 66:1851–1865.
- Cody G. D., Yabuta H., Alexander C. M. O'D., Araki T., Kilcoyne A. L. D., and The Stardust PET TEAM. 2007. Placing Comet 81P/Wild 2 organic particles into context with chondritic organic solids (abstract #2286). 38th Lunar and Planetary Science Conference. CD-ROM.
- Cronin J. R., Pizzarello S., and Frye J. S. 1987. ^{13}C NMR spectroscopy of the insoluble

- carbon of carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 51:299–303.
- Cronin J. R. and Pizzarello S. 1990. Aliphatic-Hydrocarbons of the Murchison meteorite. *Geochimica et Cosmochimica Acta* 54:2859–2868.
- Derenne S., Robert F., Binet L., Gourier D., Rouzand J. N., and Largeau C. 2002. Use of combined spectroscopic and microscopic tools for deciphering the chemical structure and origin of the insoluble organic matter in the Orgueil and Murchison meteorites (abstract #1182). 33rd Lunar and Planetary Science Conference. CD-ROM.
- Deshpande G. and Rezac M. E. 2001. The effect of phenyl content on the degradation of poly (dimethyl diphenyl) siloxane copolymers. *Polymer Degradation and Stability* 74:363–370.
- Duchesne J., Depireux J., and Litt C. 1964. Concerning the nature of free radicals in the Cold Bokkeveld meteorite. *Geochemistry international* 1, 1022–1024.
- Ehrenfreund P., Robert F., d’Hendecourt L., and Behar F. 1991. Comparison of interstellar and meteoritic organic matter at 3.4 microns. *Astronomy and Astrophysics* 252:712–717.
- Ehrenfreund P., Robert F., and d’Hendecourt L. 1992. Similarity of the infrared spectrum of an Orgueil organic polymer with interstellar organic compounds in the line of sight towards IRS 7. *Advances in Space Research* 12:53–56.
- Ehrenfreund P., Irvine W., Becker L., Blank J., Brucato J. R., Colangeli L., Derenne S., Despois D., Dutrey A., Fraaije H., Lazcano A., Owen T., Robert F., and International Space Science Institute ISSI-Team. 2002. Astrophysical and astrochemical insights into the origin of life. *Reports on Progress in Physics* 65:1427–1487.
- Flynn G. J., Keller L. P., and Miller M. A. 1998. FTIR Detection of Organic Carbon in Interplanetary Dust Particles (abstract #1157). 29th Lunar and Planetary Science

Conference.

- Flynn G. J., Keller L. P., Jacobsen C., and Wirick S. 1999. Element mapping and X-Ray absorption near edge structure (XANES) spectroscopy with a scanning transmission X-Ray microscope (abstract). *Meteoritics & Planetary Science* 34 (Suppl.):A36.
- Flynn G. J., Keller L. P., Jacobsen C., and Wirick S. 2001. FTIR and carbon-XANES examination of organic carbon in Tagish Lake: Evidence for a moderately volatile organic component (abstract #1593). 32nd Lunar and Planetary Science Conference. CD-ROM.
- Flynn G. J., Keller L. P., Joswiak D., and Brownlee D. E. 2002. Infrared analysis of organic carbon in anhydrous and hydrated interplanetary dust particles: FTIR identification of carbonyl (C=O) in IDPs (abstract #1320). 33rd Lunar and Planetary Science Conference. CD-ROM.
- Flynn G. J., Keller L. P., Feser M., Wirick S., and Jacobsen C. 2003. The origin of organic matter in the solar system: Evidence from the interplanetary dust particles. *Geochimica et Cosmochimica Acta* 67:4791–4806.
- Flynn G. J., Keller L. P., Jacobsen C., and Wirick S. 2004. An assessment of the amount and types of organic matter contributed to the Earth by interplanetary dust. *Advances in Space Research* 33:57–66.
- Gardinier A., Derenne S., Robert F., Behar F., Largeau C., and Maquet J. 2000. Solid state CP/MAS ¹³C NMR of the insoluble organic matter of the Orgueil and Murchison meteorites: quantitative study. *Earth and Planetary Science Letters* 184:9–21.
- Gingrich S. E., Diamond M. L., Stern G. A., and McCarry B. E. Atmospherically derived organic surface films along an urban-rural gradient. 2001. *Environmental Science & Technology* 35:4031–4037.
- Gourier D., Binet L., Sczypczak A., Derenne S., and Robert F. 2004. Search for EPR markers of the history and origin of the insoluble organic matter in extraterrestrial

- and terrestrial rocks. *Spectrochimica Acta Part A* 60:1349–1357.
- Greenwood R. C., Pearson V. K., Verchovsky A. B., Johnson D., Franchi I. A., Roaldset E., Raade G., and Bartoschewitz R. 2007. The Moss (CO₃) Meteorite: An Integrated Isotopic, Organic and Mineralogical Study (abstract #2267). 38th Lunar and Planetary Science Conference. CD-ROM.
- Han J., Simoneit B. R., Burlinga A. L., and Calvin M. 1969. Organic Analysis on Pueblito de Allende Meteorite. *Nature* 222:364–365.
- Hayatsu R., Matsuoka S., Anders E., Scott R. G., and Studier M. H. 1977. Origin of organic matter in the early solar system – VII. The organic polymer in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 41:1325–1339.
- Hayatsu R., Winans R. E., Scott R. E., McBeth R. L., Moore L. P., and Studier M. H. 1980. Phenolic ethers in the organic polymer of the Murchison meteorite. *Science* 207:1202–1204.
- Huang Y., Alexandre M. R., and Wang Y. 2007. Structure and isotopic ratios of aliphatic side chains in the insoluble organic matter of the Murchison carbonaceous chondrite. *Earth and Planetary Science Letters* 259:517–525.
- Ishikawa K., Tani A., Otsuka T., and Nakashima S. 2007. Transformation of gamma-ray-formed methyl radicals in methane hydrate at 10 Mpa. *Japanese Journal of Applied Physics* 46:455–460.
- Kawamura K., Suzuki I., Fujii Y., and Watanabe O. 1994. Ice core record of polycyclic aromatic-hydrocarbons over the past 400 years. *Naturwissenschaften* 81:502–505.
- Kebukawa Y., Ishikawa M., Nakashima S., Nakamura T., and Zolensky M. E. 2007. Infrared microspectroscopic mapping of organic matter in Tagish Lake meteorite for studying organic evolution during aqueous alteration (abstract #1450). 38th Lunar and Planetary Science Conference. CD-ROM.
- Keller L. P. and Flynn G. J. 2001. Matrix Mineralogy of the Tagish Lake Carbonaceous Chondrite: TEM and FTIR Studies (abstract #1639). 32nd Lunar and Planetary

Science Conference. CD-ROM.

- Keller L. P., Messenger S., Flynn G. J., Clemett S., Wirick S., and Jacobsen C. 2004. The nature of molecular cloud material in interplanetary dust. *Geochimica et Cosmochimica Acta* 68:2577–2589.
- Keller L. P., Bajt S., Baratta G. A., Borg J., Bradley J. P., Brownlee D. E., Busemann H., Brucato J. R., Burchell M., Colangeli L., d'Hendecourt L., Djouadi Z., Ferrini G., Flynn G., Franchi I. A., Fries M., Grady M. M., Graham G. A., Grossemy F., Kearsley A., Matrajt G., Nakamura-Messenger K., Mennella V., Nittler L., Palumbo M. E., Stadermann F. J., Tsou P., Rotundi A., Sandford S. A., Snead C., Steele A., Wooden D., Zolensky M. 2006. Infrared spectroscopy of Comet 81P/Wild 2 samples returned by Stardust. *Science* 314:1728–1731.
- Kissin Y. V. 2003. Hydrocarbon components in carbonaceous meteorites. *Geochimica et Cosmochimica Acta* 67:1723–1735.
- Komiya M., Shimoyama A., and Harada K. 1993. Examination of organic-compounds from insoluble organic-matter isolated from some Antarctic carbonaceous chondrites by heating experiments. *Geochimica et Cosmochimica Acta* 57:907–914.
- Komiya M. and Shimoyama A. 1996. Organic compounds from insoluble organic matter isolated from the Murchison carbonaceous chondrite by heating experiments. *Bulletin of the Chemical Society of Japan* 69:53–58.
- Krishnamurthy R. V., Epstein S., Cronin J. R., Pizzarello S., and Yuen G. U. 1992. Isotopic and molecular analyses of hydrocarbons and monocarboxylic acids of the Murchison meteorite. *Geochimica et Cosmochimica Acta* 56:4045–4058.
- Levy R. L., Grayson M. A., and Wolf C. J., 1973. The organic analysis of the murchison meteorite. *Geochimica et Cosmochimica Acta* 37:467–483.
- Matrajt G., Taylor S., Flynn G., Brownlee D., and Joswiak D. 2003. A nuclear microprobe study of the distribution and concentration of carbon and nitrogen in Murchison and Tagish Lake meteorites, Antarctic micrometeorites, and IDPs:

- Implications for astrobiology. *Meteoritics & Planetary Science* 38:1585–1600.
- Matrajt G., Borg J., Raynal P. I., Djouadi Z., d'Hendecourt L., Flynn G., and Deboffle D. 2004. FTIR and Raman analyses of the Tagish Lake meteorite: Relationship with the aliphatic hydrocarbons observed in the Diffuse Interstellar Medium. *Astronomy and Astrophysics* 416:983–990.
- Matrajt G., Caro G. M. M., Dartois E., d'Hendecourt L., Deboffle D., and Borg J. 2005. FTIR analysis of the organics in IDPs: Comparison with the IR spectra of the diffuse interstellar medium. *Astronomy and Astrophysics* 433:979–995.
- Matrajt G., Brownlee D., Sadilek M., and Kruse L. 2006. Survival of organic phases in porous IDPs during atmospheric entry: A pulse-heating study. *Meteoritics & Planetary Science* 41:903–911.
- Murae T. 1994. FT-IR spectroscopic studies of major organic matter in carbonaceous chondrites using microscopic technique and comparison with terrestrial kerogen. *Proceedings of the NIPR Symposium on Antarctic Meteorites* 7:262–274.
- Murae T. 1995. Characterization of extraterrestrial high-molecular-weight organic-matter by pyrolysis-gas chromatography mass-spectrometry. *Journal of Analytical and Applied Pyrolysis* 32:65–73.
- Nakamura K., Zolensky M. E., Tomita S., Nakashima S., and Tomeoka K. 2002. Hollow organic globules in the Tagish Lake meteorite as possible products of primitive organic reactions. *International Journal of Astrobiology* 1:179–189.
- Nakamura K., Nakashima S., Shiota D., Zolensky M. E., and Keller L. P. 2003a. In Situ Heating Behavior by Infrared Microspectroscopy of Organic Components in Tagish Lake Meteorite (abstract #1432). 34th Lunar and Planetary Science Conference. CD-ROM.
- Nakamura T., Noguchi T., Zolensky M. E., and Tanaka M. 2003b. Mineralogy and noble-gas signatures of the carbonate-rich lithology of the Tagish Lake carbonaceous chondrite: evidence for an accretionary breccia. *Earth and Planetary*

Science Letters 207:83–101.

- Naraoka H., Shimoyama A., Matsubaya O., and Harada K. 1997. Carbon isotopic compositions of Antarctic carbonaceous chondrites with relevance to the alteration and existence of organic matter. *Geochemical Journal* 31:155–168.
- Oba Y. and Naraoka H. 2006. Carbon isotopic composition of acetic acid generated by hydrous pyrolysis of macromolecular organic matter from the Murchison meteorite. *Meteoritics & Planetary Science* 41:1175–1181.
- Pizzarello S., Huang Y., Becker L., Poreda R. J., Nieman R. A., Cooper C., and Williams M. 2001. The organic content of the Tagish Lake meteorite. *Science* 293:2236–2239.
- Pizzarello S., Cooper G. W., and Flynn G. J. 2006. The nature and distribution of the organic material in carbonaceous chondrites and interplanetary dust particles. In *Meteorites and the early solar system II*, edited by Lauretta D. S., Leshin L. A., and McSween H. Y., Jr. Tucson, Arizona: The University of Arizona Press. pp. 625–651.
- Plows F. L., Elsila J. E., Zare R. N., and Buseck P. R. 2003. Evidence that polycyclic aromatic hydrocarbons in two carbonaceous chondrites predate parent-body formation. *Geochimica et Cosmochimica Acta* 67:1429–1436.
- Quirico E., Borg J., Raynal P. I., Montagnac G., and d'Hendecourt L. 2005. A micro-Raman survey of 10 IDPs and 6 carbonaceous chondrites. *Planetary and Space Science* 53:1443–1448.
- Raynal P. I., Quirico E., Borg J., Deboffe D., Dumas P., d'Hendecourt L., Bibring J. P., and Langevin Y. 2000. Synchrotron infrared microscopy of micron-sized extraterrestrial grains. *Planetary and Space Science* 48:1329–1339.
- Remusat L., Derenne S., Robert F., and Knicker H. 2005a. New pyrolytic and spectroscopic data on Orgueil and Murchison insoluble organic matter: A different origin than soluble? *Geochimica et Cosmochimica Acta* 69:3919–3932.
- Remusat L., Derenne S., and Robert F. 2005b. New insight on aliphatic linkages in the

- macromolecular organic fraction of Orgueil and Murchison meteorites through ruthenium tetroxide oxidation. 2005. *Geochimica et Cosmochimica Acta* 69:4377–4386.
- Remusat L., Pálhol F., Robert F., Derenne S., and France-Lanord C. 2006. Enrichment of deuterium in insoluble organic matter from primitive meteorites: A solar system origin? *Earth and Planetary Science Letters* 243:15–25.
- Salisbury J. W., d'Aria D. M., and Jarosewich E. 1991. Midinfrared (2.5-13.5 microns) reflectance spectra of powdered stony meteorites. *Icarus* 92:280–297.
- Sandford S. A. and Walker R. M. 1985. Laboratory infrared transmission spectra of individual interplanetary dust particles from 2.5 to 25 microns. *Astrophysical Journal* 291:838–851.
- Sandford S. A., Aléon J., Alexander C. M. O'D., Araki T., Bajt S., Baratta G. A., Borg J., Bradley J. P., Brownlee D. E., Brucato J. R., Burchell M. J., Busemann H., Butterworth A., Clemett S. J., Cody G., Colangeli L., Cooper G., d'Hendecourt L., Djouadi Z., Dworkin J. P., Ferrini G., Fleckenstein H., Flynn G. J., Franchi I. A., Fries M., Gilles M. K., Glavin D. P., Gounelle M., Grossemy F., Jacobsen C., Keller L. P., Kilcoyne A. L. D., Leitner J., Matrajt G., Meibom A., Mennella V., Mostefaoui S., Nittler L. R., Palumbo M. E., Papanastassiou D. A., Robert, F., Rotundi A., Snead C. J., Spencer M. K., Stadermann F. J., Steele A., Stephan T., Tsou P., Tyliszczak T., Westphal A. J., Wirick S., Wopenka B., Yabuta H., Zare R. N., and Zolensky M. E. 2006. Organics captured from Comet 81P/Wild 2 by the Stardust spacecraft. *Science* 314:1720–1724.
- Sephton M. A. 2002. Organic compounds in carbonaceous meteorites. *Natural Product Reports* 19:292–311.
- Sephton M. A. and Gilmour I. 2000. Pyrolysis-gas chromatography-isotope ratio mass spectrometry of macromolecular material in meteorites. *Planetary and Space Science* 49:465–471.

- Sephton M. A., Pillinger C. T., and Gilmour I. 1998. $\delta^{13}\text{C}$ of free and macromolecular aromatic structures in the Murchison meteorite. *Geochimica et Cosmochimica Acta* 62:1821–1828.
- Sephton M. A., Pillinger C. T., and Gilmour I. 1999. Small-scale hydrous pyrolysis of macromolecular material in meteorites. *Planetary and Space Science* 47:181–187.
- Sephton M. A., Pillinger C. T., and Gilmour I. 2000. Aromatic moieties in meteoritic macromolecular materials: Analyses by hydrous pyrolysis and $\delta^{13}\text{C}$ of individual compounds. *Geochimica et Cosmochimica Acta* 64:321–328.
- Sephton M. A., Pillinger C. T., and Gilmour I. 2001. Normal alkanes in meteorite : molecular $\delta^{13}\text{C}$ values indicate an origin by terrestrial contamination. *Precambrian Research* 106:47–58.
- Sephton M. A., Verchovsky A. B., Bland P. A., Gilmour I., Grady M. M., and Wright I. P. 2003. Investigating the variations in carbon and nitrogen isotopes in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 67:2093–2108.
- Sephton M. A., Love G. D., Watson J. S., Verchovsky A. B., Wright I. P., Snape C. E., and Gilmour I. 2004. Hydropyrolysis of insoluble carbonaceous matter in the Murchison meteorite: New insights into its macromolecular structure. *Geochimica et Cosmochimica Acta* 68:1385–1393.
- Sephton M. A., Love G. D., Meredith W., Snape C. E., Sun C. G., and Watson J. S. 2005. Hydropyrolysis: A new technique for the analysis of macromolecular material in meteorites. *Planetary and Space Science* 53:1280–1286.
- Schulz K. F. and Eloffson R. M. 1965. Electron spin resonance studies of organic matter in the Orgueil meteorite. *Geochimica et Cosmochimica Acta* 29:157–160.
- Studier M. H., Hayatsu R., and Anders E. 1965. Organic compounds in carbonaceous chondrites. *Science* 149:1455–1459.
- Studier M. H., Hayatsu R., and Anders E. 1968. Origin of organic matter in early solar system – I. Hydrocarbons. *Geochimica et Cosmochimica Acta* 32:151–173.

- Studier M. H., Hayatsu R., and Anders E. 1972. Origin of organic matter in early solar system – V. Further studies of meteoritic hydrocarbons and a discussion of their origin. *Geochimica et Cosmochimica Acta* 36:189–215.
- Wang Y., Huang Y. S., Alexander C. M. O'D., Fogel M., and Cody G. 2005. Molecular and compound-specific hydrogen isotope analyses of insoluble organic matter from different carbonaceous chondrite groups. *Geochimica et Cosmochimica Acta* 69:3711–3721.
- Watson J. S., Pearson V. K., Gilmour I., and Sephton M. A. 2003. Contamination by sesquiterpenoid derivatives in the Orgueil carbonaceous chondrite. *Organic Geochemistry* 34:37–47.
- Wdowiak T. J., Flickinger G. C., and Cronin J. R. 1988. Insoluble organic material of the Orgueil carbonaceous chondrite and the unidentified infrared bands. *Astrophysical Journal* 328: L75–L79.
- Yabuta H., Naraoka H., Sakanishi K., Kawashima H. 2005. Solid-state ¹³C NMR characterization of insoluble organic matter from Antarctic CM2 chondrites: Evaluation of the meteoritic alteration level. *Meteoritics & Planetary Science* 40: 779–787.
- Yabuta H., Williams L. B., Cody G. D., Alexander C. M. O'D., and Pizzarello S. 2007. The insoluble carbonaceous material of CM chondrites: A possible source of discrete organic compounds under hydrothermal conditions. *Meteoritics & Planetary Science* 42:37–48.
- Zolensky M. and McSween H.Y., Jr. 1988. Aqueous alteration. In *Meteorites and Early Solar System*, edited by Kerridge J. R. and Matthews M. S. Tucson, Arizona: The University of Arizona Press. pp. 114–143.
- Zolensky M. Barrett R., and Browning L. 1993. Mineralogy and composition of matrix and chondrules rims in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 57:3123–3148.

Zolensky M. E., Nakamura K., Gounelle M., Mikouchi T., Kasama T., Tachikawa O., and Tonui E. 2002. Mineralogy of Tagish Lake: An ungrouped type 2 carbonaceous chondrite. *Meteoritics & Planetary Science* 37:737–761.

Table 1. Infrared absorption peak positions in the contaminated samples and some simulated materials with their possible assignments.

Fig. 1. Infrared transmission-reflection spectra of 4000–2500 cm^{-1} regions of the samples pressed on aluminum plates before (thin curves) and after (thick curves) storage in the polystyrene tray with the silicone rubber mat for 14–30 hours. (a) Tagish Lake meteorite, (b) Murchison meteorite, (c) Moss meteorite, (d) antigorite, (e) muscovite, (f) montmorillonite, (g) silica gel and (h) silicon dioxide and KBr.

Fig. 2. Infrared transmission-reflection spectra of 1800–1200 cm^{-1} regions of the samples pressed on aluminum plates before (thin curves) and after (thick curves) storage in the polystyrene tray with the silicone rubber mat for 14–30 hours. (a) Tagish Lake meteorite, (b) Murchison meteorite, (c) Moss meteorite, (d) antigorite, (e) muscovite, (f) montmorillonite, (g) silica gel, and (h) silicon dioxide and KBr.

Fig. 3. Infrared transmission spectra of silica gel pressed on a KBr plate before (thin curves) and after (thick curves) storage in a polystyrene tray with silicone rubber mat for 26 hours. (a) 4000–2500 cm^{-1} regions, and (b) 1800–1200 cm^{-1} regions.

Fig. 4. Infrared transmission-reflection spectra of 4000–2500 cm^{-1} regions of silica gel pressed on aluminum plates before (thin curves) and after (thick curves) the following storage conditions for 16–26 hours: (a) in a glass petri dish wrapped by an aluminum foil, (b) in an antistatic polystyrene case, (c) fixed with adhesive tapes on a glass petri dish, which were then wrapped in aluminum foil, and (d) fixed with silicone grease on a glass petri dish, which were then wrapped in aluminum foil.

Fig. 5. Infrared transmission-reflection spectra of 1800–1200 cm^{-1} regions of silica gel

pressed on aluminum plates before (thin curves) and after (thick curves) the following storage conditions for 16–26 hours: (a) in a glass petri dish wrapped by an aluminum foil, (b) in an antistatic polystyrene case, (c) fixed with adhesive tapes on a glass petri dish, which were then wrapped in aluminum foil, and (d) fixed with silicone grease on a glass petri dish, which were then wrapped in aluminum foil.

Fig. 6. Changes with time of aliphatic C–H peak heights at 2965 cm^{-1} of silica gel stored in the polystyrene tray with a silicone rubber mat. The two different symbols represent different parts of the silica gel samples.

Fig. 7. Changes in organic peak heights upon heating of the Tagish Lake meteorite (thick curves) and antigorite (thin curves) samples contaminated by silicone rubber. (a) CH_3 peak at 2963 cm^{-1} and (b) Si-CH_3 peak at 1265 cm^{-1} of Tagish Lake (c) CH_3 peak at 2963 cm^{-1} and (d) Si-CH_3 peak at 1262 cm^{-1} of antigorite.

Fig. 8. The attenuated total reflection infrared (ATR-IR) spectra of the silicone rubber mat: 2962 and 2905 cm^{-1} bands are considered to be due to aliphatic C–H stretching vibration of CH_3 group; 1415 cm^{-1} band to Si-CH_3 ; 1257 cm^{-1} band to Si-CH_3 ; 1060 and 1007 cm^{-1} bands to Si-O ; 864 and 785 cm^{-1} bands to Si-C . The 2360 cm^{-1} band is due to atmospheric CO_2 .

Fig. 9. The attenuated total reflection infrared (ATR-IR) spectra of the adhesive tape: 2958 and 2872 cm^{-1} bands are considered to be due to aliphatic C–H stretching vibration of CH_3 group; 2931 cm^{-1} band to aliphatic C–H stretching vibration of CH_2 ; 1455 , 1395 and 1376 cm^{-1} bands to aliphatic C–H bending; 1729 cm^{-1} band to C=O ; 1237 , 1157 , 1117 , 1063 , 1023 , 940 , 840 and 758 cm^{-1} bands to C-O . The 2360 cm^{-1} band is due to atmospheric CO_2 .

Fig. 10. The infrared spectrum of volatiles from the silicone rubber mat in the air of the gas cell after 3 hours: 3250 cm^{-1} band is due to O–H stretching of water molecules, 2970 and 2905 cm^{-1} bands are due to CH_3 , 1265 cm^{-1} band to Si– CH_3 , 1080 cm^{-1} band to Si–O, and 900, 850 and 810 cm^{-1} bands to Si–C.

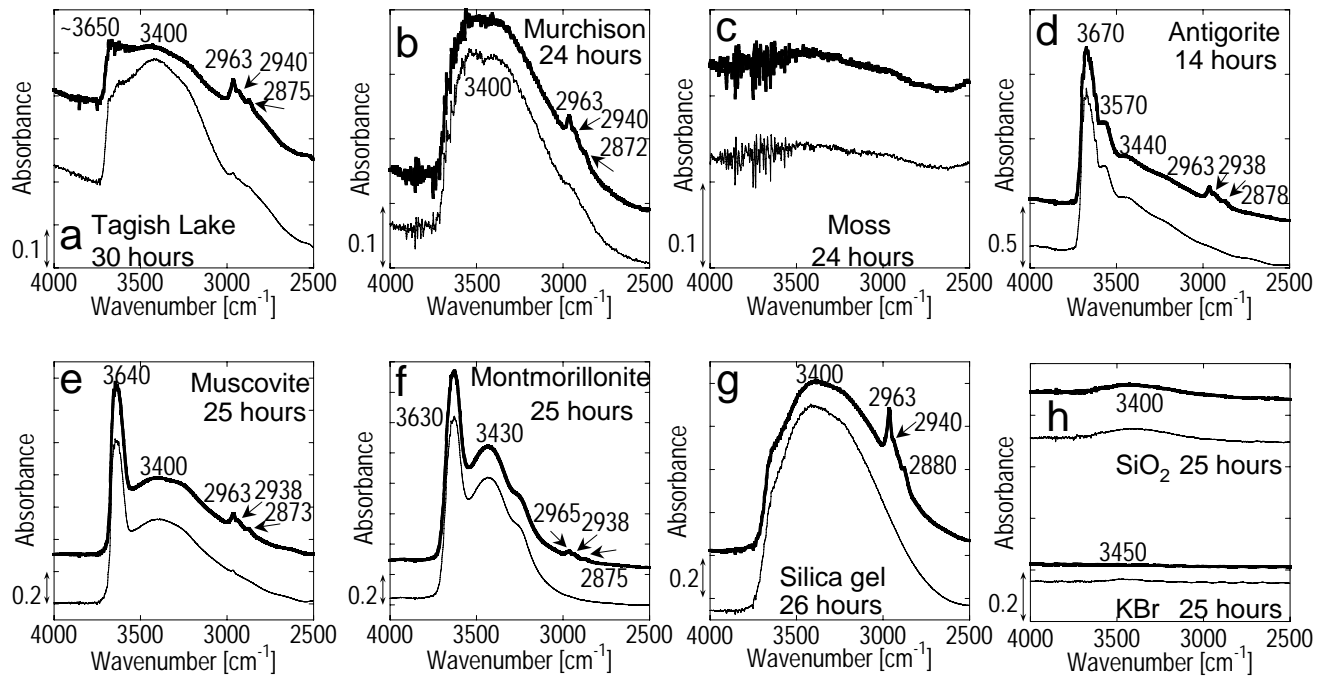
Fig. 11. The infrared spectra of 1300–700 cm^{-1} regions of volatiles from the silicone rubber mat in the air of the gas cell, immediately after the placement of the silicone rubber mat in the gas cell (0 hour), after 1 hour and 3 hours.

Fig. 12. Changes with time in infrared absorption peak heights of volatiles from the silicone rubber in the long path gas cell. (a) 2970 cm^{-1} peak due to CH_3 , 1265 cm^{-1} peak due to Si– CH_3 , 1080 cm^{-1} peak due to Si–O, and 850 cm^{-1} peak due to Si–C for 3.5 hours. (b) 850 cm^{-1} peak due to Si–C for 26 hours.

		Aliphatic C-H stretching			C=O	Overtone or combination of Si-O?	Aliphatic C-H bending				Si-CH ₃		
		CH ₃	CH ₂	CH ₃									
Silicone rubber mat	Tagish Lake	2963	2940	2875			1450					1262	
	Murchison	2963	2940	2872		1530	1460					1262	
	Antigorite	2963	2938	2878		1540	1470		1370		1405	1260	
	Muscovite	2963	2938	2873		1545	1465				1400	1260	
	Montmorillonite	2965	2938	2875		1525			1375				
	Silica gel	2963	2940	2880	1700	1520	1465		1385		1410	1262	
	Silica gel on KBr	2965	2940	2880	1705	1530	1470				1410	1262	
Adhesive tape	Silica gel	2957		2870			1480	1470	1455	1395	1367		
Silicone grease	Silica gel	2967										1410	1266
ATR-IR spectrum of silicone rubber		2962		2905								1415	1257
ATR-IR spectrum of adhesive tape		2958	2931	2872	1729			1455	1395	1376			
Volatiles from silicone rubber (gas cell IR)		2970		2905									1265

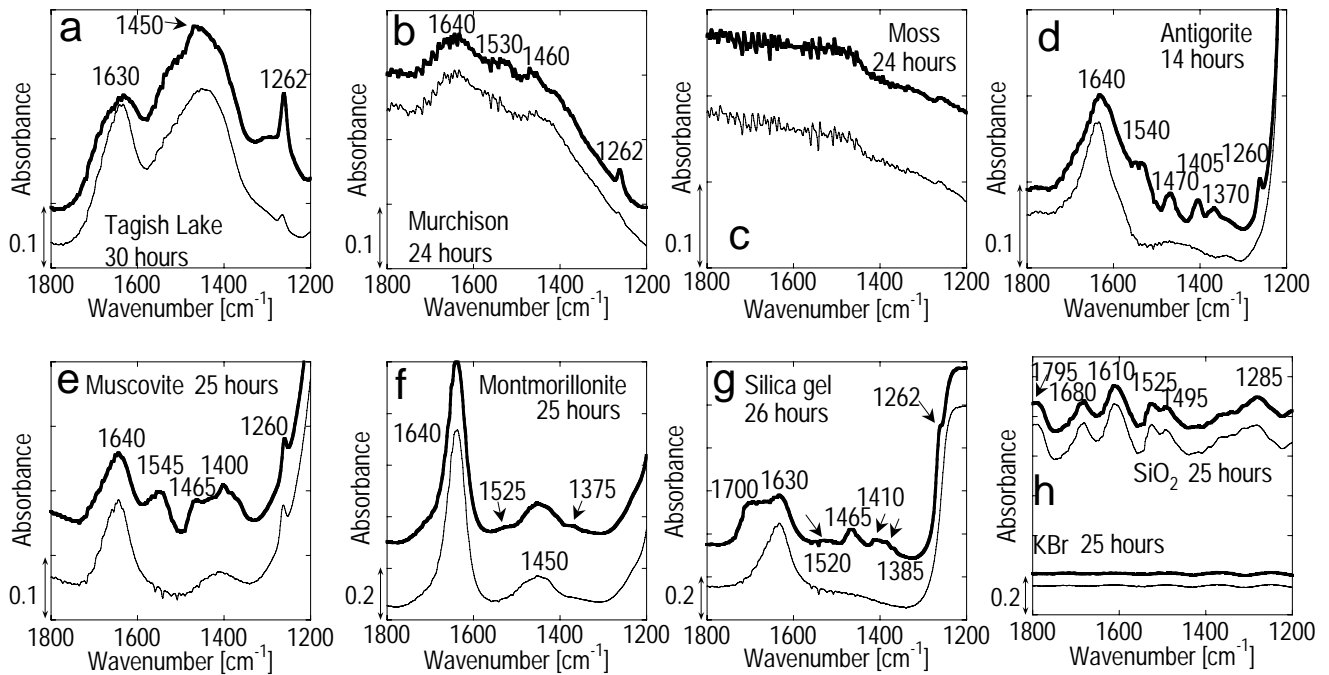
Kebukawa et al. Table 1

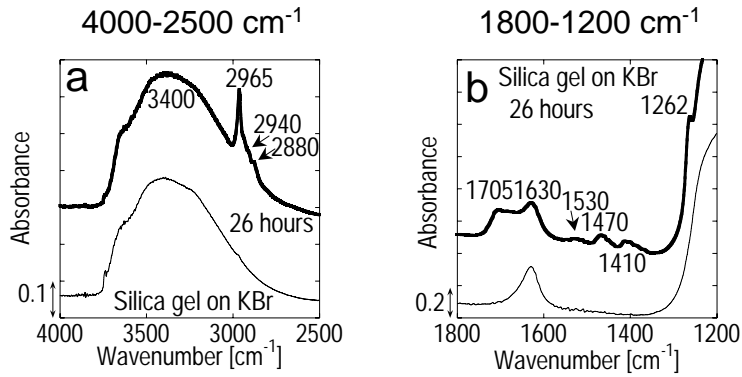
4000-2500 cm^{-1}



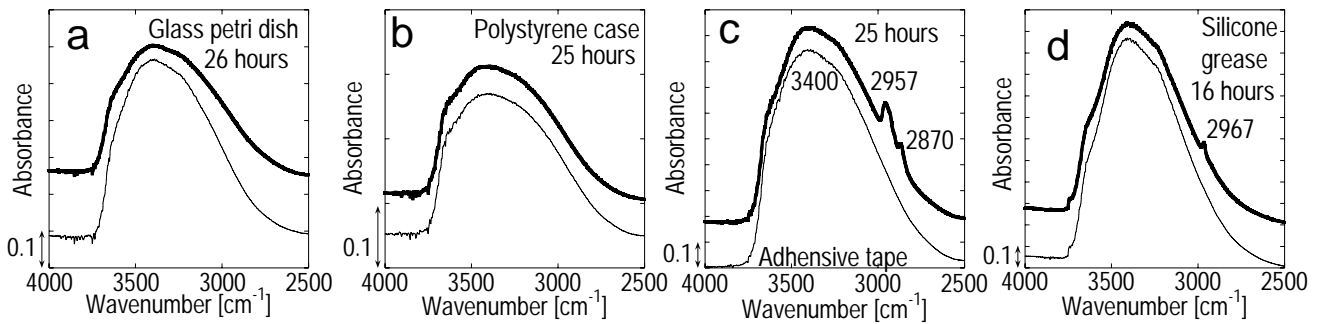
1800-1200 cm^{-1}

Fig.2

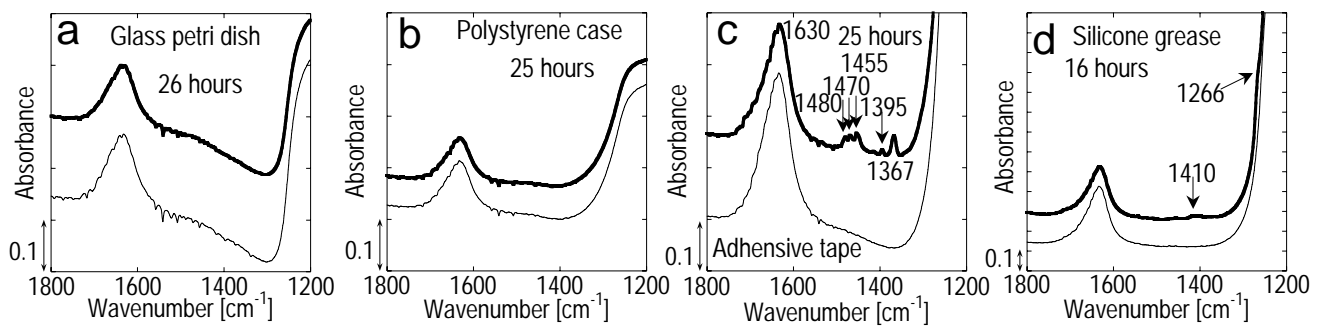


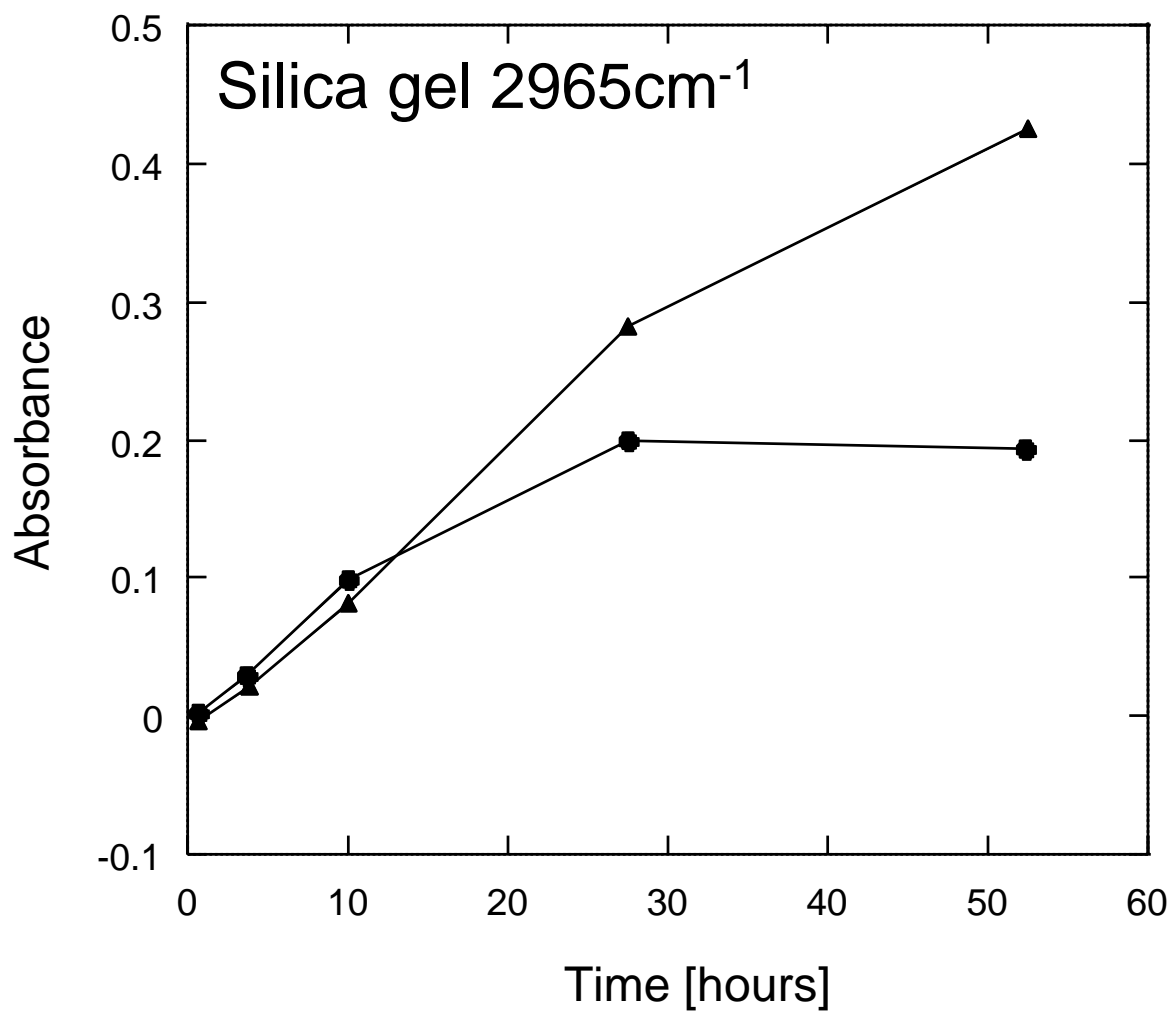


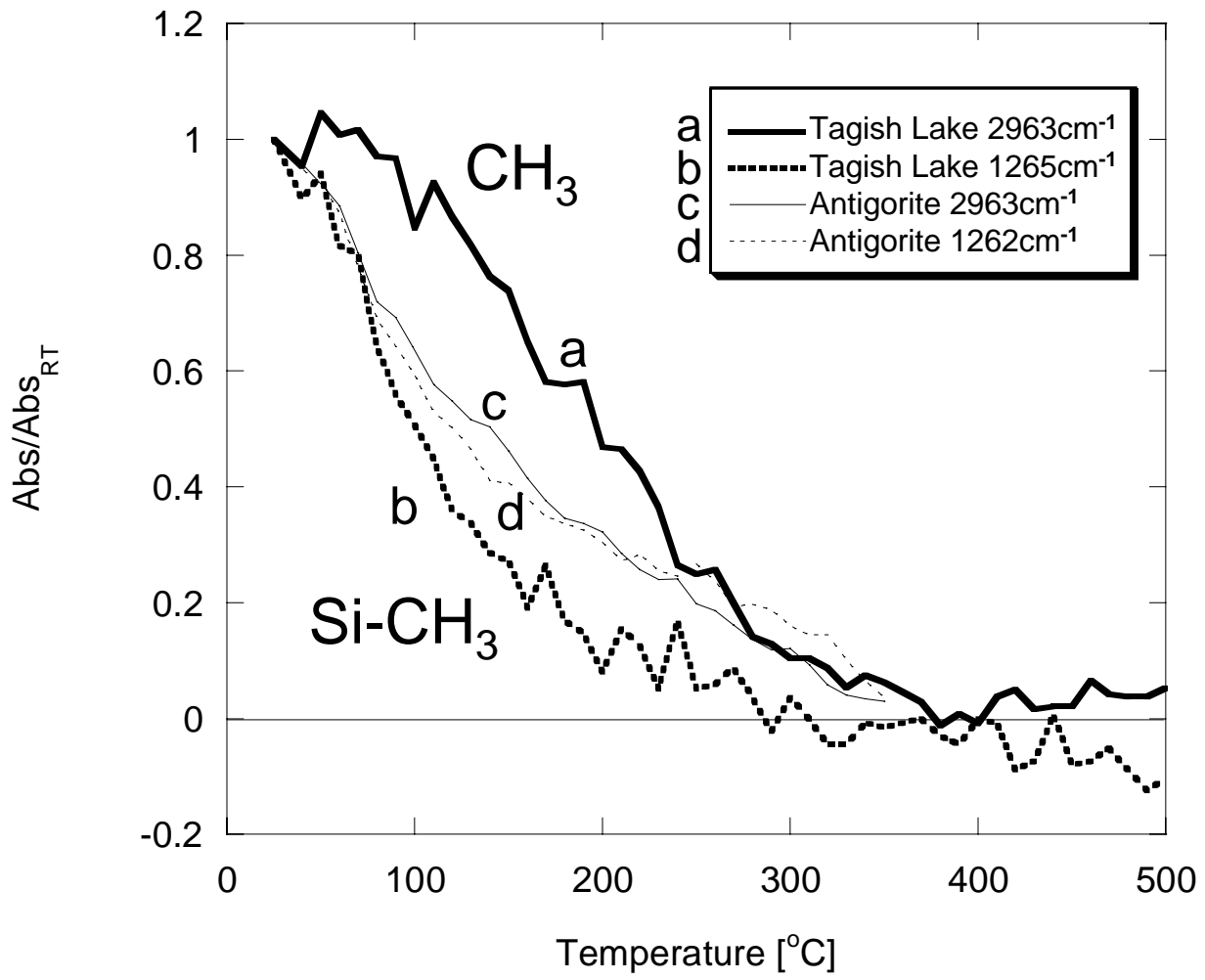
4000-2500 cm⁻¹



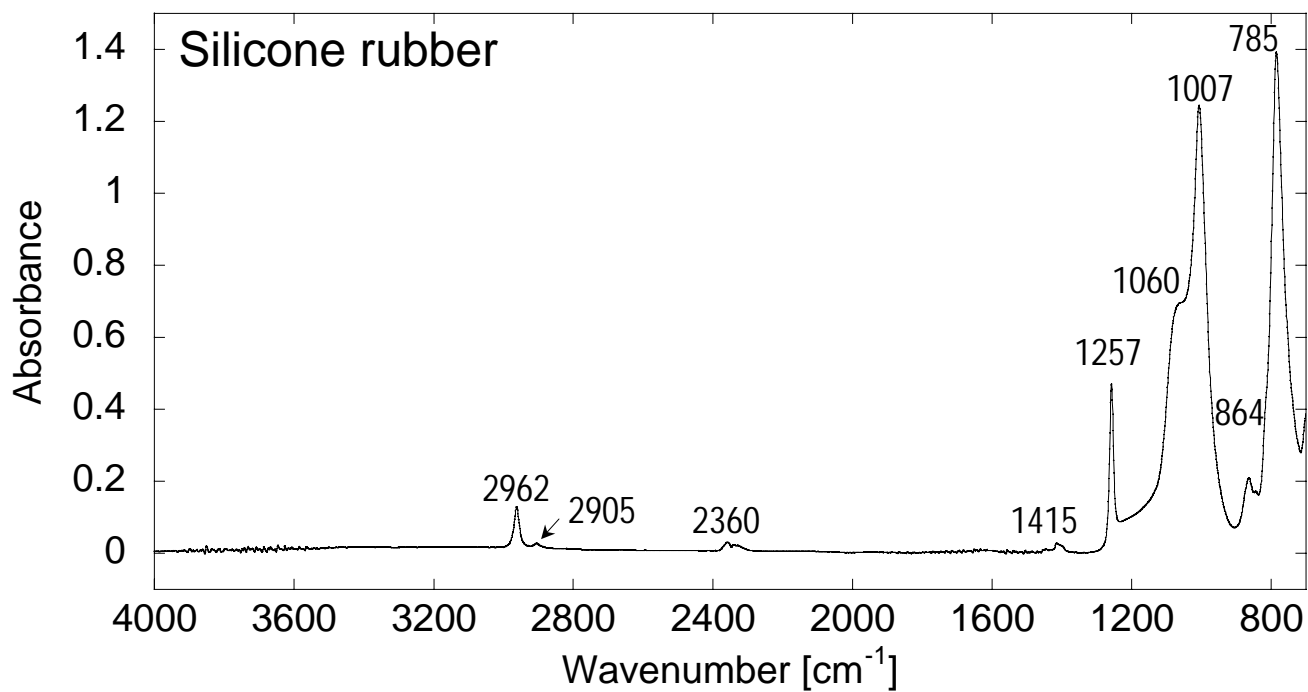
1800-1200 cm⁻¹



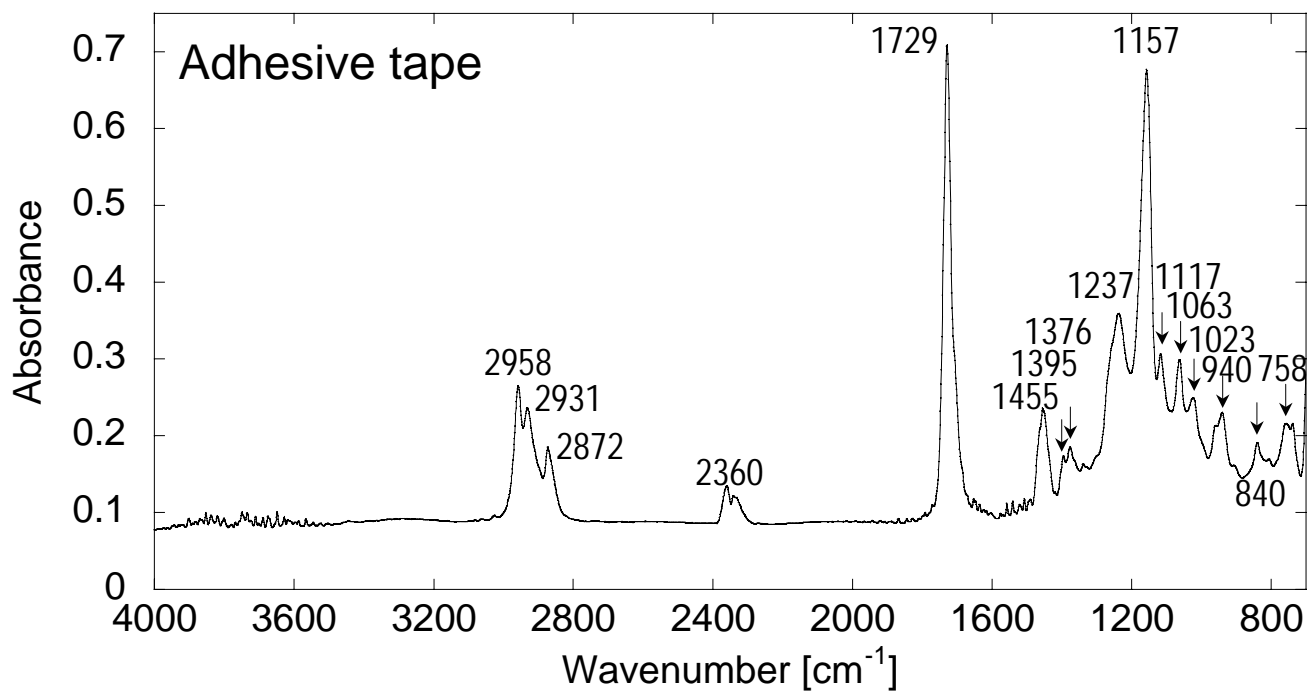




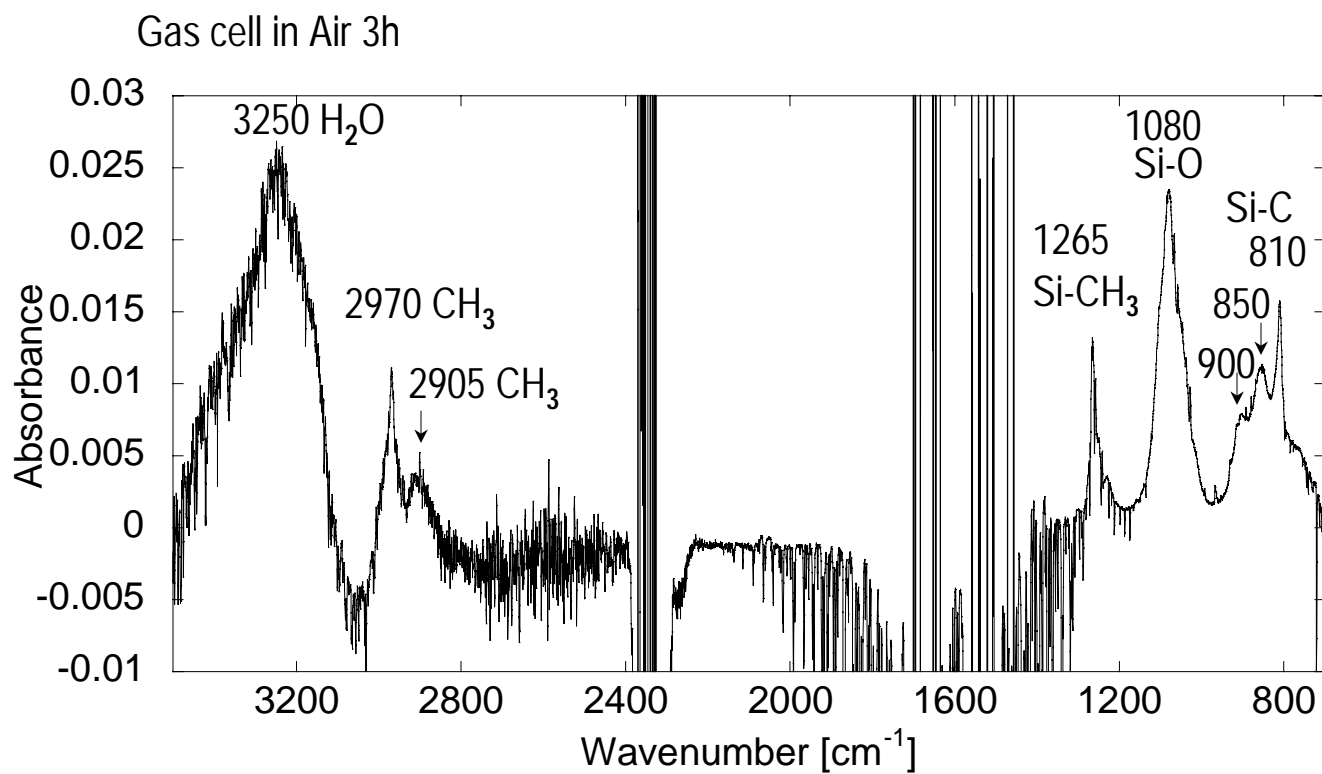
Kebukawa et al. Fig.8



Kebukawa et al. Fig.9



Kebukawa et al. Fig.10



Kebukawa et al. Fig.11

