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Probing the chemical and mineralogical characteristics of the Martian meteorite NWA 7397 through µRaman and µXRF non-destructively

Research Article

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Abstract

Martian meteorites have valuable information about past geological processes on Mars. In this particular case, the sample used was the Martian meteorite Northwest Africa (NWA) 7397. The main objective was to conduct preliminary analyses of the sample that was able to provide mineralogical characteristics in a non-destructive way. These meteorite NWA 7397 analyses were performed using two analytical techniques, µRaman and µXRF. Through the techniques used it was possible to suggest the presence of chromite, ilmenite, magnetite and forsterite minerals. These minerals seem to have a correspondence to one another in relation to the process that formed them. Thus, the information generated by these analytical techniques can contribute significantly by providing information on the history of Mars in order to have relevance to the areas of Astrobiology and Planetary Sciences.

Introduction

Martian meteorites are currently our only source material from Mars. Most of these samples are of igneous origin and form near the surface of the planet. In general, their formation is due to processes of great impact that dig and eject part of the Martian material out of the planet. Nowadays, we recognize more than 100 Martian meteorites and, in general, can describe them as basaltic-breccia, othopyroxenites, clinopyroxenites, dunites and shergotittes (Mccubbin & Jones 2015). The most common are the shergottites, which it can to be divided between basaltic, olive-phyric and lherzolitic (Goodrich 2002). Northwest Africa 7397 (hereafter, NWA 7397) is a recently found lherzolitic shergottite. Essentially, lherzolitic shergottites are expected to be derived from relatively primitive melts sampling the martian mantle. In addition, are typically characterized by two distinct textural lithologies (1) a poikilitic region consisting of coarse-pyroxene oikocrysts enclosing olivine and chromite and (2) a nonpoikilitic region comprises olivine, pigeonite, augite and maskelynite (Howarth *et al.* 2014). In this way, this meteorite could provide information about the igneous processes formed of Mars' mafic crust, as well as indirect information of martian mantle composition.

Fundamentally, it is possible to investigate the chemical and mineralogical composition of these materials ejected from the Martian surface using analytical techniques. In general, these results can help to understand the Martian environment and provide parameters for future missions to Mars (Gladman *et al.* 1996; Gladman 1997). Hutchinson *et al.* (2014) investigated the viability of studying Mars' meteorite samples through some analytical techniques, motivated by the new Mars missions, such as Exomars 2020. The aim of Rover in 2020 is to explore the environment of the red planet through modern scientific instruments that perform chemical, physical and mineralogical analyses. For Astrobiology, an area that is concerned with questions about the origin, evolution and distribution of life in the Universe (Blumberg 2003), Mars has been the focal point in exploration and pursuit of life outside the Earth by mankind. This is mainly because it is the closest place to our Solar System where we can ascertain that possibility. Finding habitable environments that may have harboured life on Mars at some point, whether present or past, has become an important scientific goal today.

The analysis of meteorite NWA 7397 from Mars, through µRaman and µXRF, had the objective of performing preliminary analysis in a non-destructive manner. Here, we report some information about the elemental chemical composition and mineralogical characteristics for the Martian shergottite NWA 7397 obtained through non-destructive processes, in other words, was maintained the physical integrity of the material/object (Nascimento-Dias *et al.* 2018). Essentially, were used two techniques to analyse the sample. Firstly, µXRF was used to obtain the elemental chemical compositions present in NWA 7397. In general, this analysis is based on simple, well-known physical X-fluorescence principles that chemical elements emit characteristic radiations when subjected to appropriate excitation (Bertin 2012; Nascimento-dias *et al.* 2017). In this way, it is possible to identify each atom present in the periodic table. Secondly, was used the technique of μRaman, which is a high spatial resolution technique that provides a fast and non-invasive way to obtain information about the molecular vibrational modes of any organic or inorganic materials, as long as the molecules are polarizable (Nasdala *et al.* 2004). In this way, it is an analytical technique by which it is possible to ascertain molecules formed by the fundamental atoms used in the system such as in the structural composition of life as Carbon (C), Hydrogen (H), Oxygen (O), Phosphorus (P), Sulphur (S), also known as 'CHONPS' moreover to other molecules, from the molecular groups present in the sample to be analysed. Furthermore, it is possible to infer and identify mineralogical structure present in the sample.

Materials and methods

Martian meteorite NWA 7397

The Martian meteorite NWA 7397 is a newly discovered, enriched, lherzolitic shergottite, the third described example of this group. In this way, it is classified as belonging to the group SNC (Shergottites, Nakhlites and Chassignites), which is a part of meteorites coming from the planet Mars. This meteorite was found near Guelmim-Es-Semara in June 2012 in Morocco by a dealer in Zagora that passed on to Darryl Pitt and David Gheesling. Its classification as a Martian shergottite was approved in January 2013 (Irving & Kuehner 2013).

This meteorite has a total of 20 g of material in the form of fragments and some polished thin slices deposited at UWB in the USA. However, the main mass remains together with Pitt and Gheesling. Basically, the NWA 7397 consists of two distinct textural lithologies (1) poikilitic—comprises zoned pyroxene oikocrysts, with chadacrysts of chromite and olivine and (2) non-poikilitic—comprises olivine, low-Ca and high-Ca pyroxene, maskelynite and minor abundances of merrillite, spinel, ilmenite and pyrrhotite (Howarth *et al.* 2014).

Finally, the fragment of this meteorite used for the development of this work have 0.104 g (Fig. 1) and was acquired with the Museum Jewels of Nature, which confirmed the authenticity with the description in the *Meteoritical Bulletin.*

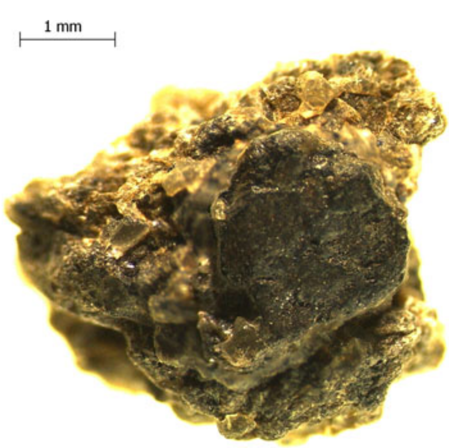

Fig. 1. Fragment of Martian meteorite NWA 7397.

μRaman

In general, the methodology used to obtain information through μRaman is based on the records of the energies of the normal modes of oscillation between the atoms that constitute the material when submitted to the monochromatic irradiation in the visible or near-infrared band. In this particular case, the development of the analysis was performed by the variation of the monochromatic beam spot position by regions of interest of the sample. In this way, the result was done by checking for possible variations in the position and shape of the peaks. In addition, it has been ascertained whether they conform to the catalogued spectra of mineral already recognized in databases or published articles.

Raman measurements were carried out with a Renishawin ViamicroRaman coupled to a Leica confocal microscope (5X, 20X and 50X objectives), available at the Brazilian Synchrotron Light Laboratory (LNLS/CNPEM). The system is equipped with 532, 633 and 785 nm excitation lasers, 1200 l/mm diffraction gratins and CCD detector and special optics and software for rapid mapping system (Renishaw Streamline®). The spectral resolution is 4 cm^{-1}. Measurements were performed with 20X objective and excitation at 785 nm, which ensured lower fluorescence background from the sample. The data treatment was made with RenishawWiRE® 4.1 software.

μXRF

The analyses of the elemental chemical composition present in the Martian meteorite NWA 7397 were carried out using a μXRF commercial System (M4 Tornado by Bruker-Nano). This system has a Rh anode X-ray tube, Polycapillary X-ray optics focus (spot sizes <25 μm for Mo-Kα) and XFlash silicon drift X-ray detector (energy resolution FWHM <135 eV at 250 000 cps for Mn-Kα and 30 mm^2 active detector). The automated scanning performed on the sample provided the detection of 21 chemical elements present at Martian meteorite.

In the development of the analysis of this sample, it was empirically verified that the parameters that best fit were 600 μA of current, 45 kV of voltage. In this way, XRF scanning in the meteorites was made shortly after we acquired these parameters that followed as patterns throughout the scan of the sample analysed. The acquisition of the XRF spectrum was done in a vacuum of 20 mbar from parameters adjusted so that the measurements were taken in a standardized way. The parameters used were the current in 600 μA, the voltage of 40 kV and in 2 cycles that had a total duration of 2 h 25 min. The low Z XRF spectra were obtained using a 12.5 μm aluminium filter and to obtain the high Z XRF spectra the 630 μm aluminium filter was used. The use of the second filter has the purpose of attenuating the noise a bit mainly in the region above 6.40 keV.

Results

μXRF results

The results obtained using the μXRF technique provided spectra that show peaks that are related to the K_α energy lines detected during the scanning process. The detected elements were: Mg (1.25 keV), Al (1.49 keV), Si (1.74 keV), P (2.02 keV), S (2.31 keV), Cl (2.62 keV),

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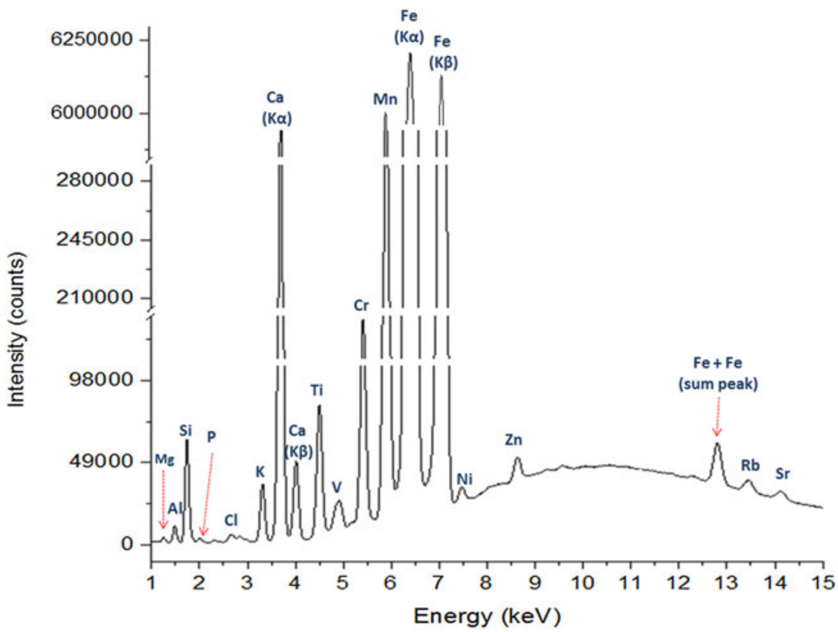

Fig. 2. XRF spectrum obtained through the low *Z* measurement of NWA 7397 meteorite.

K (3.31 keV), Ca (3.69 keV), Ti (4.51 keV), V (4.95 keV), Cr (5.41 keV), Mn (5.90 keV), Fe (6.40 keV), Ni (7.48 keV), Zn (8.64 keV), Ga (9.25 keV), Rb (13.39 keV), Sr (14.16 keV), Y (14.96 keV), Zr(15.77 keV) and line L_α Pb (10.55 keV). In Figs. 2 and 3 are presented the µXRF spectra of the Martian meteorite NWA 7397, in which it is possible to observe the result obtained from the peaks of the elements detected.

*µ*Raman results

The Raman spectra obtained from of meteorite NWA 7397 are presented in Figs. 4 and 7. The first spectrum in Fig. 4 shows peaks at 325, 478, 683 e 863 cm^{-1}. This spectrum shows to be well represented by the vibrational modes of the chromite [$FeCr_2O_4$], the ilmenite [$Fe^{+2}Ti^{+4}O_3$] and the magnetite [Fe_3O_4 (Fe^{2+} Fe_2^{3+} O_4)]. Thus, based on the results obtained in this work, it is possible to compare them with the data provided by Wang *et al.* (2004) in Fig. 5, with Table 1 of the Handbook of Minerals Raman Spectra site of Lyon University and with Fig. 6 of spectrum of the site RRUFF, you may notice certain similarities.

Apparently, the 680 cm^{-1} band has a correspondence with the grouping of the three minerals, the chromite, the ilmenite and the magnetite. According to Wang *et al.* (2004), the chromite, ilmenite and magnetite may be from a final phase of the crystallization of the meteorite from the melt of the parent body and that from the moment that the composition of the residual melt has become rich in Fe, they tend to occur together.

In Fig. 7 another spectrum of µRaman obtained from different regions of the Martian meteorite NWA 7397 is presented. In this

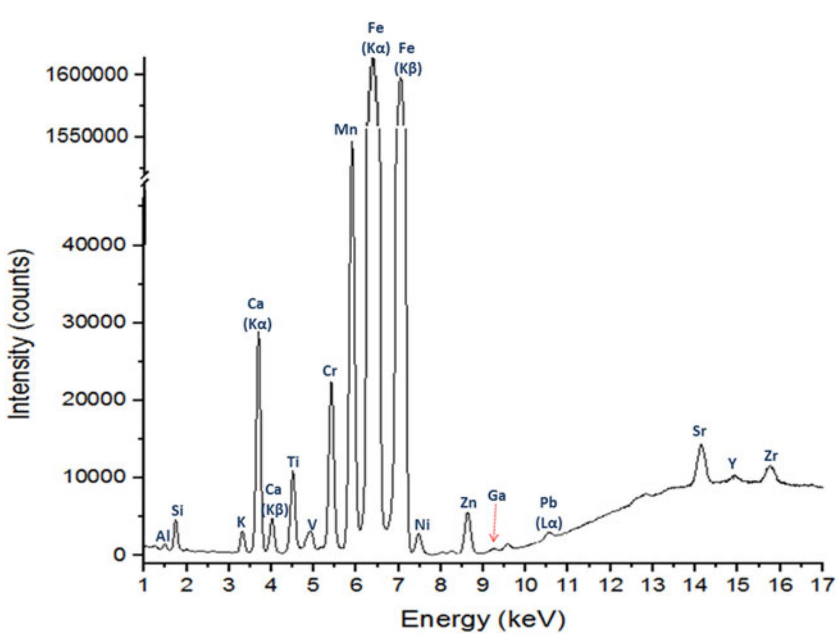

Fig. 3. XRF spectrum obtained through high *Z* measurement of meteorite NWA 7397.

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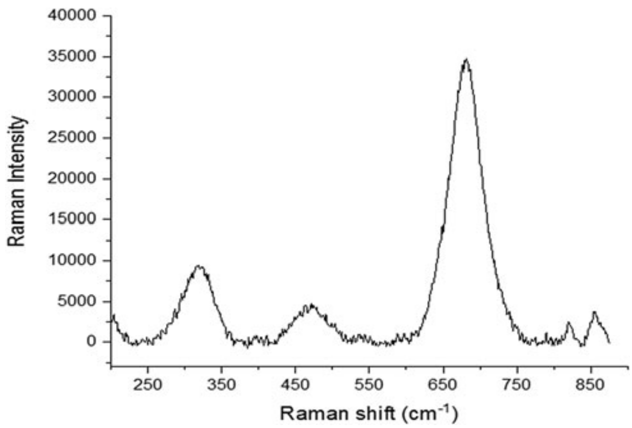

Fig. 4. Raman spectra obtained from meteorite NWA 7397.

Table 1. Expected vibrational modes of Ilmenite

Mode	Raman shift	shift versus P	shift versus T
E_g	287	2.1(2)	−0.0203(16)
A_g	345	1.7(1)	−0.0174(17)
A_g	412	2.3(1)	−0.027(3)
A_g	480	2.65(7)	−0.0285(19)
E_g	498	3.1(2)	−0.0148(16)
A_g	620	2.4(1)	−0.0192(11)
E_g	681	3.3(1)	−0.0245(5)
A_g	**799**	3.7(1)	−0.0212(5)

Raman shift in cm^{-1}, shifts versus P are in $cm^{-1}.GPa^{-1}$, shifts versus T are $cm^{-1}.K^{-1}$ (Source: Reynard *et al.* 2017).

spectrum, it is possible to observe the peaks at 820 and 850 cm^{-1}. These peaks are characterized in the NWA 7397 by the possible presence of forsterite [Mg_2SiO_4], which is a mineral of the nesosilicate class belonging to the olivine group.

Discussion

The detection of Mg, Si, Ti, Cr, Fe elements by µXRF are consistent with the minerals detected by Raman. However, even the other elements do not appear in these or through other minerals, there is no conflict between the µXRF and µRaman data. Possibly, the region-specific choices for action may have led to the detection of only those minerals.In addition, it is important to remember that the data were compared with the pure mineral spectra, ie there is also the possibility that some of these elements are embedded as small 'impurities', as doping or exsolvated elements.

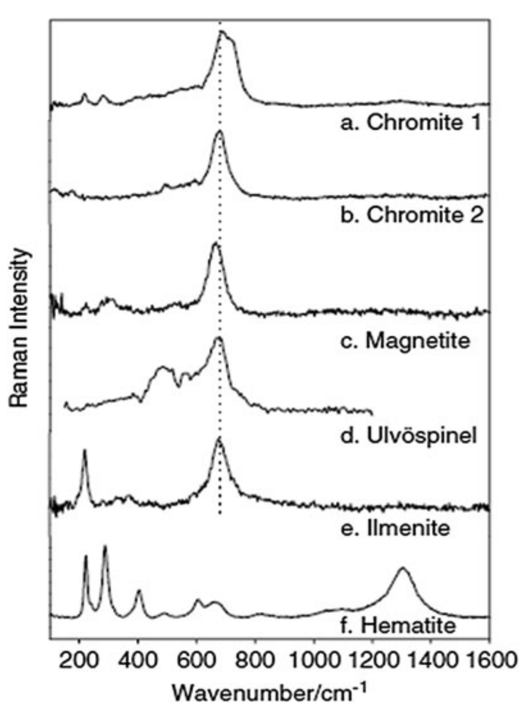

Fig. 5. Spectral images of vibrational modes of minerals in the ∼680 cm^{-1} range.

In relation to the detection of forsterite, which is a mineral of the nesosilicate class belonging to the olivine group, it may have been formed from olivines that undergo metamorphic conditions according to Bucher & Frey (1994). Fundamentally, this metamorphism would occur through processes that would involve transformations undergone by the olivines, when subjected to heat/temperature, pressure, fluids and time.

Although this mineral is observed in certain metamorphic rocks of the dolomitic group, that is, limestone rocks, the highest frequency of forsterite on Earth appears in igneous rocks. Generally, this mineral on our planet occurs associated with other minerals like magnetite, chromite, diopside, augite and others. An extremely interesting and relevant point for studies of the geological evolution of forsterite is related to the possibility of some of the material of this mineral being transformed into metamorphic magnetite (Fig. 8). In general, this occurs when igneous olivine is metamorphosed. This process produces an olivine much more magnesian and dark since part of its material, the iron, happens to be fixed in the magnetite, does not dissolve in the phases produced by the metamorphism.

Fundamentally, chromite and magnetite detected by the µRaman technique may be related to forsterite, in order to give us indications of the origin and formation of these minerals. According to Bucher & Frey (1994) the formation of magnesium forsterite without the addition of iron (Fe) generally occurs at relatively low temperatures (∼400°C) of olivine formation in metamorphism. However, the addition of Fe would lead to a considerable increase in the temperatures of olivine formation by metamorphism, which according to Spear (1995), would only occur at temperatures >800°C. Besides the forsterite having a relation with the geological evolution of the olivine, it also shows to have, at least on our planet, a relation with other minerals like magnetite and chromite, which were detected in our analyses.

Another important relation between chromite, magnetite and forsterite (olivine) is that when olivines are subjected to high pressures, they contract into a more compact structure corresponding to spinel ($MgAl_2O_4$). According to Deer *et al.* (1992), this olivine-spinel transformation in the Mg_2SiO_4 – Fe_2SiO_4 system occurs between 800 and 1200°C, these pressures being higher for the Mg rich phases and at lower pressures when the phases are Fe-rich. Thus, we have the chromite which is a mineral belonging to the spinel group, generally present in the constitution of olives rich in Mg, through the chromium in the form of tiny lamella exsolving of chromite. Magnetite may be present by means of small grains exsolvated by normal pathways, analogously when

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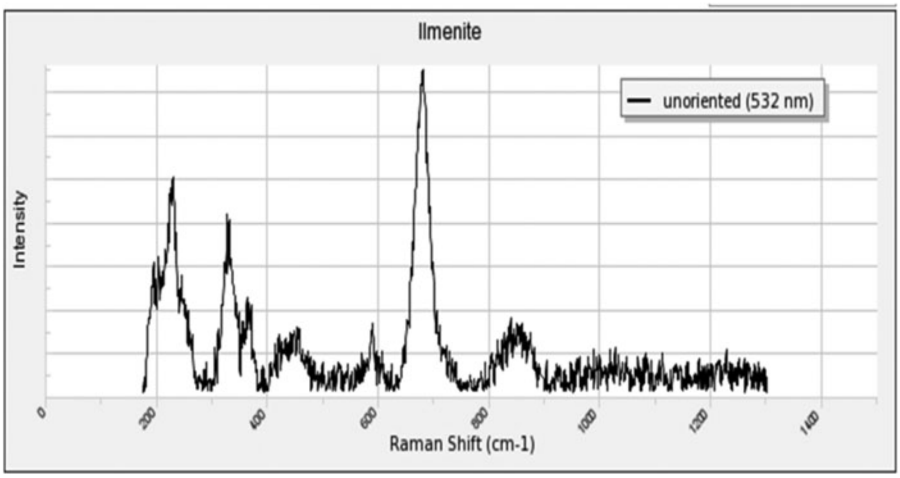

Fig. 6. Ilmenite spectrum images (Source: RRUFF Project website).

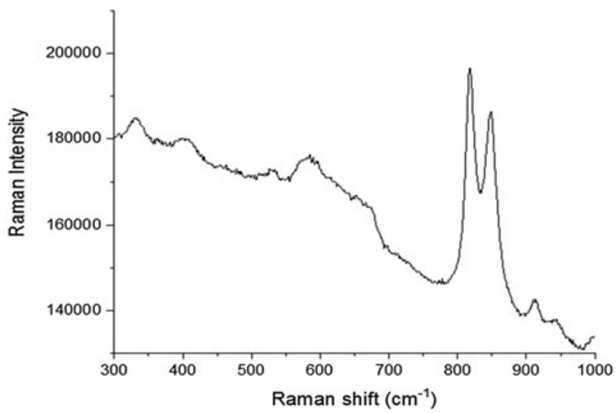

Fig. 7. Raman spectra obtained from the NWA 7397 martian meteorite.

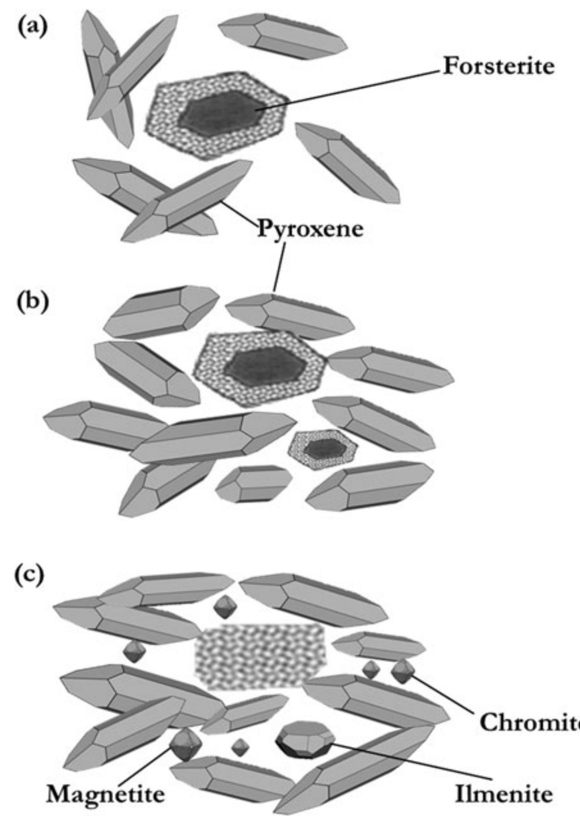

Fig. 8. Schematic illustration of the history of crystallization of minerals from forsterite to magnetite.

there is some Fe^{3+} in the material, or, as is more commonly, the oxidation alteration product of olivine.

In this way, a relation of these minerals found with astrobiology could be related to the study of the evolution of the mantle and the Martian crust. According to Szabó *et al.* (2010), igneous rocks had great importance in the Archean past of the Earth. At this time, the highest mantle temperature allowed higher melt rates, rich magmas in Mg were generated in order to reach the surface of the primitive crust and to consolidate in the form of komatitic spills, which are peculiar rocks of great interest for the study of the evolution of the mantle and the terrestrial Archaean crust. Thus, through a method of study of mineralogy compared with what we know of the Earth from what we got from the Martian meteorite NWA 7397, it may be possible in the future to help understand more about issues related to the evolution of Martian geology (Szabó *et al.* 2010).

Conclusion

Overall, it is possible to conclude that the combination of the µXRF and µRaman techniques made it possible to ascertain and suggest the mineralogical characteristics present in the NWA 7397 meteorite. All information has been obtained without the previous necessity of causing damage or alteration in the physical integrity of the meteorite in a very satisfactory way. In relation to the minerals detected in the Martian meteorite, there appears to be a correspondence in the origin and formation of the three minerals (chromite, magnetite and forsterite). The presence of these minerals in the Martian meteorite may be associated with evolutionary processes that occurred in the mantle and the Martian crust. Thus, it is possible to observe that the information obtained with XRF and Raman provided significant contributions to areas such as Astrobiology and Planetary Sciences.

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Competing financial interests. The authors declare no competing financial interests.

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