



Gestión del paisaje. Patrimonio, territorio y ciudad
Paisaiaren kudeaketa. Ondarea, lurraldea eta hiria
Landscape management. Heritage, territory and city

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Geochemical study of the NWA 6148 Martian meteorite and its terrestrial weathering processes

Imanol Torre Fernández



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Authorization of the final master's dissertation supervisor for its presentation

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In Leioa, 5th of July, 2016

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1. INTRODUCTION

1.1. The European Landscape Convention. A new way of perceiving our surroundings

Since its creation, the European Landscape Convention has supposed a change in the perception, concept and management of the landscape. Before its redaction, the concept of landscape, as nowadays we know it, was not extended. In fact, regarding its management and conservation, only a small part of it was taken into account, more precisely, the elements known as Cultural and Natural Heritage, which were considered to be more relevant elements than the rest of the landscape [1]. However, after the publication of the European Landscape Convention, the paradigm about the landscape and how it should be managed changed. The most important change that this convention brought is summed up in the definition of landscape that appears in its first article [2]: *“Landscape means an area, as perceived by people, whose character is the result of the action and interaction of natural and/or human factor”*. This statement does not only include the elements which were considered landscape in the past, but also anything that fits this definition, which could be any big region from a natural to an urban area or any small element, from an old tower to a small river section.

Regarding its management, the convention states that it must lead to the conservation of the landscapes with the aim of preserving their significant aspects, as long as they can be considered Heritage due to their natural or anthropological value [2]. Among others, it is considered as Natural Heritage any physical element which has an outstanding universal value from the aesthetic or scientific point of view [3]. This definition is fitted by the meteorites that are spread through Earth’s surface, as they are very singular and scarce elements. Taking this into account, they can be considered Natural Heritage and should be treated as such. In addition to that, their value from a scientific point of view is very high. Due to these reasons, meteorites are elements that must be conserved and preserved as they are part of our landscape, more precisely of the Natural Heritage.

1.2. Origin of Martian meteorites and the importance of their study

Traditionally, meteorites have been defined as solid objects or bodies that come from the space and fall to Earth's surface through its atmosphere [4]. However, as it is stated by A. E. Rubin and J. N. Grossman [5], this definition has several lacks. On the one hand, not every object that comes from the space is a meteorite. For example, the man-made objects, also known as space debris, may fall into Earth's surface. On the other hand, meteorites are not specific to Earth, as they have also been found in the Moon or Mars. Taking all this into account, a meteorite is re-defined as a solid object formed from a celestial body, which travels from the place on which it was formed to a region outside the gravitational field of that body, and that later collides with a body larger than itself [5].

Among all the meteorites found on Earth, the ones that come from Mars are one of the most relevant for several reasons. They are scarcer than other meteorites, having been found on Earth only 172 Martian meteorites out of 63091 meteorites [6]. The reason for this scarcity is the high fortuitous series of events that must occur to reach Earth's surface. There are several theories that explain this fact, but the most extended one is that given by H. J. Melosh in 1984 [7], who stated that all starts with a big impact event in the surface of Mars caused by a big celestial body. After this impact, which can generate a pressure up to 55 GPa and a temperature up to 1000 °C in the shock [8], large quantities of Martian rocks are ejected from the planet at high speed (Figure 1.1), reaching a height where the gravity of Mars does not affect these materials any longer. After thousands of years travelling randomly through the space, a small portion of the initial ejected material reaches Earth's gravitational field and falls into its surface as a meteorite.

As can be seen, the series of coincidences that these materials must experiment in order to reach Earth is quite large and, thus, this is the main reason for

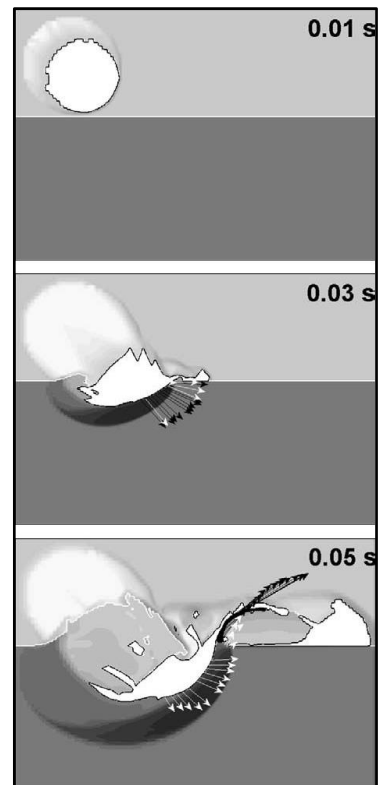


Figure 1.1. Impact of a celestial body (white) with the surface of Mars (dark grey) and the respective times after the contact. Arrows represent vectors of speed, some of them are related to the impact of the body (white) and others to the ejection of materials (black) [9].

them to be scarcer than other types of meteorites, such as asteroids (where there is not a need of an impact in the original celestial body) or the ones that come from the Moon (which they need to travel a shorter distance). Due to this scarcity its value as Natural Heritage is higher, which leads to a need of a better conservation and preservation procedures. However, this increased value is not only due to their scarcity, but also due to the studies that can be indirectly done about Mars biogeochemistry through the meteorites that come from this planet. As it was stated in the decanal report for the exploration of the Solar System, requested by NASA and written by the National Research Council from the USA (NRC) [10], there is a necessity to know more about the composition of Martian rocks. With this aim, the analysis of Martian meteorites is proposed as the best way to carry out this study.

Thanks to the analysis of Martian meteorites, among other discoveries, it has been possible to study the existence of water in the planet [11], its reservoir evolution [12] or even the possible existence of biological activity in the past [13]. In addition, regarding the study of Mars geology and the mineral composition of its surface through the analysis of meteorites, questions like how was the magmatic activity during the formation of the planet [14], which was the origin of sulfates and sulfides in Martian surface [15] or what is the periodicity of resurfacing events and geological ages [16] have been addressed.

The fact that this kind of studies can be carried out through the analysis of Martian meteorites and the fact that they are Natural Heritage makes their conservation a need. In addition, it must be taken into account that not all the materials that form the meteorite are original from the surface of Mars, since the terrestrial weathering can alter them. This is a relevant fact because due to this process, the composition of the meteorites can be altered, which could lead to a mistake in the study of Mars through these materials. In order to achieve the conservation, first of all the composition of the meteorite must be defined. Besides, any alteration that may occur to them can be detected rapidly. There are already works where these processes have been studied [17-19]. Actually, these studies can correct errors. For example, the existence of biological activity in Mars [19], which was asserted because the alterations suffered by the meteorite on Earth were not taken into account. As can be seen, the study of weathering processes in Martian meteorites is almost as important as the study of the meteorite itself.

1.3. Martian meteorites composition and classification

Although they seem to be similar, Martian meteorites usually have different compositions and structure, both among them and among all the meteorites. When they were first studied, it was obvious that they had different characteristics from the other meteorites studied until that moment [20]. First of all, their crystallization ages was fixed around 1.3 million years ago, 3 million years earlier than any other meteorite, which, taking into account the thermal evolution of asteroids, it was impossible for any celestial body. In addition, several known characteristics of the planet were ascertained in these meteorites, for example the lack of a magnetic field in Mars or its magmatic activity along the years, which differentiated them from the rest of meteorites.

With regard to the similarities among the Martian meteorites, there are some notable ones, such as the fact that they have a similar origin of formation, as all of them are igneous rocks. Moreover, all are achondrites with no chondrules in their structure. Finally, their geochemical composition is similar as they are unbrecciated augite to olivine cumulates rocks [20]. However, not every Martian meteorite is similar to each other, thus they have not exactly the same origin. Due to this fact, they can be divided mainly into three subgroups named as shergottites, nakhlites and chassignites, also known as SNC meteorites (Figure 1.2).

- Shergottites. They were named after the discovery of the first meteorite that belonged to this group, the Shergotty meteorite, fallen in Bihar, India, in 1865. Their origin is supposed to be related to the crater Mojave, which is the youngest one of Mars [21]. Although they have similar characteristics, they can be subclassified into different groups attending to various properties, for example their rare-earth elements content [22].
- Nakhlites. The first nakhlite, Nakhla meteorite, fallen in Alexandria, Egypt, in 1911, gave the name to this Martian meteorite group. Their origin is still unknown, but it is supposed to be related to one of the large volcanic zones of Tharsis, Elysium or Syrtis Major Planum (Figure 1.3) [23].
- Chassignites. They were named after the discovery of Chassigny meteorite, which fell at Haute-Marne, France, in 1815. Their Martian origin is totally unknown nowadays,

which could be due to the fact that there are only three known meteorites that belong to this group [6], not being enough to reach that kind of conclusions.

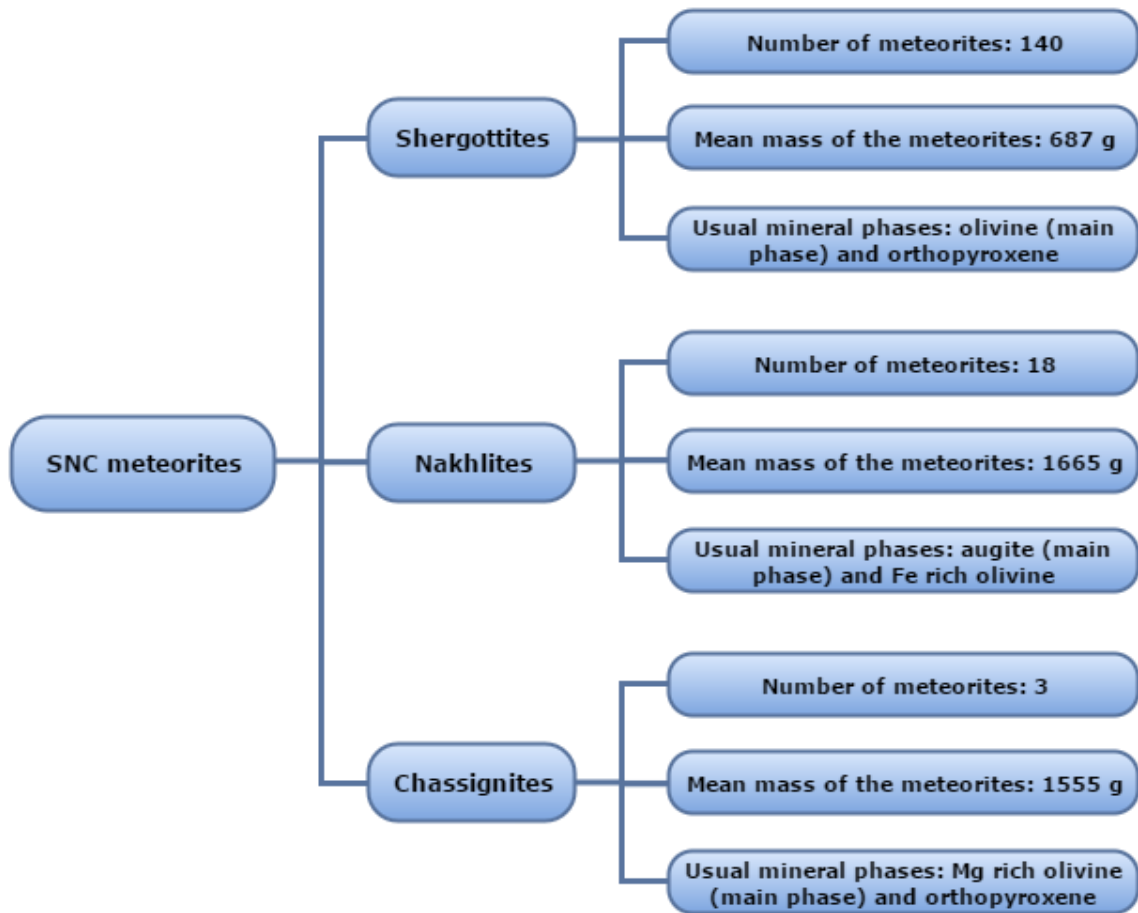


Figure 1.2. SNC meteorites classification and the number, mean mass and usual mineral phases of meteorites of each group.

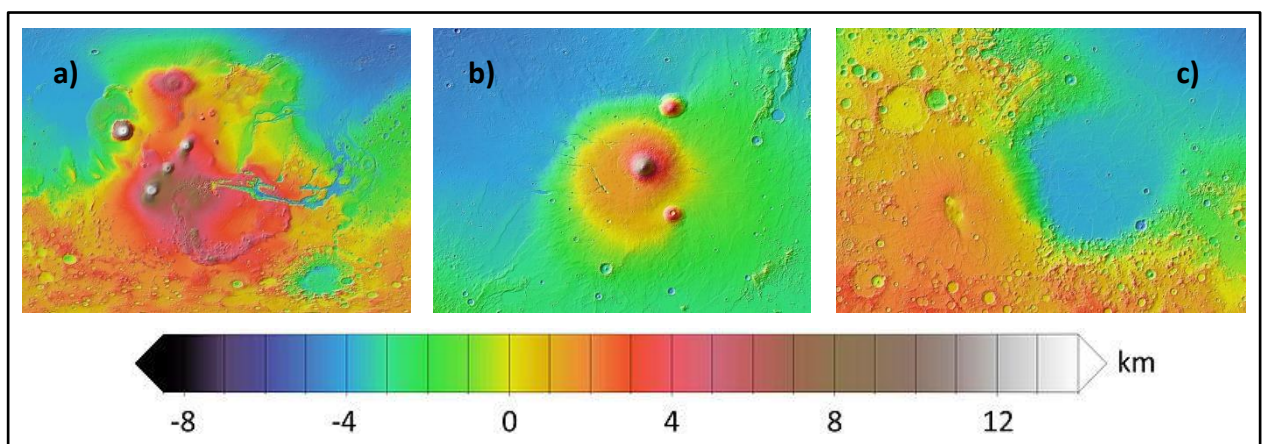


Figure 1.3. Mars Orbiter Laser Altimeter (MOLA) colored topographic map of the three possible origin regions of nakhilites: a) Tharsis, b) Elysium, c) Syrtis Major Planum [24].

1.4. NWA 6148 nakhlite

The nakhlite group of meteorites is probably the most interesting group of Martian meteorites due to the differences with the other two main groups. On the one side, their composition and structure allow the study of some Martian biogeochemical properties that cannot be studied through the other meteorites, such as the aqueous activity of the planet, due to the presence of Martian aqueous alterations in these meteorites [25]. On the other side, unlike what occurs with chassignites, enough nakhlites have been found on Earth in order to be able to compare the studies and conclusions performed about Mars through the other nakhlites. Specifically, nowadays there exist 18 different meteorites catalogued as nakhlites and, generally, they are light and present small masses (Table 1.1) [6].

Table 1.1. Name, mass, year and place where all nakhlites were found on Earth [6].

| Name | Abbreviation | Year found | Place | Mass (g) |
|------------------------|---------------------|-------------------|----------------------|-----------------|
| Governador Valadares | - | 1958 | Minas Gerais, Brazil | 158 |
| Lafayette | - | 1931 | Indiana, USA | 800 |
| Miller Range 03346 | MIL 03346 | 2003 | Antarctica | 715 |
| Miller Range 090030 | MIL 090030 | 2009 | Antarctica | 453 |
| Miller Range 090032 | MIL 090032 | 2009 | Antarctica | 532 |
| Miller Range 090136 | MIL 090136 | 2009 | Antarctica | 171 |
| Nakhla | - | 1911 | Alexandria, Egypt | 10000 |
| Northwest Africa 817 | NWA 817 | 2000 | Morocco | 104 |
| Northwest Africa 998 | NWA 998 | 2001 | Northwest Africa | 456 |
| Northwest Africa 5790 | NWA 5790 | 2009 | Northwest Africa | 145 |
| Northwest Africa 6148 | NWA 6148 | 2009 | Northwest Africa | 270 |
| Northwest Africa 10153 | NWA 10153 | 2014 | Northwest Africa | 119 |
| Northwest Africa 10645 | NWA 10645 | 2016 | Northwest Africa | 12 |
| Northwest Africa 10659 | NWA 10659 | 2015 | Morocco | 7 |
| Northwest Africa 10720 | NWA 10720 | 2015 | Mauritania | 1015 |
| Yamato 000593 | Y-000593 | 2000 | Antarctica | 13710 |
| Yamato 000749 | Y-000749 | 2000 | Antarctica | 1283 |
| Yamato 000802 | Y-000802 | 2000 | Antarctica | 22 |

Nakhlites were formed in Mars from a lava flow with a thickness between 15-120 m, which was stated by comparison with almost identical rocks original from Earth and their formation [26]. As it was stated by A. H. Treiman [23], this flow was composed of basaltic magma, which, after cooling, gave to the nakhlites the composition they have. Specifically, they are achondrite meteorites mainly formed of augite, a clinopyroxene, which is an igneous group of rocks. This augite, along with olivine, which is the other main mineral found in these meteorites, present euhedral crystals in mesostases. Nakhlites usually present a homogeneous composition in these two minerals, separately in their rims and cores, although they have small variations among the different meteorites of this group. In addition to these two minerals, nakhlites may have other phases in their composition, but in a lower proportion, which can be original Martian materials or formed on Earth due to the weathering. For example, calcite or other clay minerals can be found in nakhlites, as a product of weathering processes [27]. In contrast, titanomagnetite can be found in nakhlites [23], which is stated as a Martian original mineral.

Regarding their study, as it was mentioned before, the information obtained from these meteorites can be of relevance for the study of Mars. Due to this fact, the analyses that have been carried out in nakhlites in the last years have been progressively increasing. However, one of these meteorites has not been studied at all, the NWA 6148. As it is stated in the Meteoritical Bulletin nº 102 [28], it was found in the region of Northwest Africa and its fall was not observed. This meteorite was first documented in 2009 when A. Aaronson bought two stones that fitted together to a meteorite dealer in Erfoud, Morocco. It is possibly paired with meteorite NWA 5790, although there are not studies that confirm or deny this fact. There are only studies about the germanium dichotomy [29] and its siderophile and chalcophile element abundances [30], aside from analysis not published in scientific journals or conferences, such as its sulfur isotopic composition or its concentration of water. Due to this lack of knowledge about meteorite NWA 6148, its analysis is crucial for the reasons already mentioned in this manuscript.

In order to study this meteorite, the use of non-destructive techniques is highly recommended, as it is mentioned in the decadal report for the exploration of the Solar System [10], since there only exists a limited amount of sample and its consumption should be avoided. In addition, as it was explained previously, the possible weathering of the

Introduction

meteorite on Earth must be taken into account, as it can alter the composition or structure of the sample. In fact, the nakhlites may suffer different kinds of alterations depending on where they fell. For instance, in arid or desert areas evaporites are usually formed as a result of Earth's weathering processes [27], while in tundra areas the partial oxidation of the iron from olivines can be observed [31].

2. OBJECTIVES

As it has been explained above, the geochemical characterization of the NWA 6148 Martian meteorite could be of huge interest since they are not too many works that studied it. Through this characterization, it is crucial to distinguish the original Martian mineral phases from those that were caused by Earth's weathering processes in order to avoid misunderstandings. In the case of the weathering processes products, an explanation of their presence should be found, so that meteorites' materials are more understood. With all these in mind, for the realization of this work the following main objectives were proposed:

- 1- The study, through non-destructive techniques (SEM/EDX, Raman, SCA), of the NWA 6148 Martian meteorite with the aim of knowing its geochemical characteristics, helping to know more about the geology of Mars.
- 2- To elucidate possible terrestrial weathering processes in the meteorite using also non-destructive techniques and to explain their origin.
- 3- To test the goodness of Raman spectroscopy to characterize the metal composition of the Martian original materials using the position of the bands, as an alternative to other analysis techniques.

3. EXPERIMENTAL PROCEDURE

3.1. Description of the sample

For this work, a single sample of the NWA 6148 meteorite acquired by IBeA research group was analyzed. The sample consisted of a portion of the original NWA 6148, which fell in North West Africa region. As it was mentioned above, it is a Martian meteorite that belongs to the nakhlite group and it was first documented in 2009, weighing 270 g. The analyzed sample dimensions are about 6 x 9 x 4 cm, it weighs 0.246 g ($9 \cdot 10^{-4}$ % of the original meteorite weight) and it is a fragile rock without visible impact crust, which means it was obtained from the inner part of the NWA 6148. The sample is brownish with several greenish, black and light brown areas (Figure 3.1).

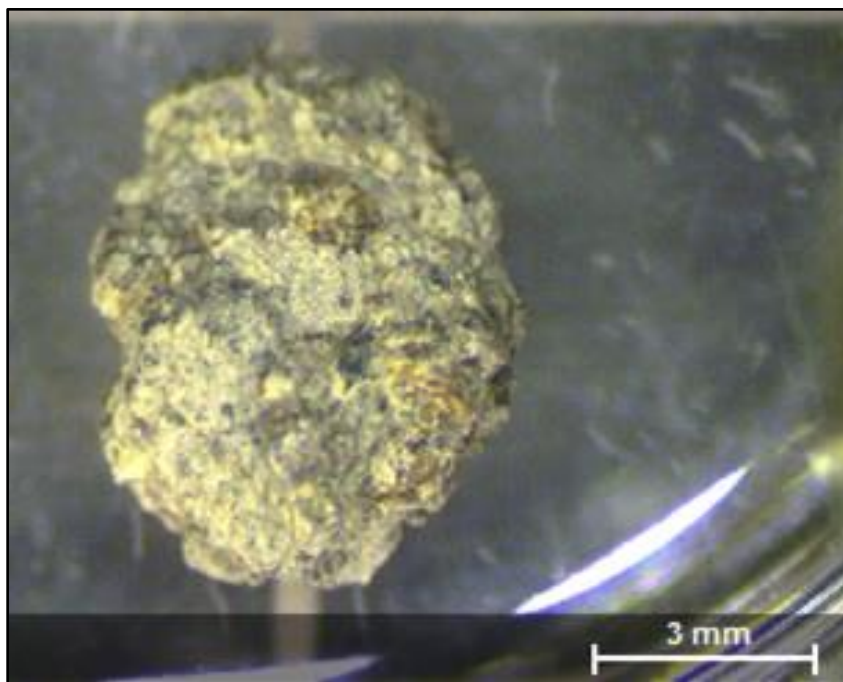


Figure 3.1. Studied sample of the NWA 6148 meteorite.

3.2. Materials and methods

3.2.1. Preparation of the sample

The sample was tried to polish to perform Raman imaging analysis. However, due to its fragility, it was impossible to polish any of its sides. Actually, the sample split into three fragments when the polishing was tried. These fragments were attached with carbon

adhesive tape to metallic pins in order to facilitate the subsequent analyses and handling (Figure 3.2). In addition, this split allowed the comparison of results between the surface of the sample with its inner part, with the aim of checking that the sample had not been contaminated during its handling.



Figure 3.2. Fragments of the initial NWA 6148 sample attached to pins with carbon adhesive tape.

3.2.2. Raman spectroscopy

An exhaustive study of the three fragments of the sample was carried out by means of Raman spectroscopy in order to obtain the molecular composition. For this aim, two different equipments were used:

- **Renishaw inVia micro-spectrometer.** A Renishaw inVia Raman micro-spectrometer (Renishaw, UK) equipped with a 532 nm excitation diode laser and a CCD detector (Peltier cooled) was used in order to carry out the measurements (Figure 3.3). The nominal power of the laser could be modulated in order to avoid the thermodecomposition of the sample from 0.0001 % to 100 % of its maximum power. During the study, there always arrived less than 20 mW to the sample.

The equipment had coupled a microscope and the lenses used were of 20x and 50x. This microscope had a camera coupled for a perfect focusing of the laser spot on the sample. In addition, the instrument was installed on an antivibratory table. The mean spectral

Experimental Procedure

resolution was around 1 cm^{-1} and the spectra were obtained in a range of $100\text{-}1800\text{ cm}^{-1}$ or $100\text{-}3200\text{ cm}^{-1}$, depending on the aim of the analysis. Besides of punctual analysis, Raman imaging analysis of certain areas of interest was carried out, whenever the surface of the sample was flat enough.

- **Renishaw RA-100 spectrometer.** A Renishaw RA-100 Raman Spectrometer (Renishaw, UK), coupled to a fiber optic microprobe equipped with a 785 nm excitation diode laser and a CCD detector (Peltier cooled) was used to carry out some analyses. The nominal power of the laser was 150 mW at the source and neutral filters allowed working at 1 %, 10 % and 100 % of the total power. The laser power was modulated depending on the spot measured in order to avoid thermodecomposition and chemical or mineralogical changes.

The microprobe mounted on a tripod (Figure 3.3) was joined to long range lenses of 20x and 50x. The equipment had coupled a micro-camera for a perfect focusing on the areas of interest. The spectra were obtained in a range of $200\text{ - }3200\text{ cm}^{-1}$ with a mean spectral resolution of 2 cm^{-1} .

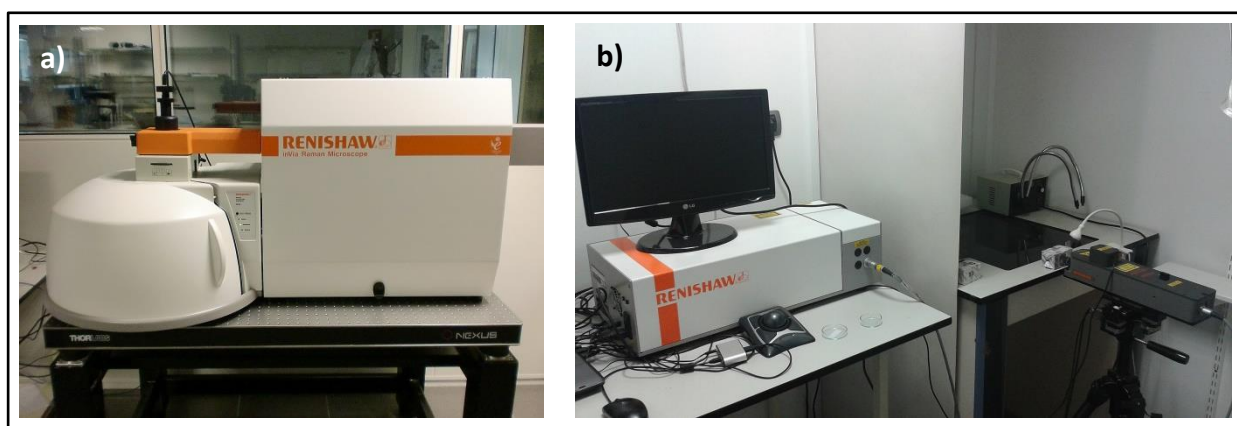


Figure 3.3. a) The Renishaw inVia Raman spectrometer provided with a 532 nm excitation laser and b) the Renishaw RA-100 spectrometer with a 785 nm excitation laser.

For the analysis with both instruments, the number of accumulations and the acquisition time were modified and optimized for each measurement in order to improve the signal to noise ratio. The calibration of both equipments was performed daily with a silicon slice, using its 520.5 cm^{-1} band. The software used for data collection was the Wire 4.2 (Renishaw, UK) and the Wire 3.2 (Renishaw, UK), for the Renishaw inVia micro-spectrometer and the Renishaw RA-100 spectrometer, respectively. For the analysis and treatment of the spectra the Omnic 7.2 software (Thermo Fisher-Nicolet, Madison, USA) was used. Data

interpretation was performed by comparison of spectra with pure standard spectra contained in the e-VISARCH [32] and e-VISART [33] spectral databases, in RRUFF on-line database [34] and in bibliography.

3.2.3. Structural and chemical analysis

In the cases where deeper study was needed, a structural and chemical analysis (SCA) was performed with a Scanning Electron Microscope – Energy Dispersive X-Ray Spectroscopy (SEM-EDS) instrument joined to a Raman spectrometer (Figure 3.4). The elemental composition determination of the three fragments of the sample was carried out using the SEM-EDS system. Coupled to this SEM-EDS system a Raman spectrometer was used in order to measure the sample in the same spot where elemental data was obtained. This interface was set up so the laser light and the Raman signal were transmitted between the Raman spectrometer and the SCA via 2 m fiber optic cables up to the SEM vacuum chamber. This fact allowed performing Raman spectroscopy measurements simultaneously with secondary electron (SE) imaging inside the SEM. Thereby, first, a scanning image of the sample surface was obtained using the SEM. Then, EDS allowed the elemental mapping of the area and, with this information, Raman laser beam was focused on the area of interest to acquire the Raman spectra. To sum up, thanks to this system the elemental and molecular information of the same micrometric spot was obtained.

In order to perform this analysis, it was used an EVO[®]40 Scanning Electron Microscope (Carl Zeiss NTS GmbH, Germany) coupled to an X-Max Energy-Dispersive X-ray spectroscopy system (Oxford Instruments, UK). SEM images were acquired at high vacuum employing an acceleration voltage of 20 KV. For a more detailed analysis, a secondary electron detector was used, reaching magnifications up to 10000x. The elemental mapping analysis was carried out using the EDS with a working distance of 8.5 mm, a take-off angle of 35° and an acceleration voltage of 20 KV.

As it has been already mentioned, there was a Raman SCA coupled to the SEM-EDS system. The instrument was a Renishaw inVia Raman micro-spectrometer (Renishaw, UK), with a Peltier-cooler (-70 °C) detector. Punctual measurements were made using a 514 nm excitation laser in the sites of interest, applying in the source a maximum power of 50 mW, being less than 20 mW in the analyzed sample. The mean spectral resolution was around 1

Experimental Procedure

cm^{-1} . The software used for the data collection was the Renishaw Wire 3.2. The system, both the SEM-EDS and the coupled Raman spectrometer, was installed on an antivibratory table and inside a temperature controlled room.

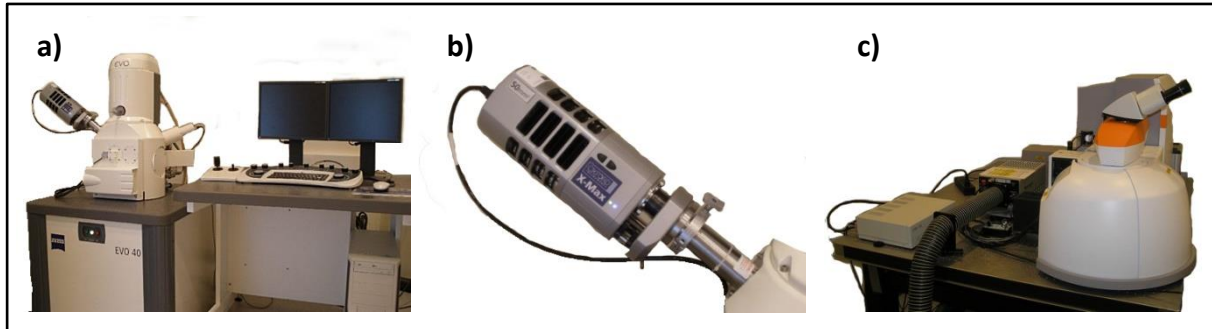


Figure 3.4. a) SEM-EDS system with b) and EDS detail and c) the coupled Raman spectrometer.

4. RESULTS AND DISCUSSION

As the main objective of this work was the geochemical characterization of the NWA 6148 meteorite, the Results and Discussion chapter has been divided in the different mineral phases that have been found in the sample, along with the results derived from each one.

4.1. Augite

As it was mentioned above, the main compound in the nakhlites group of meteorites is usually augite. As it was expected, the matrix of the analyzed sample is also formed of this mineral, which was ascertained experimentally with the Raman spectroscopy equipments (Figure 4.1). The chemical formula of this pyroxene mineral is $(Ca, Na)(Mg, Fe, Al, Ti)(Si, Al)_2O_6$. As it is seen, the augite doesn't have a defined stoichiometric formula, since it can have different proportions of the metals that form it. On the one and, the metals that form the anion, Al and Si, can have different proportion between them. On the other hand, regarding the metals that form the cations, there are two groups of metals that are related between them, the Ca and Na and the Mg, Fe, Al and Ti.

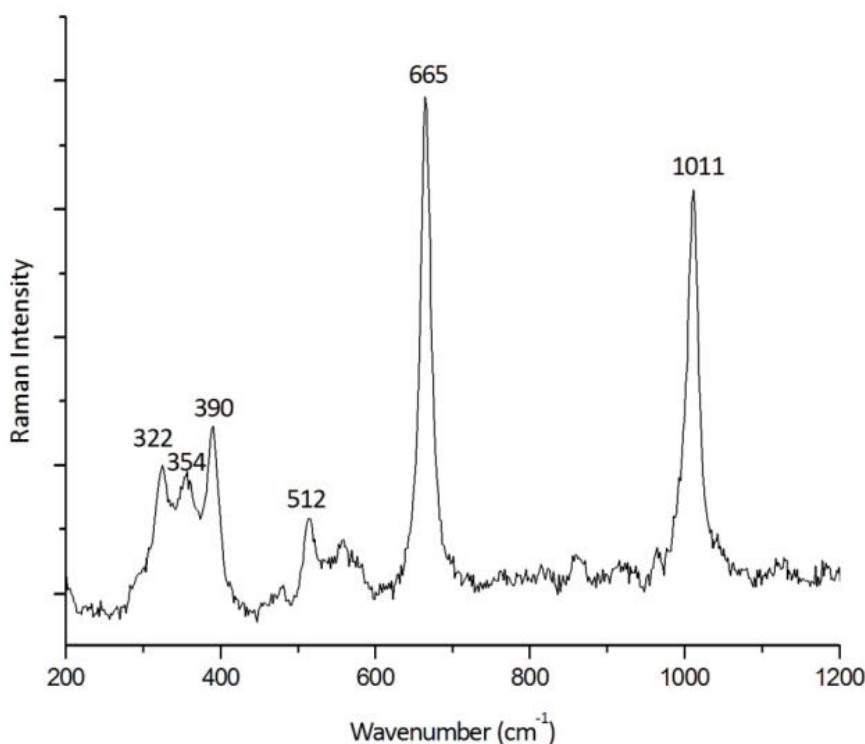


Figure 4.1. Augite Raman spectrum found in the matrix of the sample.

Results and Discussion

However, the metals Ti, Na and Al are usually in low proportion compared to the Fe, Mg and Ca, as it is usual in pyroxenes [35]. Due to this fact, this family of minerals is usually defined by its content of Fe, Mg and Ca, given as ferrosilite (Fs, $\text{Fe}_2\text{Si}_2\text{O}_6$), enstatite (En, $\text{Mg}_2\text{Si}_2\text{O}_6$) and wollastonite (Wo, $\text{Ca}_2\text{Si}_2\text{O}_6$) (Figure 4.2), respectively. These proportions are usually provided as $\text{Fs}_{xx}\text{En}_{yy}\text{Wo}_{zz}$, where XX, YY and ZZ represent the percentage of each metal over the total amount of the three. In the case of augite, as it is seen in Figure 4.2, its composition can vary from Fs_0 to Fs_{80} ,

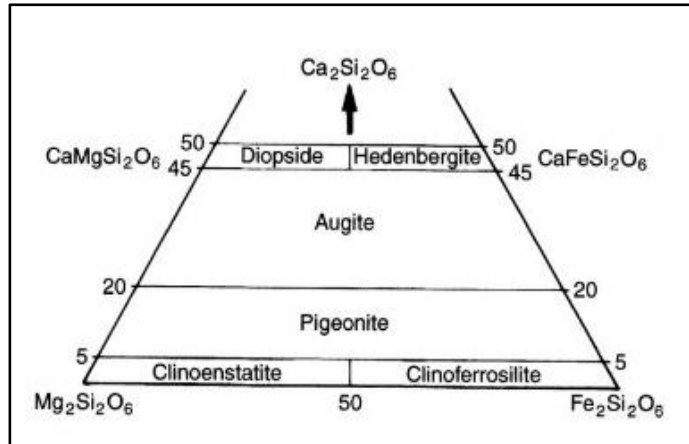


Figure 4.2. Triangular diagram showing the nomenclature of common pyroxenes in terms of their cations composition [36].

from En_0 to En_{80} and from Wo_{20} to Wo_{45} [36]. Since this mineral can have different compositions, their Raman spectra's bands change accordingly to these metal proportion changes [37]. These changes in the wavenumber where the bands appear are associated to the different stretching and bending modes of each bond present in the molecule. Specifically, its main bands (the ones around 1010 cm^{-1} and 666 cm^{-1}) and the ones that appear in the range of $500\text{-}600\text{ cm}^{-1}$ are associated to the proportion of Si and Al that form the alumino-silicate anion of the mineral. The bands associated to the metals proportion are the ones that appear in the range of $300\text{-}450\text{ cm}^{-1}$ [37].

Based on the spectra of different pyroxenes obtained by E. Huang et al. [37], it was estimated that the mean composition in Fe and Ca of the augite of the sample was Fs_{17} and Wo_{45} , respectively. The results observed in literature by means of other techniques for the augite metal composition for the NWA 6148, $\text{Fs}_{22}\text{Wo}_{43}$ [28], are very close to the ones estimated through Raman analysis in this work, as in the case of Wo it only differs in 2 % and in the case of Fs the difference is 5 %. Taking into account the results obtained experimentally, the content of Mg should be En_{38} , as it is the difference of the 100 % of the considered metals minus the estimated amount of Fs (which represents iron) and Wo (which represents Ca). However, it was not possible to estimate the amount of Mg present in the

augite through the Raman spectra, as the presence of Ti, Na and Al in the molecule interfered with the band that gives that result, as it will be explained below.

To support the obtained results and to complete them, the SCA analysis was used. First, an area where the Ca concentration was higher than the Fe concentration, which also had Mg, Ti, Na and Al, was selected and analyzed with the SEM-EDS system (Figure 4.3). Once the site of interest was defined, a Raman spectra was performed with the Raman SCA coupled to the system. With this measurement, it was verified that the area corresponded to a zone where augite was present as the only mineral phase. As it can be seen in the Figure 4.3, this pyroxene had a higher content of Ca than Fe in the NWA 6148, as the results obtained from the band position in the Raman spectra predicted.

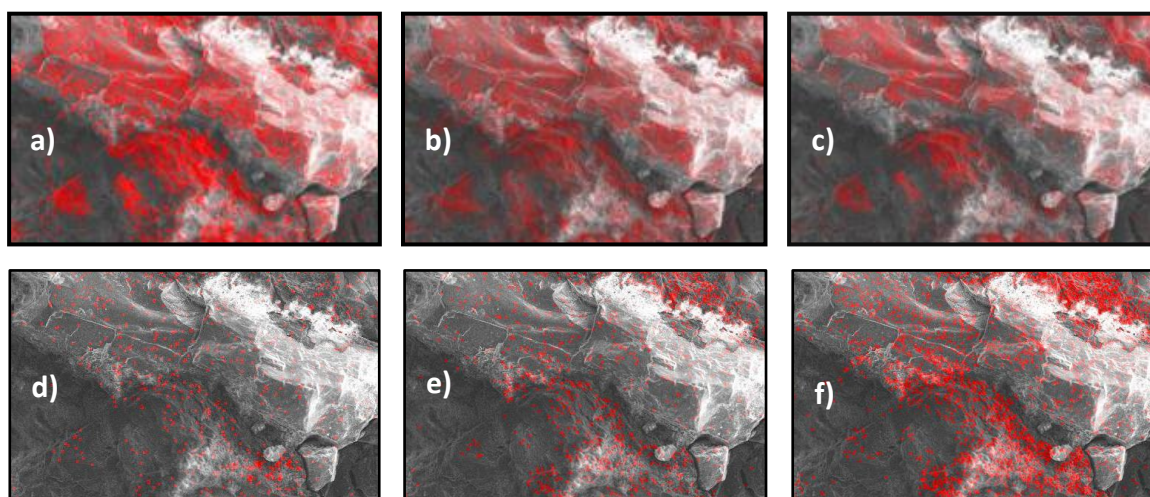


Figure 4.3. SEM image of an area with high presence of augite where there are represented in red the presence of a) Ca, b) Fe, c) Mg, d) Ti, e) Na and f) Al analyzed with EDS.

In the case of Mg content, it was observed that the amount present in the augite is lower than the Fe (17 %, following Raman data), so that would be its maximum concentration in the mineral. This fact confirmed that the estimated amount of Mg present in the mineral calculated through the Raman spectra (En_{38}) was wrong, as the Ti, Na and Al interfered in its band. However, due to this fact, it was deduced that the addition of Mg + Ti + Na + Al was the 38 % of the total of metals that formed the cations of the augite. As the Mg could have a maximum concentration of 17 %, the concentration for the addition of Ti + Na + Al had to be at least of 21 %, so that between both they reach the 38 %.

Results and Discussion

This theory was checked with the semi-quantitative results obtained with the SEM-EDS system (Table 4.1), expressed as the percentage of each metal over the total metals forming the cations. The Al is present in the augite both as a metal and forming the alumino-silicate anion. Due to this fact, the 8 % of Al content in the olivine estimated with SEM-EDS did not represent the amount of aluminum as a cation. Due to that reason, it was not possible to compare this results with the ones obtained from Raman spectra. However, the results from SEM-EDS were used to demonstrate that the amount of Mg estimated with E. Huang et al. [37] Raman spectra corresponded to Mg + Ti + Na + Al. Taking into account the addition of only the Ti and Na concentrations estimated by the SEM-EDS (6 %), it was noticed that it was more than a third part of the observed amount of Mg (15 %). This fact confirmed that the amount of Ti, Na and Al present in the augite was not insignificant in respect to the other metals, so it had to be taken into account and could mean that the 38 % that was firstly considered as Mg through the Raman bands estimation was the addition of Mg + Ti + Na + Al.

Table 4.1. Concentrations of the metals that form the augite cations observed with the SEM-EDS system.

| Element | Ca | Fe | Mg | Ti | Na | Al |
|-------------------|----|----|----|----|----|----|
| Concentration (%) | 49 | 22 | 15 | 1 | 5 | 8 |

Taking all this into account, the augite present in the NWA 6148 had a composition of $\text{Fs}_{17}\text{Wo}_{45}$. However, if not only the Fe, Mg and Ca are taken into account for the characterization of this pyroxene, but also the Ti, Na and Al, the composition was estimated to be $\text{Fe}_{17}\text{Ca}_{45}[\text{Mg}_{0-17}(\text{Ti}, \text{Na}, \text{Al})_{21-38}]_{0-38}$, although this result must not be taken as a quantitative analysis in any case.

This augite composition was compared to the ones found in literature. NWA 5790, which is the naxhlite that is supposed to be paired with the one characterized in this work, has an augite composition of $\text{En}_{33.1 \pm 1.6}\text{Fs}_{26.6 \pm 1.6}\text{Wo}_{40.3 \pm 0.6}$ [27]. The authors carried out a quantitative analysis with electron probe microanalysis (EPMA), with a set of calibration standards, for the analysis of the sample of NWA 5790. Regarding the Wo content, it has a difference of 4.7 ± 0.6 , while in the case of Fs content, it was seen that it differs in a 9 ± 1.6 % from the NWA 6148 estimated one. In both cases, especially for the calcium content (provided as Wo), it was observed that the difference was not considerable. It must be taken into account that

the characterization obtained for the augite of the NWA 6148 in this work is an estimated one, that it has not been proved that this meteorite is paired with NWA 5790 (so a different augite composition for both nakhlites is possible) and that in the article of T. Tomkinson et al. [27] Ti, Na and Al were not taken into account. They stated that Ti, Na and Al were present in the augite composition of their NWA 5790 sample, but they did not consider them for the characterization of this mineral phase and gave their results as $En_{Y\gamma}Fs_{Xx}Wo_{Zz}$. Taking all these facts into account, it is believed that the characterization of this mineral phase through Raman spectroscopy is a good approach. However, further work should be developed in this area in order to obtain a calibration set were Ti, Na and Al are taken into account.

4.2. Olivine

As it was mentioned above, the second most common mineral phase present in nakhlites is olivine, which chemical formula is $(Mg, Fe)_2SiO_4$. The first time this compound was found in the analyzed sample was by means of Raman spectroscopy, in which spectrum the primary bands of the olivine were observed ($817-819\text{ cm}^{-1}$, $841-847\text{ cm}^{-1}$) along with some of its secondary bands (909 cm^{-1} and 522 cm^{-1}) (Figure 4.4). However, in contrast with the augite, the wavenumber where the maximum intensity of the bands of olivine appeared varied from one spectrum to another.

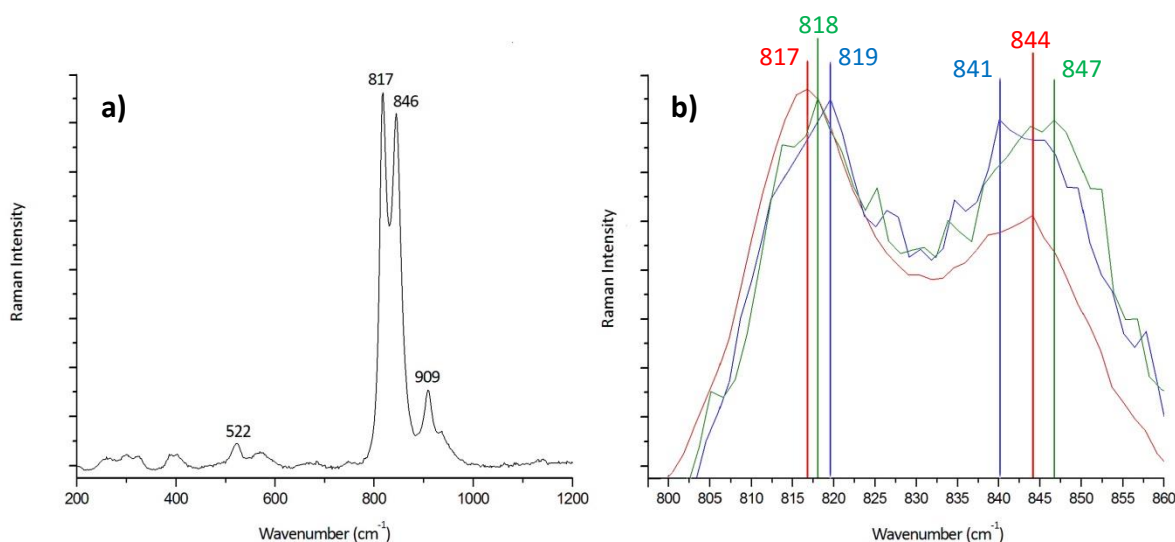


Figure 4.4. a) Olivine Raman spectrum found in the matrix of the sample and b) a zoom in of the $800-860\text{ cm}^{-1}$ range, where it is observed the wavenumber variation in the olivine spectra.

Results and Discussion

In this case, the two main bands present in the spectra, which appear in the range of 841-847 cm^{-1} (K_1) and 817-829 cm^{-1} (K_2), are related to the Si-O symmetric stretching and to the Si-O asymmetric stretching, respectively [38]. This variation in the position of the band is related to the proportion of Fe and Mg present in the mineral, given as content of fayalite (Fa, Fe_2SiO_4) and forsterite (Fo, Mg_2SiO_4), respectively. These proportions are provided as $\text{Fo}_{xx}\text{Fa}_{yy}$, where XX and YY represent the percentage of each metal over the total amount of the two. The fact that the wavenumber of the main bands of olivine varied experimentally lead to the conclusion that there were different types of olivines regarding the proportion of Mg and Fe present in the matrix of the NWA 6148 meteorite sample. In order to characterize them, 4 different calibration curves were considered (Equation 1-4), obtained from two articles [38, 39] where the correlation of the position of the two main bands is studied regarding %Mg, where %Mg is given as a decimal fraction and is defined as $\text{Mg}/(\text{Mg}+\text{Fe})$.

$$\%Mg = -610.65 + 1.3981K_1 - 0.00079869K_1^2 \quad \text{Equation 1}$$

$$\%Mg = \frac{-38847.1256 + 86.9086K_1 - 0.048382K_1^2}{100} \quad \text{Equation 2}$$

$$\%Mg = -3715.8 + 8.9889K_2 - 0.0054348K_2^2 \quad \text{Equation 3}$$

$$\%Mg = \frac{-484679.0451 + 1172.7260K_2 - 0.70923K_2^2}{100} \quad \text{Equation 4}$$

These calibration curves were tested in the laboratory with a commercial standard of olivine, which had a composition of $\text{Fo}_{89}\text{Fa}_{11}$, characterized with X-ray diffraction (XRD) and wavelength dispersive X-ray fluorescence (WD-XRF). 10 different grains of this olivine were measured with Raman spectroscopy and the wavenumbers of the bands obtained were introduced in the four calibration curves. Then, the mean value of the results obtained with each equation was calculated, with the confidence interval at 95 % of confidence, taking into account the uncertainty associated to each calibration curve and the standard deviation of the results. Observing the obtained results (Table 4.2), it was decided that the Equation 1 was the one that suited better with the real values of the olivine standard, as the result obtained with it were very accurate and had the lowest uncertainty.

Table 4.2. Results of the composition of the standard of olivine using the four considered calibrations.

| Composition of olivine | Equation 1 | Equation 2 | Equation 3 | Equation 4 |
|------------------------|------------|------------|------------|------------|
| Fo (%) | 89 ± 3 | 91 ± 6 | 89 ± 5 | 96 ± 5 |
| Fa (%) | 11 ± 3 | 9 ± 6 | 11 ± 5 | 4 ± 5 |

After deciding which calibration curve was the one that gave the best results for the olivine commercial standard, the composition of the olivines present in the meteorite sample were calculated using the selected calibration curve. The composition range of the olivines found was $FO_{25.4\pm 3}Fa_{74.6\pm 3} - FO_{55.3\pm 3}Fa_{44.7\pm 3}$, where the confidence interval is given as the uncertainty of the calibration curve. As it could be seen, the olivines present in the sample had, for the most part of the range, a higher content of iron than magnesium, which correspond to the usual proportions found in nakhlites, as it was explained above. Furthermore, the olivine composition that is stated in literature for the NWA 6148 is $FO_{42.0}Fa_{58.0}$ for the core of grains of olivine and $FO_{25.5}Fa_{74.5}$ for the rims of the grains [28]. Experimentally, it was not possible to differentiate the cores and the rims of the grains of the analyzed olivine. However, olivines with the richest iron content found experimentally ($FO_{25.4\pm 0.3}Fa_{74.6\pm 0.3}$) match perfectly with the composition of the olivines in the rims ($FO_{25.5}Fa_{74.5}$). This high concentration of iron in the olivine would gradually decrease until reaching the center of the core of the grain, which would explain the presence of different proportions of Fe and Mg found in the sample. For these olivine grain cores, where the highest amount of Mg is found in the mineral phase, the experimentally found composition ($FO_{55.3\pm 0.3}Fa_{44.7\pm 0.3}$) differs significantly from the one stated in literature ($FO_{42.0}Fa_{58.0}$). This difference could be explained because in literature not all the olivine grains were studied and, as the NWA 6148 nakhlite is heterogeneous in this mineral composition, new olivine with a higher content of Mg could have been found in the cores of the grains in this work.

Regarding other nakhlites, after the finding in this work of these magnesium rich olivine grain cores, the NWA 6148 has become the nakhlite with the greatest amount of magnesium in the core of its olivine grains, with a 55.3 %. The second one is the NWA 817, with a 43 % of magnesium in the core of its olivine grains [40]. As it can be seen, there exists a notable

difference between both compositions, which could lead to think that some nakhlites may have more magnesium content in olivines than it was thought and stated in bibliography.

4.3. Cobalt (II, III) oxide

The first time the sample was analyzed with the SEM-EDS system cobalt was seen in some isolated areas of one of the meteorite fragments (Figure 4.5). As it is known, cobalt is usually found in nature as a minor trace of other mineral phases, especially in copper and nickel minerals, although in some cases it can be found as the main component, as cobaltite, skutterudite or safflorite [41]. However, as it can be seen in Figure 4.5, in the analyzed sample there are only a few small areas with presence of Co. In addition, the cobalt is not distributed homogeneously through the area, fact that would be observed if the metal appeared as an impurity in another mineral phase. All these facts lead to think that the analyzed area was composed of at least one compound where the cobalt was the main metal. Using the Raman SCA coupled to the SEM-EDS system the spectra of that area was obtained (Figure 4.6).

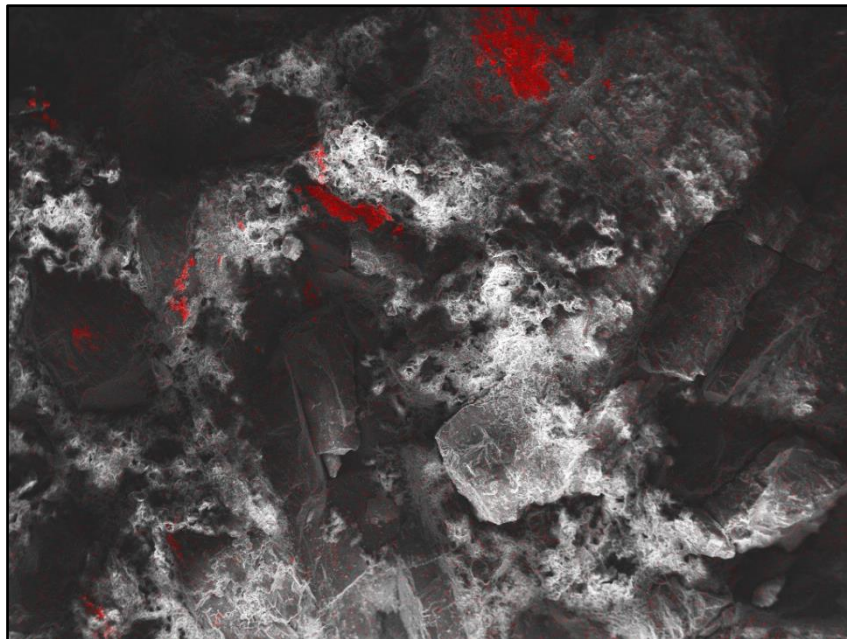


Figure 4.5. SEM image of one side of one of the NWA 6148 fragments and the Co presence (red) analyzed with EDS.

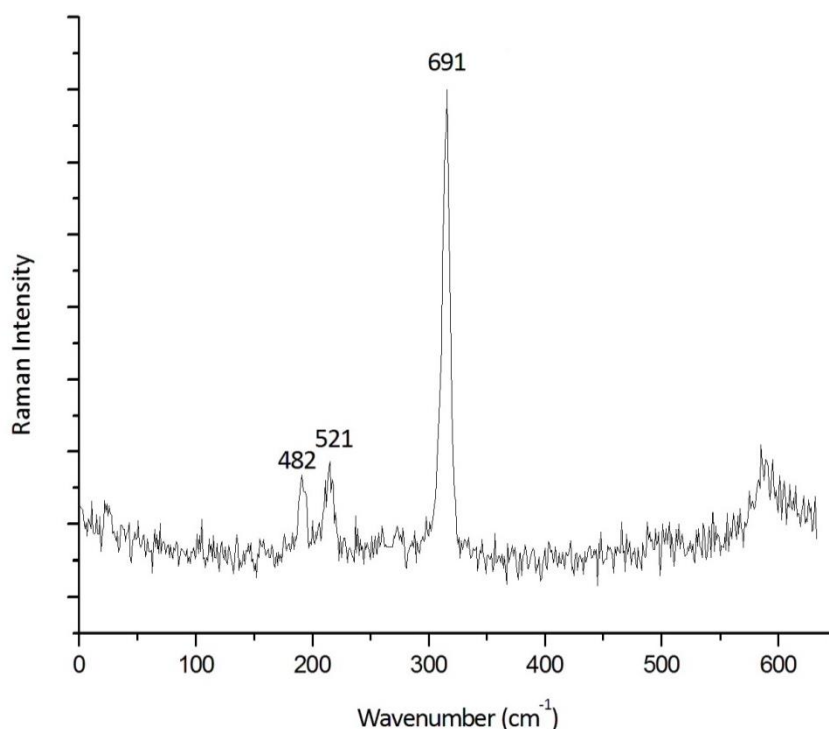


Figure 4.6. Raman spectra obtained in the highest Co presence spot by means of SCA device.

As can be seen, the signals of the compound present in that area appear at 482, 521 and 691 cm^{-1} , which coincide with the main and the two most intense secondary Raman-active modes of the Co_3O_4 (691 cm^{-1} , 618 cm^{-1} , 521 cm^{-1} , 482 cm^{-1} , 194 cm^{-1}) [42]. This cobalt (II, III) oxide is a mixed valence black compound with antiferromagnetic properties [43]. This oxide is well known for its catalytic properties in some industrial reactions, as for example in the oxygen reduction reaction [44]. Among others applications as a catalyst, it is one of the most promising ones in the renewable-energy technologies field [44]. Regarding its presence in meteorites, it is not stated in literature that this oxide has been observed earlier in any kind of meteorite. Taking into account also the fact that it was isolated and only appeared in a located area of the sample, the first hypothesis was that it was a contamination caused during the handling of the meteorite at some point.

This hypothesis was discarded once this cobalt compound was observed with the Renishaw inVia micro-spectrometer, as it was seen that the oxide was integrated in the matrix of the sample, as it will be explained later. An area rich in Co_3O_4 different than the one seen with

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the SEM-EDS system was observed. In this case, the area was much larger than the one previously shown, about 200 x 150 μm (Figure 4.7), so an intensive analysis of the zone was carried out by punctual analysis with the Renishaw inVia micro-spectrometer in order to check how the cobalt (II, III) oxide was distributed on the area. Even though the sample surface in that area was mainly black, both the black areas and also the shiny white areas provided the spectrum of the Co_3O_4 . Moreover, not all the compounds found corresponded to the cobalt (II, III) oxide. Concretely, spots of pure Co_3O_4 and spots of a mixture of Co_3O_4 and augite were identified (Figure 4.8). Furthermore, as it can be observed, there were areas that had different proportions of cobalt (II, III) oxide and augite, since the relation of intensities between the bands of these compounds varied. This difference in proportions of the Co_3O_4 and the augite was observed through all the area present in Figure 4.8 and not only in a single spot, which meant that the Co_3O_4 was integrated in the sample matrix along with the augite. Besides, both minerals belong to the same grain, as the laser spot has a diameter of about 3 μm and the analyzed grain has an area of about 200 x 150 μm , so it could not have measured two different grains by error. All these facts lead to think that the Co_3O_4 was already in the structure of the meteorite, so the hypothesis that stated that it was a contamination caused during the handling of the sample was discarded.

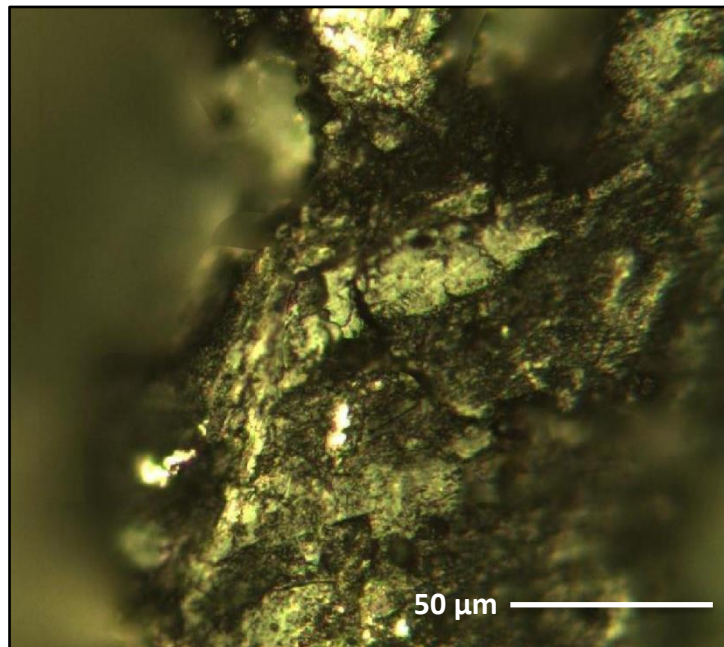


Figure 4.7. Co_3O_4 zone microphotography taken with the Renishaw inVia micro-spectrometer

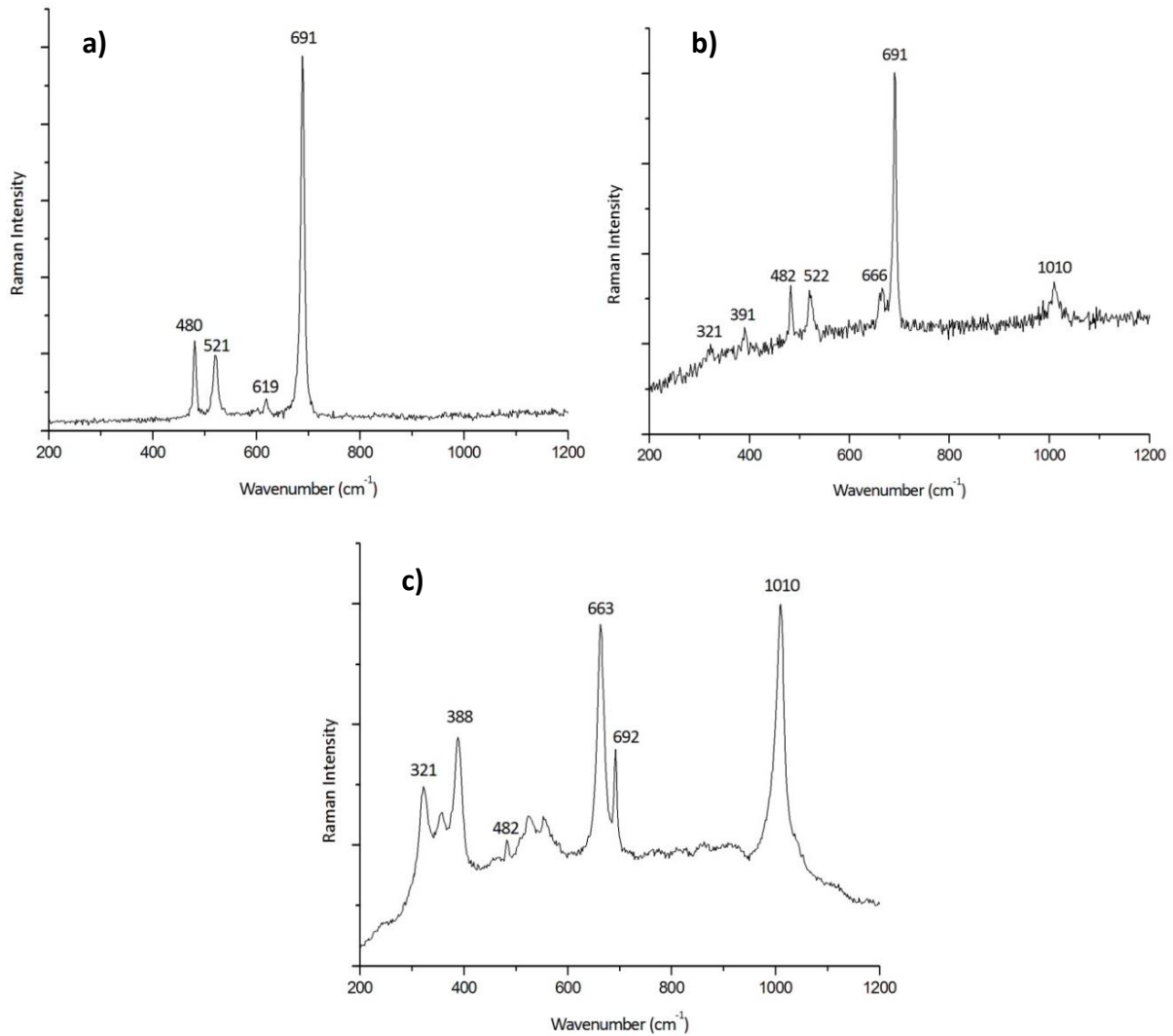


Figure 4.8. Raman spectra of three punctual analysis of a Co₃O₄ rich area in which a) there is only presence of Co₃O₄, b) there is presence of Co₃O₄ and augite and c) there is presence of augite and Co₃O₄ at a different proportion than b).

Due to all these facts, the conclusion reached was that the Co₃O₄ is present in the meteorite not due to contamination during the handling of the analyzed sample. However, the presence of cobalt in any group of Martian meteorites is not stated in the revised literature. Due to this fact, bibliography was revised in order to find another explanation that could support the presence of this compound in the sample. Regarding its origin, as it was explained above, the NWA 6148 nakhlite was first documented when it was purchased from a meteorite dealer in Erfoud, Morocco. Although its fall was not observed, it is known that it occurred in the region of Northwest Africa. Revising bibliography, it was found that there is a geographic range in Morocco where rocks are rich in cobalt, that is the so-called Anti-Atlas range [45]. In fact, in this range, the Bou-Azzer mine can be found, which is the only mine in

the world that extracts cobalt as a primary product. In addition, the city of Erfoud, where the meteorite was first documented, is located on the Northeast limit of the Anti-Atlas range, only 325 km away from Bou-Azzer (Figure 4.9). Taking into these facts, it is thought that the meteorite could fall in the Anti-Atlas range, impacting into an area rich in cobalt. Due to the heat and pressure generated in this impact, the cobalt would have integrated into the structure of the NWA 6148 nakhlite meteorite, forming the cobalt (II, III) oxide. This would explain the presence of cobalt along with augite in different proportions in the same grains of the sample, as well as the fact that in literature there is not stated the presence of cobalt in any Martian meteorite. If this hypothesis is true, the Co_3O_4 would not be an original compound from Mars but one formed because of the impact of the NWA 6148 with the terrestrial surface. In order to ascertain this conclusion, oxygen isotopes analysis will be carried out in the future to compare the results provided by this technique with the oxygen isotopes ratios of Martian and Earth's minerals.

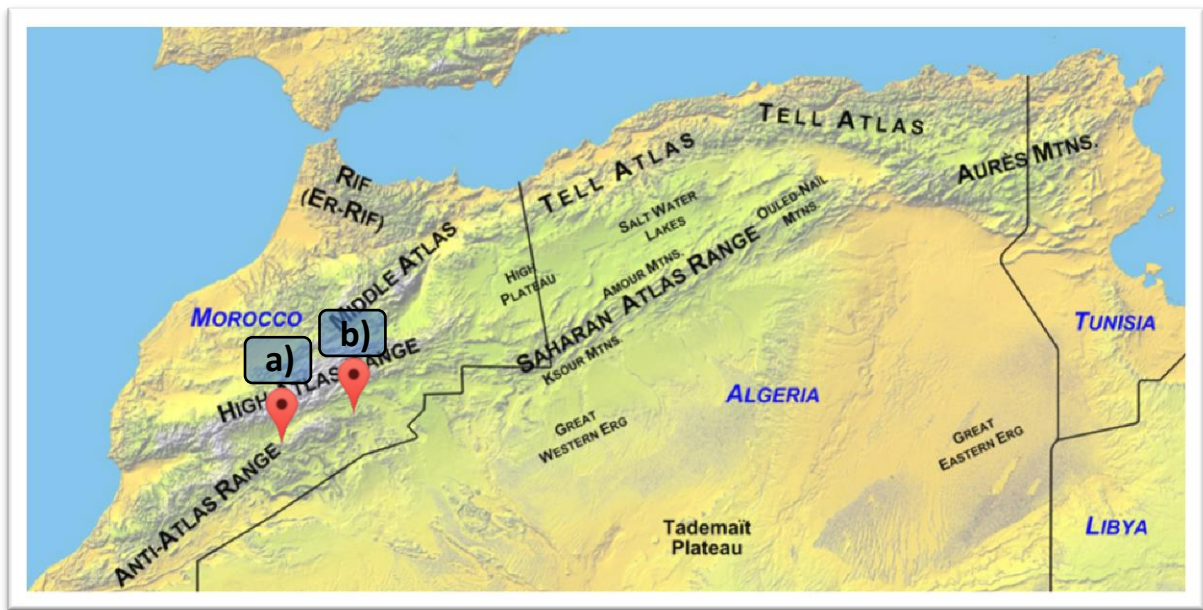


Figure 4.9. Northwest Africa, where the NWA 6148 nakhlite was found, with a) Bou-Azzer mine and b) Erfoud city pinpointed in the map, being 325 km away from each other.

4.4. Calcite

Although is not mentioned in literature as an original compound from Mars found in meteorites, calcite (CaCO_3) was observed in the NWA 6148 sample through Raman spectroscopy (Figure 4.10). It is known that calcite is present in Mars surface, as it was detected by Phoenix Mars lander [46]. However, the usual explanation given for the

presence of this carbonate in nakhlite meteorites is due to terrestrial weathering in desert areas [27, 47-49]. In the case of the NWA 6148 sample analyzed, it was detected only in a few spots of the sample and its Raman bands intensity was always very low, which lead to think that it was present in the sample in a low relative presence. Moreover, the fact that it was found in a few areas distributed through all the sample meant that the process which made this mineral appear in the NWA 6148 meteorite had occurred only in a few locations of it and in a similar way in the entire meteorite, which could mean that this process only takes places in determined meteorite areas as it will be explained later.

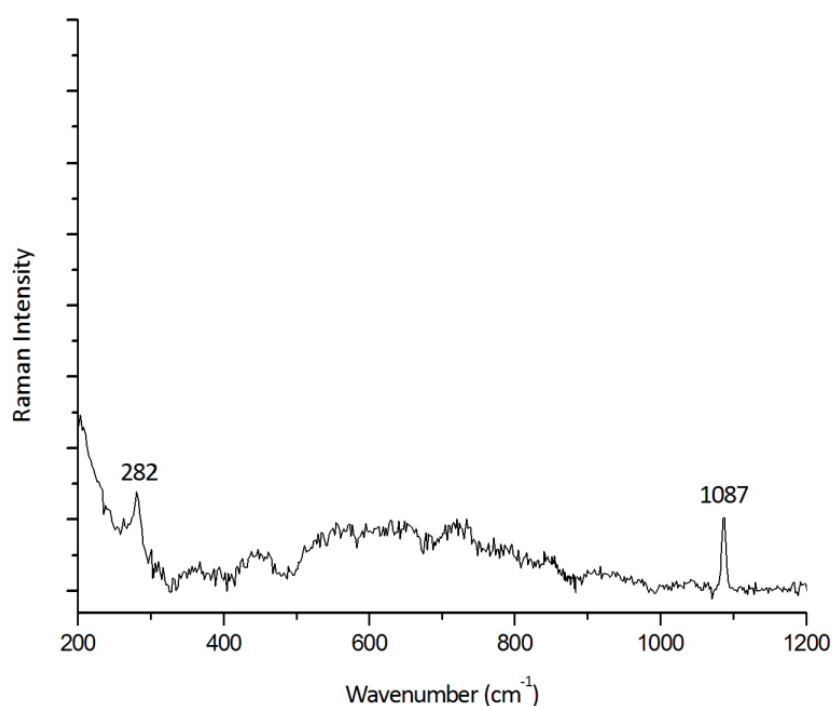


Figure 4.10. Calcite spectrum found in the NWA 6148 sample.

As it was mentioned above, the NWA 6148 meteorite fell in Northwest Africa, probably in the Anti-Atlas range, as suggests the presence of cobalt (II, III) oxide. This area, as well as almost every zone in Northwest Africa, is constituted by a desert environment. Moreover, as it was mentioned above, it is known through literature that calcite is usually found in meteorites in these kind of areas, since it crystallizes by the evaporation of water, rich in carbonates, that may flow through the veins of the meteorite [27], being a clear example of a weathering product formed on Earth.

A good analog to explain this process is the formation of desert roses. These objects are found in desert areas and have a rose-like form. Their formation is related to the evaporation of water and their rose-like form to the wind [50]. When water is evaporated in the desert due to high temperatures, the compounds dissolved in it, usually gypsum and barite, reach a supersaturation state and start to precipitate. While precipitating, they act as cement, uniting the surrounding sand grains and forming a hard solid structure. This structure, thanks to the wind, adopts several forms while the gypsum or the barite precipitate, being the rose-like forms the most common [50].

Similarly, calcite can be formed in meteorites due to this weathering process. In the case of meteorites, the water would travel through its veins, evaporating afterwards and forming the mentioned calcite. This process of formation would explain the fact that calcite is scarce in the sample, as it would be only present in the veins or porous of the NWA 6148.

4.5. Organic compounds

A couple of organic compounds were observed while performing Raman imaging in a grain of olivine. As it could be seen in Figure 4.11, in both cases besides of olivine the spectra presented several bands in the range of 1050-1650 cm^{-1} . This region of the Raman spectra is typical of organic compounds, so it was thought that these zones would correspond to one. As it was seen in the Raman imaging (Figure 4.11), both organic compounds were isolated and in a particle-form like. This led to think that the presence of both compounds had been produced during the handling of the sample, so its appearance was associated to contamination. Regarding its identification, due the complexity of the bands a it has been impossible to characterize it with Raman spectrometry.

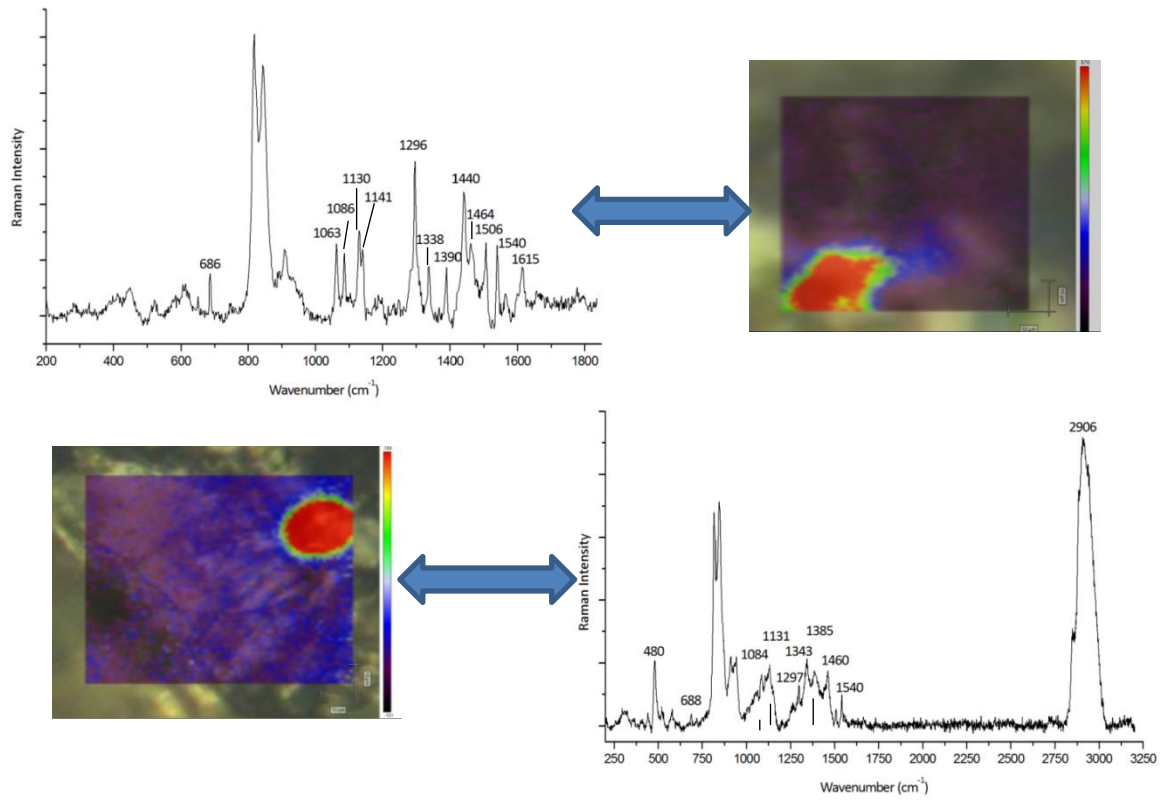


Figure 4.11. Raman spectrum of two areas where organic compounds were found with its corresponding Raman imaging.

5. CONCLUSIONS

The geochemical characterization of the NWA 6148 Martian meteorite has been meaningful in order to develop a deeper knowledge of the mineral composition present in Mars surface through the original Martian materials found in the analyzed sample. In addition, weathering processes that may alter the meteorites during their fall, in their impact and during their stance on Earth's surface until they are found have been studied. Besides, Raman spectroscopy has been tested as an alternative methodology to perform not only the mineral phases characterization, but also their metal composition estimation through the Raman spectra bands position.

The main objective of this work, the characterization of the NWA 6148 nakhlite, was carried out, finding augite as the main mineral phase of its matrix. Olivine was also found with a significant relative presence. In a lower relative presence, Co_3O_4 , calcite and some organic compounds were observed. On the one hand, after doing a literature review, augite and olivine were taken as original Martian mineral phase. On the other hand, calcite, cobalt (II, III) oxide and several organic compounds were considered as compounds formed on Earth due to weathering processes.

The bands position of Raman spectra were used for the determination of the cationic metals present in the Martian original mineral phases. With this approach, it was observed that the augite present in the NWA 6148 sample was the usual one found in this group of Martian meteorites. However, in the case of olivine, several olivines with a higher content of Mg than the one stated in literature in the grain cores for the nakhlite meteorites were found. Nevertheless, olivine grain rims had similar iron and magnesium proportions as other nakhlites. Besides, after an intensive study, it was selected the calibration curve for the olivine magnesium and iron characterization that suited better with the commercial olivine standard. Thanks to this study, it was proved the goodness of Raman spectroscopy not only to characterize the molecules present in the sample, but also to determine the different metal proportions in the mineral.

After characterizing the Martian original mineral phases, an explanation for the presence of the other compounds found in the sample was searched. In the case of cobalt (II, III) oxide, it was the first time that a cobalt compound was found in a Martian meteorite, and its

presence was explained through the integration of the Co_3O_4 in the meteorite after its impact with Earth's surface. This fact helped to determine that the fall area of NWA 6148 was the Anti-Atlas range, as it is a geographic range rich in cobalt. In order to reach this conclusion, the use of SEM-EDS with the SCA device was crucial, since thanks to the SEM-EDS the cobalt rich area was spotted and the Raman analysis could be carried out in the same spot. This methodology has been found to be very useful for the analysis of these kind of samples, since they allow an elemental and molecular analysis in the same spot.

Calcite was also found as a terrestrial weathering product. In this case, it formed due to the evaporation of carbonate rich water that flowed through the veins of the meteorite. Lastly, several organic compounds were found in the sample, which were considered contamination of the meteorite during its handling due to the shape and abundance on the sample.

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7. APPENDIX

7.1. Scientific publications

7.1.1. Congresses

International congress. Oral communication:

Authors: I. Torre-Fdez, J. Aramendia, L. Gomez-Nubla, K. Castro, J. M. Madariaga

Congress: GeoRAMAN-2016. XII International Conference.

Place and date: Novosibirsk, Russia, 9/06/2016 – 15/06/2016

Title: Raman analysis of the NWA 6148 Martian meteorite: olivine characterization and its differences with other nakhlites



Resumen/Laburpena/Summary

The NWA 6148 meteorite was found in the region of Northwest Africa and is one of the 18 Martian meteorites catalogued as nakhlites. Due to their scarcity and their Natural Heritage value, their study is essential and provides relevant information about Mars' surface composition. However, even if their study could result crucial, there are almost no studies about this nakhlite and there is a lack of knowledge about meteorite NWA 6148.

In this work, a sample of the NWA 6148 meteorite was analyzed by means of Raman spectroscopy and Scanning Electron Microscopy coupled to Energy Dispersive Spectroscopy (SEM-EDS) coupled to a Raman spectrometer (SCA analyzer). Regarding the Martian original materials, augite and olivine were observed. Their metal composition was estimated through Raman bands position, obtaining a common composition for augite and for olivine grain rims, but discovering several olivine grain cores with the greatest magnesium content among nakhlites. Regarding terrestrial weathering products, calcium was identified, which was formed due to carbonate rich water evaporation in desert areas. Besides, a cobalt compound was discovered for the very first time in a Martian meteorite, the Co_3O_4 , which integrated in this nakhlite's structure after its impact on Earth's surface. Finally, several organic compounds were observed in the meteorite sample, which were related to contamination during its handling.