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Raman and Infrared Spectroscopic Tentative Identification of Organic Traces in Sadiya (LL5) Ordinary Chondrite

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Abstract. We report here for the first time the possible presence of organic compounds in Sadiya (LL5) ordinary chondrite using micro-Raman and infrared spectroscopic technique. The micro-Raman spectrum exhibits the diamond and graphite peaks correspondingly at 1331 cm^{-1}, 1349 cm^{-1} and 1588 – 1618 cm^{-1}. The full wave at half maximum value of about 18 cm^{-1} for Sadiya indicating the nature of disordered phase involved shock metamorphism in the meteorite samples. The diamond and graphite peaks intensity ratio (~0.53) indicates the disordered nature of graphite. The infrared spectrum in the range 2700–3000 cm^{-1} indicates the presence of CH_3 asymmetric stretching, and CH_2 symmetric and asymmetric stretching modes due to aliphatic hydrocarbons. This study has strong implications in understanding of the organic compounds in extra-terrestrial materials.

Keywords: Sadiya meteorite, Raman, infrared, organic compound.

1 Introduction

Meteorites are an important source of extraterrestrial matter, their chemical and physical characteristics, texture and internal structure contribute to our understanding of the birth and early history of our solar system [1]. The primitive meteorites contain abundant amounts (up to 1500 ppm) of nanodiamonds [2, 3]. The main formation process of the meteoritic nanodiamonds may be either in chemical vapour deposition or in shock origin (e.g., [4]). These nanocrystalline carbon materials (presolar grains) have to be considered amorphous or glassy carbon, and are either inorganic or consist of hydrogenated aromatic macromolecular organic carbon in the Raman spectroscopic literatures (e.g., see [5-8]). Alternatively, the carbon in primitive chondritic meteorites is present as organic material in the form of solvent –soluble and –insoluble components [9, 10]. Raman spectroscopy is a non-destructive technique that can yield information on the structural order of polyaromatic organic matter when applied at low laser power. Therefore, it is used to investigate insoluble organic matter from a range of chondritic meteorites, and a suite of interplanetary dust particles [11-13]. Raman analysis of insoluble organic matter has been already discussed by various authors in different meteorites [14-17], as well as of interplanetary dust particles [18-20] and returned samples from the Stardust Mission [21, 22]. The organic compounds in the dense interstellar clouds exhibit infrared absorption features at ~2880 cm^{-1} or 3.4 μm [23,24]. The existence of similar features (at 3.4 μm interstellar band) in Dergaon meteorite by infrared spectroscopy has been discussed by Saikia et al. [10].

This study demonstrates the presence of organic tracers in Sadiya LL5 ordinary chondrite which fell at Natun Balijan village of Sunpura, Sadiya (27°50'09''N; 95°51'34''E), India, on 5th June 2017 (04:30 pm IST)[25] using Raman and infrared spectroscopic technique. Commonly Organic carbon including PAH are found in carbonaceous meteorite. However the organic carbon in ordinary chondrite is very rare. In our study we present our new results on occurrence of organic carbon in ordinary chondrite.

2 Experimental

All the sample preparation was performed in ultra-clean conditions. To prevent from the environmental artefact contaminations, such as mud, the sample was carefully checked by optical microscopy. To avoid any surface contamination and the fusion crust we fragmented the sample (~20 mg) and took only pieces coming from its interior. The Raman spectra were collected on bulk powdered meteorite samples using an Ar ion laser laser with a power of ~5 mW, which used an excitation source having wavelength 488 nm coupled with a Jobin-Yvon Horiba LabRam-HR Micro-Raman spectrometer equipped with an Olympus microscope with 10X, 50X and 100X objectives, using the method described elsewhere [26, 27]. The powdered sample was homogenized in spectrophotometric grade KBr (1:20) in an agate mortar and was pressed 3mm pellets with a hand press. We tried to minimize the grinding time to avoid the deformation of the crystal structure, the ion exchange and the water absorption from atmosphere. The infrared spectra was acquired using Perkin-Elmer system 2000 FTIR spectrophotometer with helium-neon laser as the source reference, at a resolution of 4 cm^{-1}. The spectra were taken in transmission mode in the region 400−4000 cm^{-1}. The room temperature was 29°C during the experiment. The 800−1100 cm^{-1} (10μm) and 800−400 cm^{-1} (20μm) region of the infrared spectra facilitate an understanding of the relative nature of the SiO_4 tetrahedra. Particular interest is directed towards the presence of trace of organic compound in the spectral region around 2800-3000 cm^{-1}(3.4μm), due to the aliphatic functional CH_2 and CH_3 groups.

3 Results and Discussion

The compositional, mineralogical and Raman spectroscopic analyses of Sadiya meteorite have been discussed by Saikia et al. elsewhere (see [25]). The olivine and pyroxene composition of Sadiya meteorite are determined as: $Fa_{28.97}$; $Fo_{71.03}$; $Fs_{24.47}$; $En_{74.03}$ and $Wo_{1.5}$. The Raman spectra exhibit two characteristics peaks of olivine at 820 cm^{-1} and 850 cm^{-1} and three characteristic peaks of pyroxene at 335 cm^{-1}, 679 cm^{-1} and 1004 cm^{-1}. The olivine and pyroxene phases have already been discussed by the author in [25], therefore, the emphasis is given to the carbon phases in the Raman spectra of the meteorite.

Figure 1 displays different carbon phases observed in Raman spectra in between 1100–2000 cm^{-1}. In general, the Raman spectra of nanodiamonds reveal two broad bands centred at 1326 cm^{-1} and 1590 cm^{-1} [26]. The first-order Raman band (F_{2g}) of diamond occurring at ~1332 cm^{-1} corresponds to carbon *sp3* bonding (the main C–C bond vibration in diamond) and the band (E_{2g}) at ~1590 cm^{-1} is assigned to carbon *sp2* bonding graphitic structures [28]. The peaks exhibiting in the Raman spectrum (Fig.1) at 1331 cm^{-1}, 1349 cm^{-1} and 1588–1618 cm^{-1} attributed to diamond and graphite (D and G carbon bands), respectively. The peak intensity is generally used as a signature of crystalline quality. The relative intensities of these two bands reflect the degree of ordering [29]. The peak intensities of these bands are relatively low, which indicate strong background fluorescence. Depending on the degree of disordering and orientation of the graphite grain, a second band around 1350 cm^{-1} and a shoulder at 1620 cm^{-1} of lower intensity is present [30], which can be observed in the Raman spectrum of Sadiya meteorite at 1349 cm^{-1} and 1618 cm^{-1}. The relative intensities of the 1349 cm^{-1} and 1588 cm^{-1} peaks reflect the degree of ordering or disordering [29]. The Raman peak position 1618 cm^{-1} is the evidence of disordered graphite in the Sadiya meteorite (Fig. 1).

The peak appearing at 1331 cm^{-1} is accepted for diamond, such Raman peaks at ~1318–1333 cm^{-1} for apparently shock-produced diamond inside graphite nodules from Canyon Diablo were found by Miyamoto [31]. Diamond formation by chemical vapour deposition at low pressures and high temperatures is also possible in stellar atmospheres where the nanodiamonds of chondrites [32] were generated. The artificially produced chemical vapour deposited nanocrystalline diamonds exhibit two significant bands at 1150 cm^{-1} and 1450 cm^{-1} [33]. Similar peak at 1455 cm^{-1} is observed in Sadiya spectra. Therefore, it may be believed that the formation of nanodiamonds in Sadiya is similar to this process (chemical vapour deposition).

In general, FWHM 10–120 cm^{-1} is characteristic for shock-induced diamonds [31]. We measured FWHM value for Sadiya as 17.5 cm^{-1} which reflects the nature of shock metamorphism in the meteorite samples. The intensity ratio of the Raman diamond (I_D) and graphite (I_G) peaks in graphitic carbon was attributed by Wopenka et al. and ranging for fairly well ordered graphite ($I_D/I_G < 0.5$), disordered graphite ($0.51 < I_D/I_G < 1.1$), and glassy carbon ($I_D/I_G > 1.1$) [22, 34]. We measure the intensity ratio of diamond and graphite peaks of Sadiya and found to be ~0.53. It implies to the evidence of disordered nature of graphite in Sadiya. The peaks at 1455 cm^{-1} and 1490 cm^{-1} are related to phonon modes with q_0, which are activated by the disorder induced by small grain sizes in nanocrystalline or amorphous diamond [35].

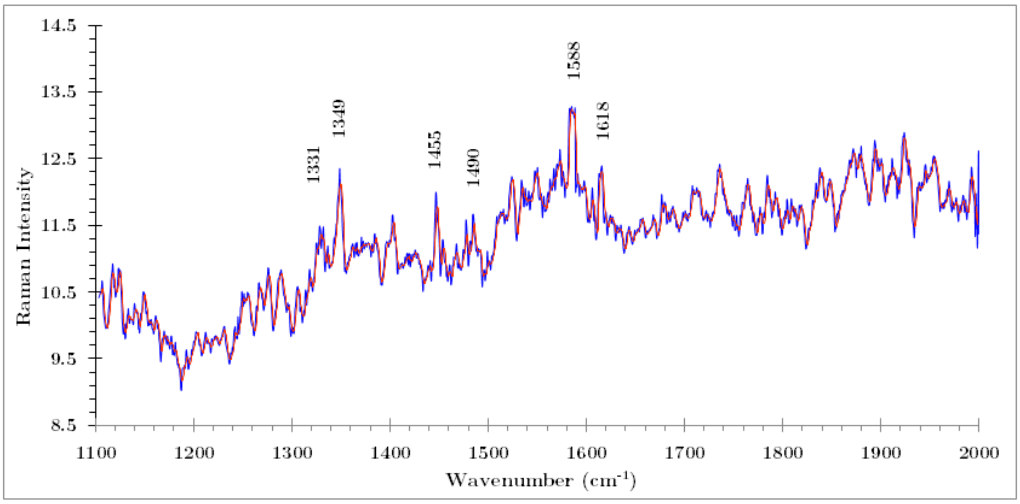

Figure1. Raman spectrum of graphite nodule in Sadiya meteorite sample showing two peaks, at 1349 cm^{-1} and peak at ~1588–1618 cm^{-1}. The diamond peak appears at 1331 cm^{-1} (see Appendices).

The infrared spectrum of Sadiya (Fig. 2) reveals numerous absorption bands in 400-1400 cm^{-1} indicating the presence of silicates. The observed band at 508 cm^{-1} can be interpreted as Si-O and Mg-O vibration modes in enstatite ($MgSiO_3$) with slight shifts in the matrix [36, 37]. Generally, below 500 cm^{-1} (e.g. the observed peaks between 465-494 cm^{-1}) olivines containing different divalent cations (M-SiO_4, where M is Mg^{2+}, Fe^{2+}, Mn^{2+}, or Ca^{2+}) exhibit a fairly uniform infrared spectrum in which individual bands are sensitive to cation composition [27]. The Si-O asymmetric stretching vibration (TO2-T2O5) is observed in between 974-1057 cm^{-1}. The peaks arise in between 916–974 cm^{-1} is assigned to the Si-O asymmetric vibration (TO3), whereas the peak arises at 879 cm^{-1} due to (T2O7-TO4). The appearance of these bands is due to the Si-O mode originating from different silicate (mostly meta- and ortho-silicates) present in the meteorite. The observed bands at 684, 722, 874, 918, and 1057 cm^{-1} can be attributed to pyroxene.

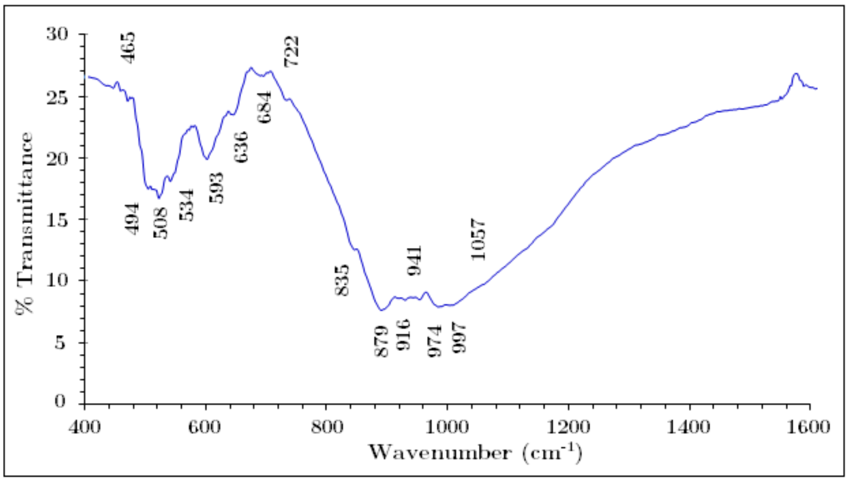

Figure 2. The infrared spectra of Sadiya meteorite in the spectral region 400-1600 cm^{-1}, silicate is recorded in 400-1000 cm^{-1} region.

The organic aliphatic C-H stretching features in meteorites have been observed by many authors (e.g. [38-40]). During their studies, three major peaks are found in the 2700-3000 cm^{-1} region, corresponding to aliphatic hydrocarbon stretching features. The pair of peaks at 2922 cm^{-1} and 2851 cm^{-1} corresponds to the asymmetrical and symmetrical stretching vibrations of CH_2 in an aliphatic hydrocarbon. The peaks at 2958 cm^{-1} and 2865 cm^{-1} correspond to the asymmetrical and symmetrical stretching vibrations of CH_3 also in an aliphatic hydrocarbon [38-40]. The infrared spectrum of the Sadiya meteorite in the range 2700-3000 cm^{-1} is shown in Fig. 3. The observed peaks at 2920 cm^{-1} and 2848 cm^{-1} correspond to the asymmetrical and symmetrical stretching vibrations of CH_2, whereas the peak at 2957cm^{-1} arises due to the asymmetrical stretching vibrations of CH_3 [10]. The C-H bending vibrations of aliphatic hydrocarbons are generally observed at ~1466 cm^{-1} and ~1379 cm^{-1}, but these peaks are not observed in the present analyses. Extraterrestrial organic compounds present in carbonaceous chondrites known to exhibit large structural diversity, which is a feature contrasting with terrestrial biogenic organic compounds [41]. Potiszil et al. have carried out high pressure spectroscopic measurements on organic materials and suggested that the formation of the hydrogen bonds has implications for the origination of macromolecular organic matter (MOM) in the extraterrestrial materials. Such high-pressure-induced hydrogen-bond formation is likely a process by which aromatic MOM precursors could have cross-linked to generate the organic polymers found within extraterrestrial bodies [42].

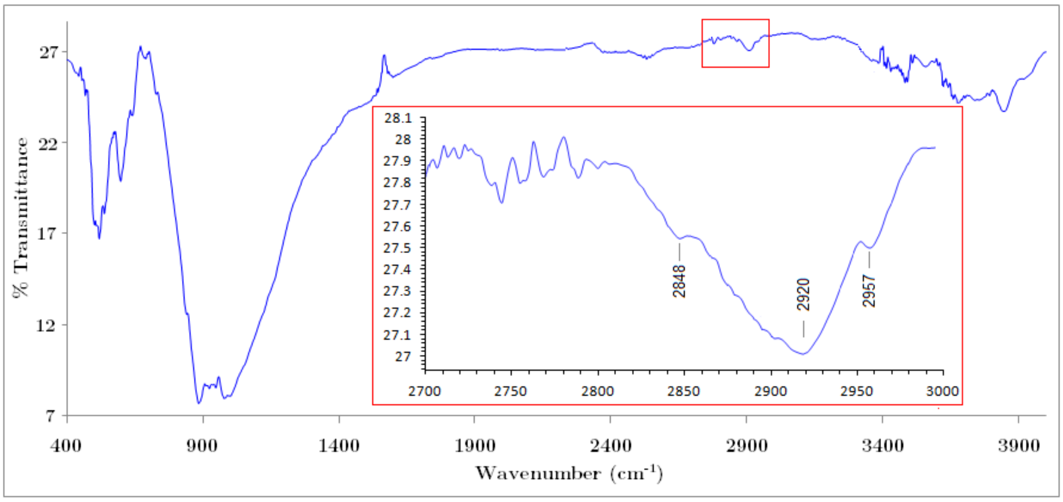

Figure 3. The infrared spectra of Sadiya meteorite in the spectral region 400-4000 cm^{-1}, C-H features is recorded in 2800-3000 cm^{-1} region (Inset).

4 Conclusion

The Raman and infrared spectroscopic results provide the first evidence for the possible existence of organic compounds in Sadiya meteorite. The Raman spectra exhibit the diamond and graphite (D and G carbon bands) peaks correspondingly observed at 1331 cm^{-1}, 1349 cm^{-1} and 1588–1618 cm^{-1}. The peak intensity of these peaks reflects the degree of ordering. The Raman peak position 1618 cm^{-1} is the evidence of disordered graphite in the Sadiya meteorite. The peak appears at 1331 cm^{-1} is accepted for diamond. The presence of 1455 cm^{-1} in Raman spectra indicates that the formation of nanodiamonds in Sadiya is similar to the chemical vapour deposition process. The full wave at half maximum value 17.5 cm^{-1} reflects the shock metamorphism in the meteorite samples. The diamond and graphite peaks intensity ratio (~ 0.53) indicates the disordered nature of graphite in Sadiya. The infrared analysis is consistent to the Raman spectroscopic results. The weak absorption bands found in 2700-3000 cm^{-1} of Sadiya are indicative to organic compounds. Infrared spectra indicate the presence of aliphatic hydrocarbons in the Sadiya meteorite. Similar organic features have been observed by Lawless et al. and Saikia et al. in H type ordinary chondrites [10, 43].

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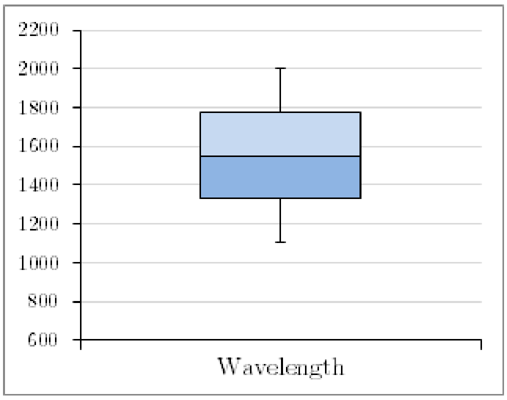
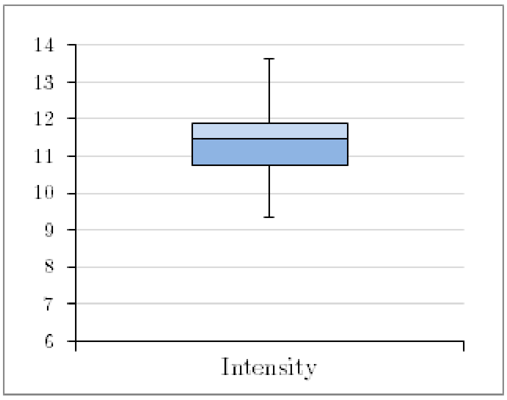
Appendix 1:

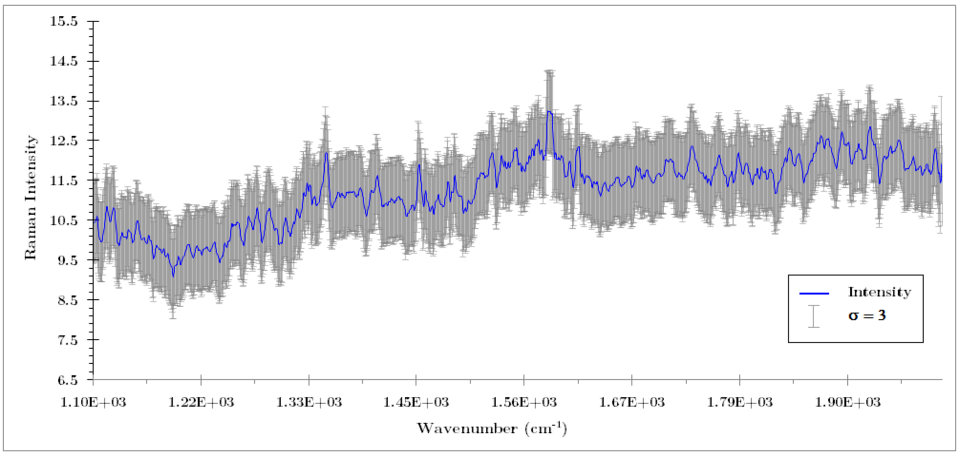
Box-whisker plot for wavelength and intencity of the Raman spectra of Sadiya meteorite which is shown in Figure 1.





	Wavelength	**Intensity**
Min	1103.505127	9.02513657
Q1	1327.628815	10.7398189
Median	1552.037109	11.4648919
Q3	1775.876312	11.9008698
Max	2000.000000	13.2854107
Box 1 -Hidden	1327.628815	10.7398189
Box 2 -Lower	224.4082947	0.72507303
Box 3-Upper	223.8392029	0.43597794
Whisker Top	224.1236877	1.3845409
Whisker Bottom	224.1236877	1.7146823

Appendix 2:



This figure represents the variation of intensity of Raman spectra (Figure 1) at standard deviation (σ=3).