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Submicron Distribution of Organic Matter of Carbonaceous Chondrite Using Near-field Infrared Microspectroscopy

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Carbonaceous chondrites are known to contain up to a few wt % organic carbon. Organic materials are disseminated in the clayish matrix, and some of them have been reported to be in the form of submicron organic globules. However, little is known about the nature of these microscopic organics. The organic matter distribution of the Bells (CM2) carbonaceous chondrite has been studied using a near-field infrared (NFIR) microspectrometer. Organic matter distribution and mineral associations at the submicron scale spatial resolution were observed.

Carbonaceous chondrite meteorites contain up to a few wt % organic carbon.[1] These meteorites are known to be the most primitive meteorites and contain records of the early solar system. The larger fraction of the organic carbon (70–99%) is a complex and insoluble macromolecular material.[2] Organic matter in carbonaceous chondrites is reported to be strongly associated with clay minerals, which may have had important trapping and possibly catalytic roles in the evolution of organics in the early solar system.[3] The microscopic distribution of organic matter has been studied by scanning electron microscope (SEM) observation with osmium labeling,[3] Raman spectroscopic imaging,[4] and transmission electron microscopy (TEM) combined with electron energy-loss spectroscopy (EELS).[5] Despite these studies, the detailed nature of microscopic organics is still not known, because methods for organic characterization at the submicron scale are lacking.

Fourier transform infrared (FTIR) microspectroscopy is useful for characterizing both organic and mineral structures. However, its spatial resolution is limited to $\approx 10\,\mu m$ at maximum.[6] Near-field infrared (NFIR) microspectroscopy has recently been developed to permit infrared spectral mapping beyond the optical diffraction limit with a spatial resolution of several hundred nanometers.[7] This method is, therefore, expected to measure nondestructively the distribution of organic polar functional groups including H-bearing ones together with those for hydrous minerals.

Here we apply this new high-resolution NFIR microspectroscopy to the analysis of organic matter in the Bells meteorite (an unusual CM2 chondrite), which is one of the most primitive chondrites by their isotopic compositions.[8]

We use near-field (NF) optics combined with FTIR (NFIR microspectrometer: Jasco NFIR-300N).[7] The ceramic infrared light source from the FTIR is focused by a Cassegrainian mirror onto a probe tip (having 1 µm curvature) placed within several tens of nm of a sample surface. The probe tip scatters NF signals localized around the probe-sample region, and another Cassegrainian mirror collects the scattered light onto a mercury–cadmium–telluride (MCT) detector.

Matrix fragments (a few ten micrometers) of the Bells CM2 carbonaceous chondrite were embedded in elemental sulfur for ultramicrotomy. The sample was then sliced into 300-nm thick sections and deposited onto an aluminum plate.

Figure 1 shows a conventional FTIR spectrum of a slice of the Bells meteorite and NFIR spectra of different portions of the same slice on the aluminum plate. Most of the weak IR absorption bands in the conventional transmission–reflection spectra can be observed in the NFIR spectra.

The band at $3620\,cm^{-1}$ is considered to be due to structural O–H of hydrous minerals, while the band around $3300\,cm^{-1}$ is probably due to O–H stretching vibrations of molecular water. Bells is known to contain abundant phyllosilicates, particularly serpentines, and tochilinite (a sulfide–hydroxide mineral).[9] The band around $2880\,cm^{-1}$ is due to aliphatic C–H vibrations. The band at $1025\,cm^{-1}$ is due to Si–O stretching vibrations of phyllosilicates. The 2960 and $1260\,cm^{-1}$ bands are due to CH_3 and $Si–CH_3$, respectively. These two bands are due to contaminants from silicone grease fixing the aluminum plate holding the sample onto the sample stage. The conventional FTIR spectrum (Figure 1a) taken before using silicone grease had much lower intensity of $2960\,cm^{-1}$ band compared to NFIR spectra (Figures 1b and 1c) and did not show $1260\,cm^{-1}$ band. The bands around $3900–3600\,cm^{-1}$ are considered to be noises of water vapor in the atmosphere.

Figure 2 shows NFIR spectral imaging of the Bells meteorite on the aluminum plate at 0.21 µm steps for $4.0 \times 2.1\,\mu m^2$ area. The band depths (downward peak heights in reflectance with linear baselines) were determined for $2880\,cm^{-1}$ due to aliphatic C–H, $3300\,cm^{-1}$ due to molecular H_2O, $3620\,cm^{-1}$ due to structural O–H, and $1260\,cm^{-1}$ due to contaminated $Si–CH_3$.

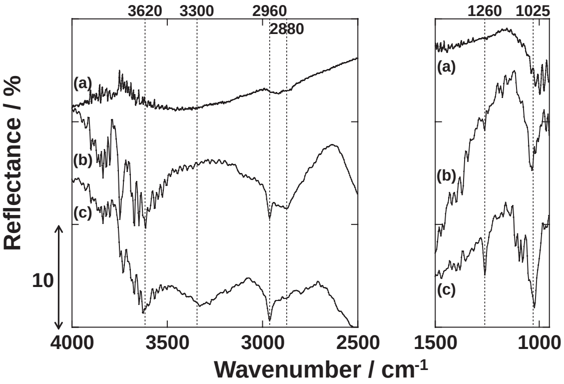

Figure 1. (a) Conventional FTIR spectrum of a slice (about 300-nm thick) of Bells meteorite. (b,c) Representative NFIR spectra for an organic-rich point (mark B in Figure 2), and a water-rich point (mark C in Figure 2), respectively.

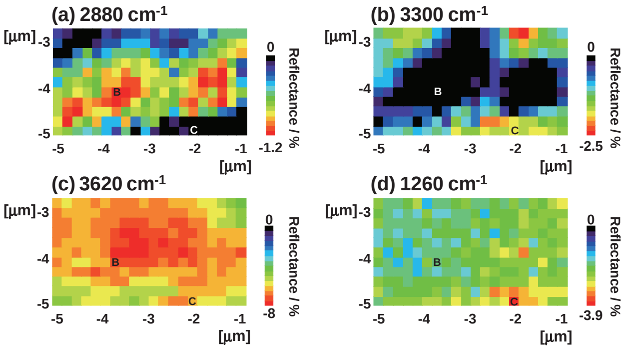

Figure 2. NFIR spectral imaging of the band depths of (a) 2880 cm^{-1} due to aliphatic C–H, (b) 3300 cm^{-1} due to molecular O–H, (c) 3620 cm^{-1} due to structural O–H, and (d) 1260 cm^{-1} due to contaminated Si–CH_3.

The contaminants (1260 cm^{-1}: Si–CH_3) are commonly distributed in the area with some high spots (Figure 2d). Structural O–H (3620 cm^{-1}), probably due to phyllosilicates, is also ubiquitously distributed with a highly concentrated portion at the center (Figure 2c). The molecular H_2O (3300 cm^{-1}) is lacking at two areas on the right and left sides (Figure 2b). Aliphatic C–H at 2880 cm^{-1} appeared to be distributed in the above water-free areas (Figure 2a). This distribution is clearly different from that of contaminants (1260 cm^{-1}: Si–CH_3). Therefore, aliphatic C–H at 2880 cm^{-1} is considered to be indigenous to the meteorite.

Bunch and Chang[10] reported that carbonaceous matter in altered CM matrices is largely associated with poorly characterized phases (PCP) which are later found to be coherent tochilinite–serpentine intergrowth.[11] Pearson et al.[3] suggested that organic matter is strongly associated with phyllosilicates among CM chondrites. The association of organic matter with phyllosilicates observed by the present NFIR agrees with these previous works.

The other organic functional groups such as C=O and C=N could not be detected owing to strong absorption of water vapor fluctuation in the atmosphere in the 1800–1500 cm^{-1} region. Therefore, the aliphatic C–H rich areas in Figure 2a were considered to represent the organic-rich areas. The organic-rich portions seemed to be around 1 micrometer in size (Figure 2a). However, their boundary might be blurred by the contribution of transmitted–reflected light other than NFIR signals at the surface. Therefore, the organic-rich areas might be smaller than 1 µm or several hundreds of nm in size (yellow to red regions in Figure 2a). These portions might, therefore, correspond to submicron organic globules found in CI, CM, and Tagish Lake meteorites.[12,13] These organic globules are thought to be amorphous carbon, and some of them contain functional groups such as C=O and C=N based on TEM-EELS.[13] In the Bells meteorite, such organic globules less than 1 µm in diameter are quite abundant in the serpentine–saponite matrix according to our TEM observation. Figure 3 shows a typical bright field TEM image of organic globules ubiquitously distributed in the Bells meteorite. These globules in Bells are often filled, and hollow ones such as those found in Tagish Lake are less common.[14] Since we cannot use the same slice for the TEM observation and NFIR measurement, it remains unknown whether the structures shown in Figure 2 are organic globules or not.

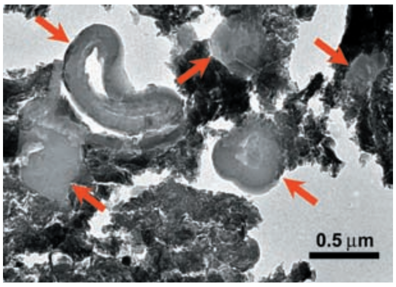

Figure 3. A typical bright field TEM image of five organic globules from Bells CM2 meteorite embedded in saponite matrix. Scale bar is 0.5 µm. Microtomed slice different from that analyzed by NFIR.

Organic matter is likely to accrete with anhydrous minerals to chondrite parent body. Then aqueous alteration would yield hydrous minerals such as phyllosilicates. The chondritic organic matter could have been protected by phyllosilicates during parent body aqueous alteration and subsequent thermal metamorphism. The submicron scale characterization of organic matter and its association with hydrous minerals would elucidate the evolution history of extraterrestrial organic matter. Further improvement of the present NFIR method would provide more information on the nature of microscopic organic matter by the organic functional groups other than aliphatic C–H such as C=O.

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