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Study of organic compounds present in the NorthWest Africa 6148 Nakhlite by means of Raman spectroscopy

Imanol Torre-Fdez, Patricia Ruiz-Galende, Julene Aramendia, Leticia Gomez-Nubla, Kepa Castro, Silvia Fdez-Ortiz de Vallejuelo, Gorka Arana, Juan Manuel Madariaga
University of the Basque Country (UPV/EHU), Barrio Sarriena, s/n, 48940 Leioa, Spain (imanol.torre@ehu.eus)

Abstract

Even though the rovers of the upcoming missions to Mars already have specific instruments for the analysis of organic compounds, Raman spectroscopy is also a suitable technique to provide supplementary information to these other instruments. In this work, several bubbles containing organic compounds have been detected using this technique on the NWA 6148 Martian meteorite. The bubbles contain a complex mixture of carboxylic acids, along with other organic compounds. Raman spectroscopy was used in the high resolution image mode to draw the shape of the bubbles in the context of an olivine matrix.

1. Introduction

Since one of the main objectives of the upcoming Mars missions (ExoMars 2020 from ESA and Mars 2020 from NASA) is to elucidate the possible existence of past life in the planet, instruments and techniques capable of detecting and identifying both organic compounds and biomarkers are essential. The main instrument designed with this purpose in the ExoMars 2020 rover is the MOMA. However, other instruments that are present in the rover could be used, as well, with this aim as a secondary or support technique. They would be used to contrast and confirm the information obtained from MOMA regarding organic compounds. In this work we illustrate how Raman spectroscopy can be useful to detect and characterize prebiotic, abiotic or biotic organic compounds.

In order to test the capabilities of the technique in this regard, the NorthWest Africa (NWA) 6148 nakhlite was studied. As a Martian meteorite, the mineral distribution and morphology is like that on the Red Planet, thus, its study provides information of what kind of results Raman spectroscopy can provide when studying organic compounds in Martian rocks.

2. Sample description

The analysed NWA 6148 sample weights 0.246 g and has dimensions of about 5x7x3 mm. It has not visible impact crust and is brownish with several greenish, black and light brown areas. As other nakhlites, it is mainly composed of augite formed from basaltic magma. It also contains olivine rich in iron as the second most abundant mineral. A complete geochemical study of this sample can be found in literature [2].

3. Methodology

To carry out the study of the organic compounds present in the NWA 6148, an InVia confocal micro-Raman spectrometer (Renishaw, UK) was used. A 532 nm excitation laser was employed to acquire the spectra, both in a point by point and high resolution image mode. The WiRE 4.2 software (Renishaw, UK) was used to process and obtain the information of interest from the Raman images.

In order to find the bubbles and cavities where the organic compounds were present, a SEM-EDS instrument was used with an SCA interface, which allows performing Raman analysis in the desired spots of the SEM-EDS images.

4. Results and Discussion

After an in-depth analysis of the NWA 6148 sample, several bubbles containing organic compounds were detected. Figure 1 shows one of the mentioned bubbles with the Raman image mapping the organic signature bands. The Raman image is composed of 4280 individual spectra, from which almost 500 are the ones with bands of organic compounds (in red in Figure 1, each pixel of the Raman Image corresponds to an individual spectrum).

As can be observed, Raman spectra can be difficult to interpret in terms of organic molecules, especially

if there is more than one compound present simultaneously in the same spot. However, in the case of this bubble, the ν(C-C) stretching vibrations of carboxylic acids of 8 or 10 atoms of carbon are observed in the 1062, 1085 and 1129 cm^{-1} bands. Moreover, the 1295 cm^{-1} band is typical of $\delta(CH_2)$ twist vibrations of these acids and the bands at 1389, 1461 and 1505 cm^{-1} are assigned to $\delta(CH_2)$ or $\delta(CH_3)$ deformations, all of them typical from linear saturated carboxylic acids [1].

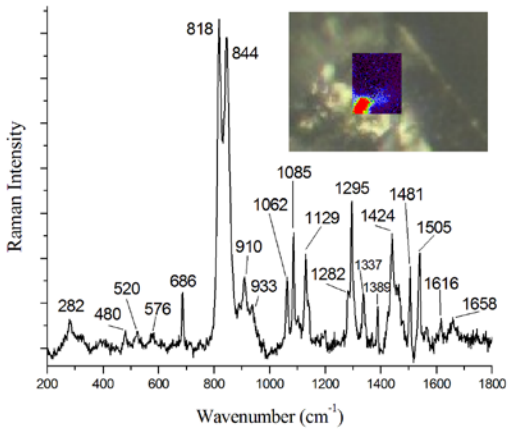

Figure 1. Average Raman spectrum of a mixture of organic compounds contained in a bubble (red), over the Raman signature of an olivine matrix.

Nonetheless, if several spectra are analysed separately and not as an average spectrum of the whole bubble, more differences can be appreciated. Table 1 shows the normalized area, using the 1295 cm^{-1} band area as a normalizing factor, of several Raman bands corresponding to three Raman spectra from a bubble from the NWA 6148. As it can be observed, several areas of the different bands are not proportional from one to another. For instance, the 1062 and 1129 cm^{-1} bands (ν(C-C) stretching vibrations, correlated with the number of carbon atoms in the organic acid chain), is much larger in spectrum 1 than in 2 or 3. However, in the case of the bands assigned to $\delta(CH_2)$ or $\delta(CH_3)$ deformations of linear carboxylic acids, the 1389 cm^{-1} band is larger in spectrum 1, although in the case of the 1505 cm^{-1} it is the smallest one. Other bands, such as the ones at 520 or 686 cm^{-1} are similar from one spectrum to another. All these facts mean that even though the initial guess could not be wrong (carboxylic acid of short chains is present in the bubble), the bubble could be filled by a complex mixture of compounds of similar nature.

Table 1. Normalised area of some organic signature bands of three different Raman spectra obtained from an analysed bubble.

Raman band (cm^{-1})	Normalized Band Area		
	Spectrum 1	Spectrum 2	Spectrum 3
520	0.70	0.43	0.20
686	0.27	0.30	0.54
1062	5.00	0.49	0.98
1085	0.40	0.49	0.46
1129	3.83	0.59	1.20
1295	1.00	1.00	1.00
1337	2.83	0.56	1.16
1389	7.60	0.18	0.61
1461	2.65	0.96	3.63
1505	0.13	0.41	0.38

5. Conclusions

Raman spectroscopy has been proven as a useful technique in order to study bubbles or cavities where organic compounds are present in Martian meteorites. In the current example, it was possible to characterize the nature of the organic compound present in the sample. In addition, it was observed that the bubble has a complex mixture of organic compounds, mainly saturated carboxylic acids. As a disadvantage, Raman spectroscopy has nowadays difficulties to characterize organic compounds of the same nature, as well as to quantify said compounds. For that purpose, new developments are required.

Acknowledgements

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