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Detection of organic or inorganic material in Martian meteorite Zagami by vibrational spectroscopy?

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Abstract

Zagami is a basaltic shergottite well characterized among Martian meteorites. For this reason, it is used as a reference sample to verify the feasibility of the vibrational spectroscopy techniques. In general, these techniques seeking extract spectral signatures from individual mineral present in the meteorite samples. Among some FTIR results were detected organic compounds in the Zagami meteorite and recorded in some articles. Based on these results, an analysis of a Zagami meteorite sample was performed using FTIR and Raman spectrometry. Examining the fragment of Zagami meteorite using the FTIR technique, it was possible to identify the same band of 2920 and 2850 cm⁻¹ described by other references, which were interpreted as organic components and were recorded such as aliphatic hydrocarbon. Another unusual result in Martian meteorite was the detection of the 1300 cm⁻¹ band using Raman. The main reason for this peculiarity is that band is characterized in meteorites as a D band. Generally, this band is attributed to structural defects and the disordering of carbon. However, care should be taken when interpreting Raman spectra around 1300 cm⁻¹ and FTIR spectra 2950-2840 cm⁻¹ of the sample from oxidizing environments such as Mars. Misconceptions can occur during the interpretations of the bands, and this can lead to incorrect identification. Thus, an analysis of the mentioned peaks, such as chemical and mineralogical assignments, will be provided and suggested in order to compare the results that mentioned the presence of organic compounds in the Zagami meteorite.

Introduction

Martian meteorites are considered important pieces of geological material from Mars. Although most of the geological records have been destroyed, as happened on Earth, the geological evolution of the Martian surface, its physical information and chemical characteristics can still be studied through the Martian meteorites (Nimmo and Tanaka, 2005). In general, Martian meteorites are divided into Shergottites, Nakhlites and Chassignites (SNC). The SNC meteorite group includes igneous rocks (basalts and cumulates) which generally contain evidence for shock impact metamorphism, such as glass veins and cracks.

Zagami meteorite is a very famous shergottite, and has been well studied (McCoy et al., 1999; Wang et al., 1999; Nyquist et al., 2001). Some of these studies detected organic compounds in the Zagami meteorite and recorded in some articles (Anderson et al., 2005; Palomba et al., 2006). Thus, one of the main intentions of this work is to analyse the spectral signature obtained by vibrational spectrometry and compare the result with spectral compositions of the same sample that reported the presence of organic compounds.

According to Anderson *et al.* (2005), infrared spectroscopy would be an obvious choice as part of an instrument for analysing Martian samples. In particular, the molecular bond information provided by vibrational spectrometry, such as Raman and FTIR, adds powerful interpretive information to methods that yield only elemental composition.

Finally, it can be said that this research conforms to the focal point for searching for traces of life in the Solar System, which is Mars. The main reason for this attribution to Mars is because of its geological similarity and proximity to Earth. Thus, information obtained from Martian meteorites may provide important implications for the study of life or habitability conditions that might have existed in the Solar System. However, it is worth noting that although there are results pointing to the existence of organic compounds in Martian meteorites, such as in Zagami meteorite, it is always necessary to carefully ascertain such attributions.

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Materials and methods

Martian Zagami meteorite

The Zagami meteorite fell on 3 October 1962 about 1.2 km from Zagami Rock, Katsina Province, Nigeria (Graham *et al.*, 1985). In 1985, the main mass of 18 kg was first sent to studies in the Geological Survey of Nigeria in Kaduna, but since 1988 when Robert Haag (meteorite dealer) obtained a large piece of the Zagami meteorite, it was cut and distributed widely. Zagami is a basaltic shergottite that with a crystallization age of 180 Ma (e.g. Shih *et al.*, 1982; Jones 1986; Nyquist *et al.*, 2001) can be placed among the youngest SNC meteorites, considerably younger than the average Martian crust.

SNC ejection mechanism has been explained also for the most common near-normal impacts, for the crater of hundreds to few km in size (Vickery and Melosh, 1987; Carr and Head, 2010). The space exposure ages of Zagami suggest that it was ejected from the surface by the same impact event that launched Shergotty, Los Angeles and QUE94201 about 2.7–3.1 Ma ago (Eugster *et al.*, 1997; Nyquist *et al.*, 2001). In general, the sample Zagami meteorite in Fig. 1 analysed in this work (rectangular shape measuring about $1.0 \times 0.7 \times 0.2$ cm)

Although Zagami meteorite is quite distinct petrologically and chemically from the rest of the basaltic achondrites, and Shergotty are texturally and mineralogically similar to terrestrial diabases, plagioclase has been shocked to maskelynite (Stolper and McSween, 1979). The meteorite is texturally heterogeneous, with several distinct lithologies dominated by the so-called Normal Zagami (NZ) lithology. In the NZ lithology, pyroxene crystals, with an average grain size 0.24-0.36 mm, are arranged with maskelynite grains in a preferential orientation which gives the meteorite its characteristic foliation texture. The average mineral modal, for the NZ lithology, varies in the following intervals: pyroxene 70-80%, maskelynite 10-25%, minor phases 4-9% (e.g. Stolper and McSween, 1979; McCoy et al., 1999). In addition, some fine black glass veins apparently were formed by 'shear spillage during shock' (Langenhorst and Poirier, 2000), and could contain rare recent information on high-pressure phases.

The fragment of Zagami meteorite used for development in this work was provided by the Rio de Janeiro National Museum (UFRJ), which confirmed that the sample of Zagami meteorite corresponds to the mineralogy and textured description in *Meteoritical Bulletin* (Graham *et al.*, 1985)

FTIR

In this work, Fourier transform infrared (FTIR) spectrometer was used (Alpha II, Bruker Optics, Ettlingen, Germany). The spectra of the sample were collected under environmental conditions in the range between 4000 and 400 cm⁻¹, with a resolution of 4 cm⁻¹ and acquiring an average of 128 scans. In addition, Hyperion 3000-VORTEX 70 was used. This equipment has a diamond attenuated total reflectance (ATR) accessory and OPUS software (v. 6.5, Bruker Optics) was used for instrumental control and for spectral acquisition.

The analysis of the Martian meteorite fragment followed some procedures/protocols, which will be listed and explained. First, a tablet containing only potassium bromide (KBr) was prepared. This type of material has a 100% transmission window in the range of the number of waves (4000–400 cm⁻¹) for FTIR.

Based on this, a measure was taken to obtain the infrared spectrum of the KBr chip only. The purpose of this measure is to



Fig. 1. Fragment of Martian meteorite Zagami used in this work.

remove any negative contribution or impurity that may be present in the device or in the KBr used. Thus, the results obtained containing the analyte disregard these possible contributions during the measurements. Potassium bromide, in this case, acts as a kind of what can be called 'white' or 'background'. Subsequently, all this information will be subtracted from the final spectrum.

The published article database was used to compare the result obtained with that of the reference as an analysis method such as Palomba *et al.* (2006), Brolly *et al.* (2016), Lakshmi Reddy *et al.* (2015).

μRaman

Data were obtained using the μ Raman Confocal Bruker Senterra equipment coupled to an Olympus microscope. (lenses $10\times$, $20\times$, $50\times$ and $100\times$), available at UFJF Chemistry department. Measurements were made with the $50\times$ objective lens. In addition, the system is equipped with 532, 633 and 785 nm excitation lasers, but in this work, a 633 nm laser was specifically used. The output power was 20 mW and integration time 10 s, with a spectral resolution of 1 cm $^{-1}$.

It is noteworthy that the limitations in the analyses performed lie in possible interference of fluorescence and Raman scattering of the object under consideration. Basically, this can cause a large noise in the spectrum, causing no Raman peaks or low-intensity peaks for some constituents.

Results

FTIR

Infrared (IR) spectra of the Martian Zagami meteorite were acquired in the mid-infrared (MIR) region (from 4000 to 400 cm⁻¹). Although the FTIR technique is not commonly used to study minerals in meteorites, important information regarding sample composition can be obtained. Thus, the data obtained from the Chemistry department of UFJF of the Zagami meteorite will be presented below in Fig. 2.

FTIR spectrum shows the bands in the higher wavelength region at 1642, 1742, 2850, 2920 and 3455 cm⁻¹ and lower wavelength region at 500, 635, 672, 725, 880, 936, 962, 1050, 1344 and 1400 cm⁻¹. Based on this result, a comparative analysis was performed between spectra in order to characterize and try to provide the chemical composition.

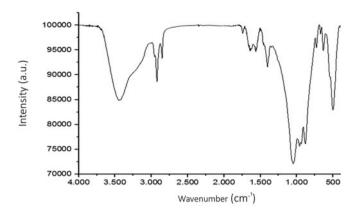
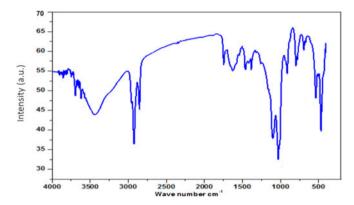


Fig. 2. FTIR spectrum obtained from the Martian meteorite fragment.



 $\textbf{Fig. 3.} \ \ \text{Reference spectrum by Lakshmi Reddy } \textit{et al. (2015)} \ \ \text{to compare with the result obtained.}$

The characterization of the chemical compound obtained from Zagami meteorite by IR was investigated and compared with the spectrum of Lakshmi Reddy *et al.* (2015) in Fig. 3. The reference spectra Cui *et al.* (2013) and Lakshmi Reddy *et al.* (2015) used to perform the comparative analysis with the spectrum obtained from the Zagami meteorite are described together with the spectrum of the fragment analysed in Table 1.

μRaman

The analysis of the Martian Zagami meteorite was performed by varying the point position of the beam by sample regions. The Raman spectrum shows in Fig. 4 a composition of the frequencies 220, 290, 325, 400, 666, 1004 and 1328 cm⁻¹.

For purposes of comparison and characterization of the obtained compound, spectra of terrestrial mineral samples were collected from literature sources or from the database cited in the text. The peak of the spectra is described and compared with two spectra of pure minerals used as references in Table 2.

Based on the comparison between the obtained data and the references, the iron oxide compound and the Hedenbergite mineral (CaFe $^{+2}$ Si₂O₆) appear to be part of the Zagami meteorite sample. In addition, it is possible to attribute a possible intergrowth between both minerals because of how the spectra are mixed and overlapping some peaks such as $660 \, \mathrm{cm}^{-1}$ (iron oxide) and $667 \, \mathrm{cm}^{-1}$ (Hedenbergite) or $1005 \, \mathrm{cm}^{-1}$ (iron oxide) and $1007 \, \mathrm{cm}^{-1}$ (Hedenbergite) as illustrated in Fig. 5.

Table 1. Peaks obtained compared with data from published reference articles: Reference A is Lakshmi Reddy *et al.* (2015) and Reference B is Cui *et al.* (2013)

FTIR Zagami (cm ⁻¹)	Iron oxide FTIR (cm ⁻¹)	Iron oxide FTIR (cm ⁻¹)
(This work)	(Reference A)	(Reference B)
3450	3445	3400
2927	2925	2924
2850	2853	2850
1742	1746	-
1632	1628	1632
1400	1464	1453
1344	1384	1383
1050	1030	-
962	-	-
920	913	-
880	-	892
725	798	795
685	695	-
635	-	635
510	536	-

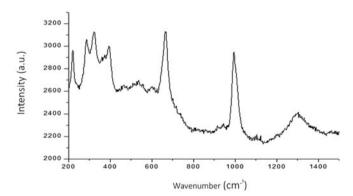


Fig. 4. Raman spectrum obtained from the Zagami meteorite.

Table 2. Data with the peaks obtained and comparison with the data of pure minerals also obtained through Raman dp RRUFF database

Raman Zagami (cm ⁻¹)	Iron oxide Raman (cm ⁻¹)	Hedenbergite Raman (cm ⁻¹)
(This work)	(Reference RRUFF)	(Reference RRUFF)
220	223	-
285	292	-
324	-	325
400	409	395
666	650-670	667
1006	1005	1007
1328	1300	-

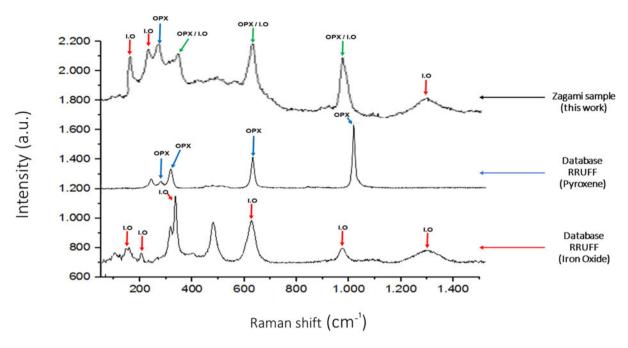


Fig. 5. Comparative spectrum between the result obtained from the Martian meteorite fragment and the pure minerals from the RRUFF database.

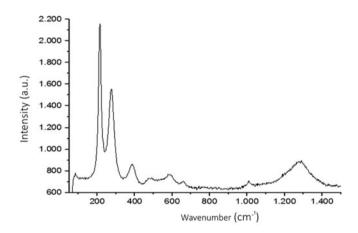


Fig. 6. Second Raman spectrum obtained from the Zagami meteorite.

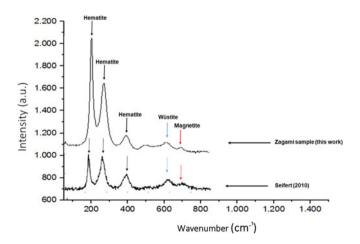


Fig. 7. Comparative spectrum between the result obtained from the Martian meteorite fragment and the spectrum obtained by Seifert *et al.* (2010).

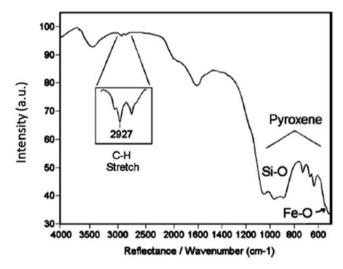


Fig. 8. Image of a spectrum obtained and published by Anderson *et al.* (2005) when it presents the presence of organic matter in the Martian meteorite Zagami.

In Fig. 6, another Raman spectrum of the Zagami meteorite is presented. Raman spectrum shows the bands in the wavelength region at 1300, 600, 660, 400, 275 and 220 cm⁻¹.

According to Seifert *et al.* (2010), Hematite can sometimes be found along with the minerals of magnetite and wustite. The Raman spectrum shows in Fig. 7 a composition of the Zagami meteorite sample along with the spectrum obtained by Seifert to demonstrate by comparison the presence of Hematite, Magnetite and Wustite in the Martian meteorite.

Discussion

Interpreting the results of vibrational techniques

The results presented above show the potential of vibrational techniques for mineral discrimination in a heterogeneous sample,

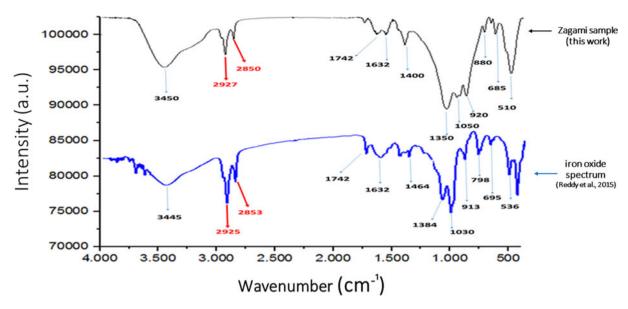


Fig. 9. Comparative spectrum between the result obtained from the Martian meteorite fragment and the spectrum obtained by Lakshmi Reddy et al. (2015).

such as the Martian meteorite Zagami. In the following section, we will discuss in detail the spectral behaviour in our sample, trying to restrict its chemistry and/or structure. The main intention of this work is to analyse the spectral signature obtained by vibrational spectrometry, and compare the result with spectral compositions of the same sample that reported the presence of organic compounds. Some of these studies detected organic compounds; according to Anderson *et al.* (2005), using FTIR recorded the presence of aliphatic structures in the Zagami meteorite (Fig. 8).

Furthermore, according to Palomba *et al.* (2006), similar results were obtained confirming this kind of variations across the sample. Still according to the authors, this could be an indication that the organic and water resources in Zagami are due to heterogeneous compounds. However, a possible presence of contaminating material from the time of collection should not be ruled out, even if the authors mentioned above are not in favour of this possibility. Although this work obtained the same band 2927 cm⁻¹, our interpretation is slightly different on the presence of organic compounds. Perhaps you can suggest a second interpretation in relation to this vibrational mode that is not linked to a carbon bond. It is what tries to be exposed next (Fig. 9).

A broad band at 3450 cm⁻¹ in the mineral is assigned to OH stretching (*v*3) of structural hydroxyl groups and a probable existence of water present in the sample. This indicates the possibility of the hydroxyl linkage between octahedral layers. Furthermore, at 1742 and 1632 cm⁻¹ a sharp and intense band is observed, which is due to *v*2, the asymmetric OH stretch (deformation mode) of water and is a structural part of the mineral. The sharp band observed at 1400 cm⁻¹ may also be due to OH stretch of water.

We would like to draw attention specifically to the band at 2920 cm⁻¹. It is possible that this 2927 cm⁻¹ band appeared due to the iron oxide in the sample. However, the interpretation of this band may have been mistakenly attributed to the presence of organic compounds/aliphatic carbon bonds. According to Bikiaris *et al.* (2000), due to the presence of minerals of iron oxide group, such as hematite and magnetite, the band 2920 and 2850 cm⁻¹ can be assigned to the FeOOH functional group.

In this functional group, ferrihydrite $(Fe^{III}(OH)_3)$ and goethite can be cited.

The maximum sharp absorption band at 1050 cm⁻¹ is a characteristic of Si-O-Fe and Si-O-Si stretching vibration, which plays an important role in the sample, and the band observed at 920 cm⁻¹ is assigned to OH deformation mode of Fe-OH. In the low wave number (below 700 cm⁻¹) region, iron oxide has the following IR absorptions: Fe-O stretches (lattice modes of FeO6) in the region of 600–700 and 450–475 cm⁻¹. Accordingly, the two bands observed at 685 and 635 cm⁻¹ are attributed to the Fe-O stretching mode (Vahur *et al.*, 2010). According to Gupta *et al.* (2014), the band observed at 510 cm⁻¹ corresponds to *v*2, the deformation mode of Fe-O-Si group. In general, according to Lakshmi Reddy *et al.* (2015), a band at 1356 cm⁻¹ could be due to overtone of *v*4 of SiO₄ (Table 3).

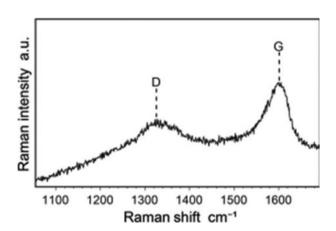
In addition, another result that corroborates the previous assignments is the complementary Raman data. The presence of iron oxide was detected through Raman, and this mineral would be associated with a possible intergrowth with the ferromagnesian Hedenbergite mineral, belonging to the pyroxene group. Furthermore, other results showed the detection of Hematite, Wustite and Magnetite. In both Raman results, a peculiar band at 1300 cm⁻¹ draws attention. That band also is characterized in meteorites as a D band, which is attributed to structural defects.

In general, according to Brolly *et al.* (2016), Raman spectroscopy of carbonaceous materials occurs at two wavelength bands. The first, known as 'first-order bands' occur between 1100 and 1800 cm⁻¹ (Tuinstra and Koenig, 1970). The spectra of organic material in this order is characterized by two main bands; the graphitic (G) band, which occurs at 1600 cm⁻¹; and the disordered (D) band, which occurs around at 1300 cm⁻¹, as shown in Fig. 10.

According to Beyssac *et al.* (2002), D band is a specific frequency of poorly ordered carbon. In general, the band area reduces with stiffening of the aromatic planes and is attributed to in-plane defects, e.g. heteroatoms or structural defects. However, according to Brolly *et al.* (2016), the hematite 2LO

Table 3.

Region (cm ⁻¹)	Function group	Vibrational mode
3450	ОН	Stretching
2927	FeOOH	
2850	FeOOH	
1742	ОН	Asymmetric stretch
1632	ОН	Asymmetric stretch
1400	ОН	Stretch
1344	SiO ₄	Overtone
1050	Fe-O-Si/Si-O-Si	Stretch
962	Si-O	Stretch
920	Fe-OH	OH deformation mode
880	Si-O	Stretch
725	Si-O	Stretch
685	Fe-O	Stretching
635	Fe-O	Stretching
510	Fe-O-Si	



 $\textbf{Fig. 10.} \ \ \textbf{Illustrative representation of bands D and G}.$

mode, which is attributed to defects in the hematite lattice, occurs in the same frequency of the carbon D band (A1g mode). Hematite 2LO mode occurs around $1320\,\mathrm{cm^{-1}}$ and is very intense, and overlaps the carbonaceous spectra (Fig. 11). Thus, at $1320\,\mathrm{cm^{-1}}$ it could be misinterpreted as a specialized vibrational mode in the presence of organic matter. However, none of the alternatives can or should be discarded.

Hypotheses and astrobiological implications

Although the presence of aliphatic structures in a Martian meteorite may seem peculiar, detection is possible and should not be ruled out or considered unfeasible. In this section, some alternative hypotheses will be presented regarding the detected bands whether they come from organic matter or not.

Firstly, it is important to emphasize because the band related to the structural defects of carbon (Band D) and hematite (2LO

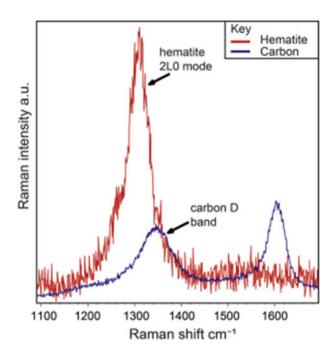


Fig. 11. Illustrative representation of 2LO mode of hematite.

mode) occur at the same frequency; it is not possible to make a direct and clear distinction about what is actually being detected. However, taking as a premise the results obtained, it is still possible to have relationships between the carbon and the analysed meteorite sample, whether direct or indirect.

Experiments with the mixtures of iron (Fe) minerals and organic matter have already been carried out in order to understand the relationship between both materials (Posth *et al.*, 2013). According to Posth *et al.* (2013), several paths of magnetite production were observed from the mixture of hydrated iron oxide and CH_2O (Fig. 12).

However, care must be taken when interpreting magnetite as Banded Iron Formations (BIF), a marker for the primary presence of organic matter. According to Ohmoto (2003), reactions between Fe^(III) and Fe²⁺ minerals in hydrothermal areas (reactions (1)–(2)) can also form magnetite.

$$2Fe(OH)_3 + Fe^{2+} \rightarrow Fe_3O_4 + 2H_2O + 2H^+$$
 (1)

$$Fe_3O_4 + Fe^{2+} + H_2O \rightarrow Fe_3O_4 + 2H^+$$
 (2)

Figure 13 shows three possible trajectories of hematite and magnetite formation formed from mixtures of mineral and organic matter of Fe^(III) in the proportions of high concentration of mixture between organic matter and iron oxide, low concentration of mixture between organic matter and oxide, in addition to no concentration of organic matter and iron oxide.

Conclusion

It was not possible to totally rule out the possible presence of aliphatic structures in the Martian meteorite. Although this chemical compound is unlikely to be an endogenous component actually present in the Zagami meteorite, there are some

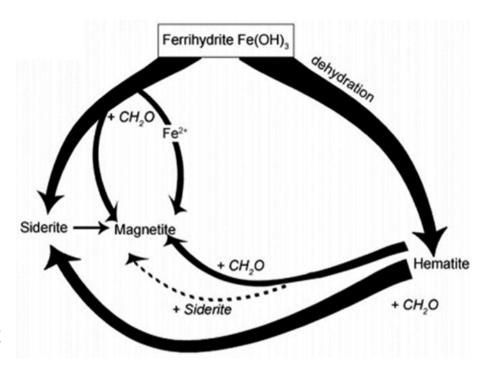


Fig. 12. Schematic system of magnetite and hematite production from different possible processes by Posth *et al.* (2013).

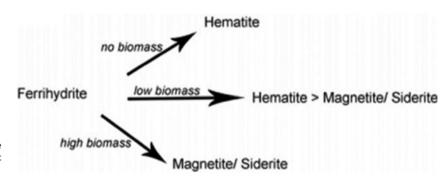


Fig. 13. Representation of three different trajectories for the formation of hematite and magnetite with high, low or without organic matter present in the process of Posth *et al.* (2013).

alternatives. (1) It could refer to possible contamination. Although certain researches that have detected the same results deny this possibility, this cannot be ignored. Although the material has not been manipulated by hand and has been sterilized, the contamination may have occurred during the process of obtaining data, e.g. own interaction of CO₂ from the air.

However, this organic compound can be of endogenous origin and not be the result of contamination. This was also a possibility presented in the discussions. In this case, the aliphatic structure could be a contribution of compounds like $\mathrm{CH}_2\mathrm{O}$ as a remnant of chemical processes that would have occurred in the past and that can generate these aliphatic compounds.

Finally, the final purpose of this work, based on the results obtained, was to try to present a second interpretative alternative in relation to the previously published data. Based on references from published articles and comparative analyses carried out with the present work, it was possible to obtain another bias and interpretation. The bands 2920 and 2850 cm⁻¹, according to these compared analyses, can be attributed to a possible functional group FeOOH due to the presence of minerals of the iron oxide group, such as hematite, magnetite, ferrihydrite and goethite.

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