

## RESEARCH ARTICLE

# Utilization of nondestructive techniques for analysis of the Martian meteorite NWA 6963 and its implications for astrobiology

Bruno L. do Nascimento-Dias<sup>1</sup>  | Davi F. de Oliveira<sup>1,2</sup>  | Alessandra S. Machado<sup>2</sup>  |  
Olga M.O. Araújo<sup>2</sup> | Ricardo T. Lopes<sup>2</sup>  | Marcelino J. dos Anjos<sup>1,2</sup>

<sup>1</sup>Physics Institute Armando Dias Tavares, University of State of Rio de Janeiro, Rio de Janeiro, Brazil

<sup>2</sup>Nuclear Instrumentation Laboratory, PEN, COPPE, UFRJ, Rio de Janeiro, Brazil

## Correspondence

Bruno L. do Nascimento-Dias, Physics Institute Armando Dias Tavares, University of State of Rio de Janeiro, Rio de Janeiro, RJ, Brazil.  
Email: bruno.astrobio@gmail.com

Martian meteorites are excellent study materials for understanding the present and past of Mars, as they are important historical astrophysical artifacts because they possess information about Martian geological evolution and physical and chemical characteristics. In our case, we analyzed the NWA 6963 Martian meteorite classified as basaltic shergottite because of its chemical structure. A computerized microtomography ( $\mu$ CT) study in the NWA 6963 Martian meteorite provided us with 2D and 3D images that were extremely useful for ascertaining the internal structure of the analyzed sample and gave us the opportunity to find a crumpled material with a very peculiar structural format. In addition, it was possible to observe through the  $\mu$ CT that this encrusted material also has a completely different density of the meteorite. Calcium, strontium, and potassium were detected qualitatively, among others through the technique of X-ray fluorescence.

## 1 | INTRODUCTION

Mars is a rocky planet very similar to Earth. In this way, if we can understand how their planetary evolution occurred, through comparative analysis, we could generate generalizations of physical processes in the formation between the planets and also obtain possible hints of how could be the initial history of our planet and also of the red planet.<sup>[1,2]</sup> Although most of the geological records have been destroyed, just 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.<sup>[3,4]</sup>

Fundamentally, we can see meteorites as rocks of great importance because of the vast amount of information they can give us about the primordial material that formed the planets of our solar system.<sup>[5,6]</sup> Thus, through the objects ejected from the Martian surface, such as NWA 6963, it is possible, through analytical techniques,

to investigate chemical, physical, and geological information, which can help, for example, to define requirements for missions to Mars.<sup>[7,8]</sup>

Finally, another interest very special related to Mars is the possibility that the planet has been habitable, that is, have had the conditions necessary for life to have established itself in the past. Thus, to search for these types of information, the Martian meteorites are of extreme relevance because through them are made research related to the interior of the planet.<sup>[9]</sup> It also studied the possible presence of water by analyzing the composition of volatile chemical elements in Martian meteorites<sup>[10]</sup> and the origin and age of the Martian crust,<sup>[11–13]</sup> and there are researches related to the search for fossils, bacteria, or traces of organic compounds in Martian meteorites.<sup>[14–17]</sup>

Thus, we will try to emphasize and demonstrate in this work the discovery we made and the importance of using nondestructive analytical techniques such as  $\mu$ CT

and X-ray fluorescence (XRF) in the preliminary analysis to obtain information on fragments of meteorites. For this, we will demonstrate the efficiency of both techniques by the findings that were made by combining the XRF analyses with the imaging results of the  $\mu$ CT technique.

## 2 | MATERIALS AND METHODS

### 2.1 | Martian meteorite NWA 6963

The sample analyzed and studied in this research was a fragment of about 4 mm of the Martian meteorite NWA 6963, which is considered an igneous rock of basaltic origin, due to its mineralogical composition and texture characteristics. This meteorite was found in September 2011 in Morocco, more precisely in Guelmim-Es Semara and is classified as an achondrite belonging to the group SNC (Shergottites, Nakhlatite, and Chassignites), being recognized more specifically such as a shergottite among the groups of meteors from red planet because of its chemical structure and attested as a meteorite from Mars due to the oxygen isotopes.<sup>[18,19]</sup>

For the development of this project, a fragment of this meteorite was acquired with Paulo Anselmo Matioli, geologist and curator of the Museu Joias da Natureza, which confirmed its mineralogical correspondence and textured description in the *Meteoritical Bulletin*.<sup>[19]</sup>

### 2.2 | Micro-CT

The images were obtained through the Skyscan/Bruker apparatus, model 1173. The samples were verified in all three spatial planes through the apparatus model 1173, composed of a microfocus X-ray tube with high-voltage source, an acrylic sample port, in which the NWA 6963 meteorite was fixed inside the equipment to prevent movement during the image acquisition process, and a CMOS-based flat panel detector (2,240 × 2,240 pixels) connected to a control computer, both used in the reconstruction of the images.

The scanning of the NWA 6963 Martian meteorite was obtained from the following parameters; 50 kV of voltage, 160  $\mu$ A, isotropic pixel size of 5.70  $\mu$ m, angular pitch of 0.4°, 1,000 ms of exposure time, using an aluminum filter of 1 mm thickness and with an acquisition time of 1 hr 35 min.

After the scanning, the data are quantitatively analyzed using CTAn (porosity and density); the tomographic projections are then reconstructed using the InstaRecon® software Version 1.3.9.2. This program generated the 3D images, which were formed from the two-dimensional slices of the sample generated during the acquisition process and which were converted into

an orderly stack, thus generating a 3D image. The DataViewer Version 1.5.2.4 program was used for visualization and evaluation in 2D (linear measurements) of the coronal, transaxial, and sagittal axes. Then, the software CTVOX Version 3.2 was used for the three-dimensional visualization and for the external and internal anatomical analysis of the materials obtained after the rendering process. All software used were proprietary from Bruker microCT.

### 2.3 | X-ray fluorescence

The determination of the qualitative chemical composition present in the NWA 6963 Martian meteorite was obtained through the portable model ARTAX 200, with a molybdenum anode and with a collimation aperture of 200  $\mu$ m. The first result containing the first elements Si, Ca, Ti, Cr, Mn, Fe, and Zn was detected from a spot beam at a randomly chosen location, because the initial objective was to obtain the best voltage, current, and time parameters to detect as many elements as possible with better quality and with the lowest background noise possible in the spectrum.

In the development of the analysis of this sample, it was empirically verified that the parameters that best fit were 400  $\mu$ A of current and 50 kV of voltage. In this way, XRF scanning in the NWA 6963 Martian meteorite was made shortly after we acquired these parameters that followed as patterns throughout the scan of the sample analyzed. Fundamentally, the scanning was done by changing the spot beam to different areas, in which the measurements of a locally chosen spot were first taken. Subsequently, the beam was moved a second point in another region in which a new measurement was performed. This procedure was then repeated so that we could sweep point-to-point to a vast region of NWA 6963 meteorite.

Thus, we were able to obtain the qualitative elemental chemical composition of the Martian meteorite NWA 6963, in which the elements Si, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Y, and Z were detected through this methodology. These being placed here in order of atomic radius of the periodic table. The obtained X-ray fluorescence spectra were evaluated by the AXIL software of the QXAS package for peak deconvolution and subtraction from the radiation background.<sup>[20–22]</sup>

## 3 | RESULTS AND DISCUSSION

The imaging results that were generated from the NWA 6963 Martian meteorite were extremely satisfactory because they provided us with images of inclusions in

the meteorite, which we hoped to obtain through this technique. However, it also provided us with a surprising result of images of certain structures with very peculiar shapes encrusted inside the NWA 6963 Martian meteorite. This finding was made from a 3D image model (Figure 1a), obtained through the image reconstruction feature. In addition, through the acquisition of the images and the 3D reconstruction feature, we were able to obtain additional information related to the density (Figure 2a), porosity (Figure 2b,c), and the internal structure of the analyzed Martian meteorite (Figure 1a–d).

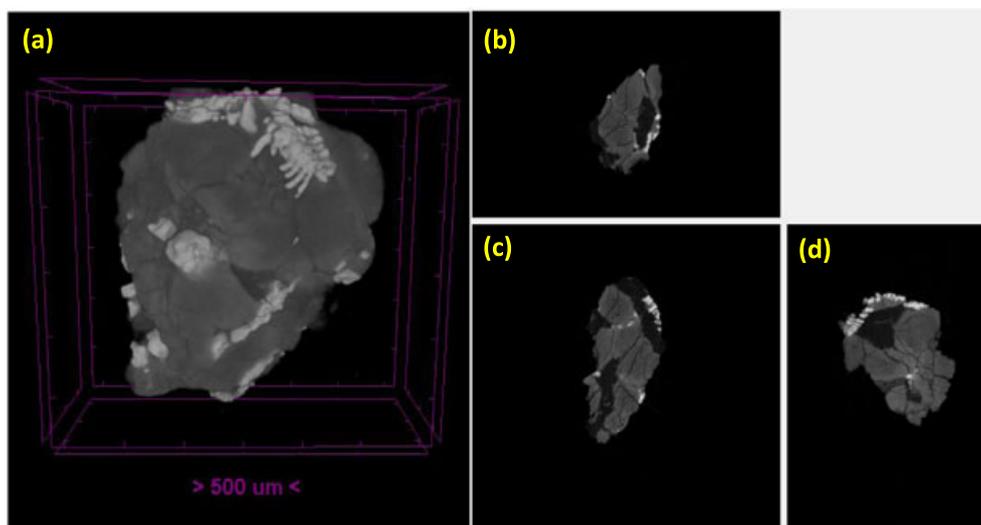
It was possible to obtain an estimate of the chemical composition of NWA 6963 Martian meteorite (Figure 3). We were able to obtain results that provided us qualitative information of the chemical elements that are present in the sample analyzed and collect this information locally through the variation of a point beam in different areas of our interest in the meteorite NWA 6963.

### 3.1 | Imaging

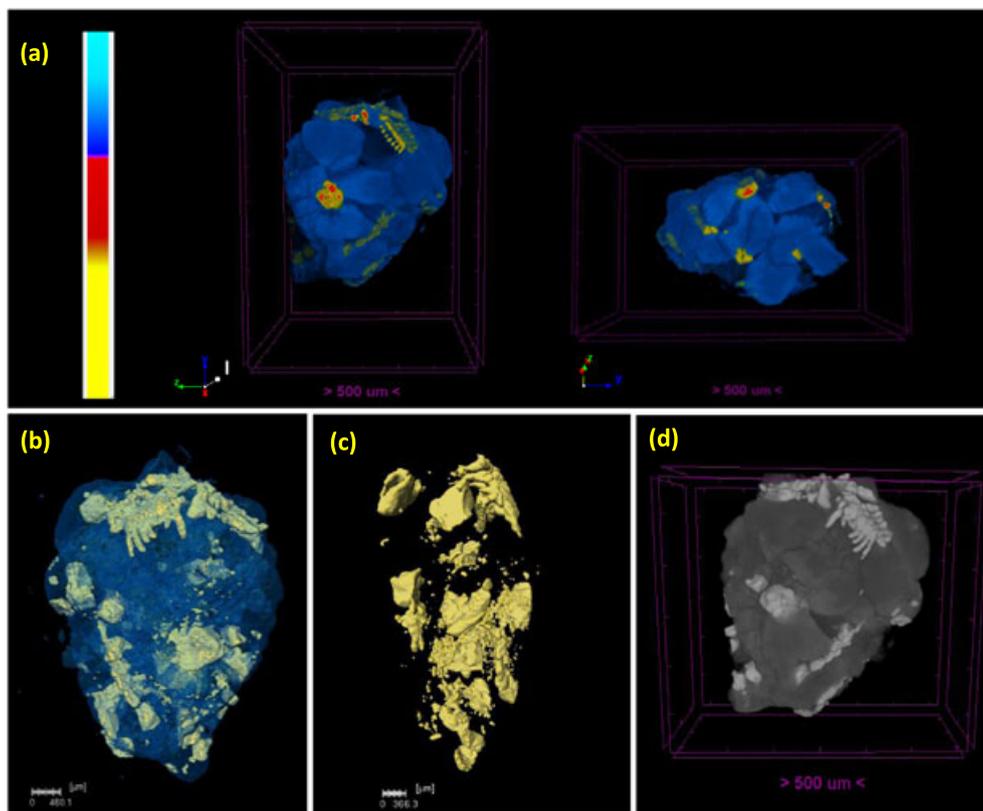
By means of imaging research, we are able to analyze internal cuts of the material, that is, hundreds of microtomographic cross sections are made that allow the internal three-dimensional visualization of samples that would otherwise not be observable. With this, we are able to obtain various sample data such as the proportions of materials, quantify particle volumes, and/or areas in an automated manner.<sup>[23]</sup> In general, these technological instruments are based on the X-ray attenuation equation, thus having the same operating principle, in which the object is positioned between an

X-ray source and an X-ray detector, in a system of rotation.<sup>[24]</sup>

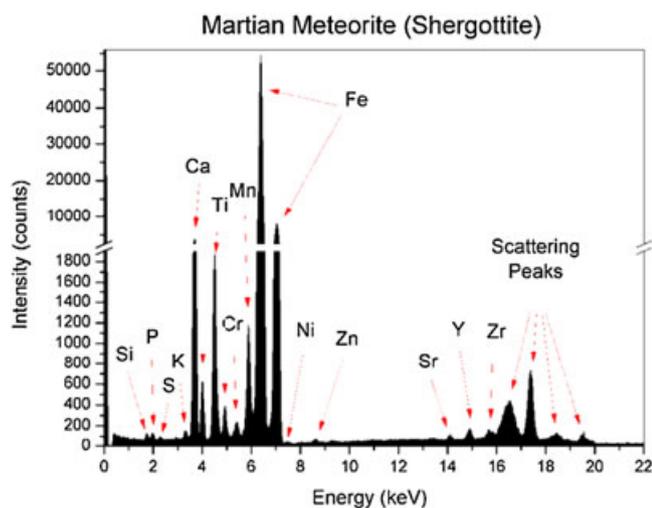
Through the image acquisition process and with the aid of the rendering feature to reconstruct a 3D image model, we were able to obtain information of materials that were embedded inside the NWA 6963 Martian meteorite with higher quality and definition, indicating in which region these materials were specifically found. These encrusting materials attract a lot of attention because of their rather peculiar structural shape because they are not spheroidal structures such as the chondrules generally found in some types of known chondrite meteorites or filamentary structures that could be characterized as grooves, vessels, or possible differentiation between geological materials. In fact, the encrusted material presents a differentiated structure, because it appears to have a well-behaved formation, even possessing a distinct density in relation to the rest of all the material of the NWA 6963 Martian meteorite. Thus, all analysis of density, porosity of the meteorite NWA 6963, and the encrusted material were made through images that had distinct color shades, in order to provide a better understanding and facilitate the differentiation of analyzed elements (Figure 2) we have, for example, the image of density (Figure 2a), in which the elements were differentiated by different colors, the elements of blue being those of lower density, red of intermediate density, and yellow of the elements of higher density. Furthermore, the total porosity was also calculated in relation to the total volume of the analyzed material, which is 2.38%, with the total volume of the analyzed material being 4.75 mm<sup>3</sup>. Finally, we try to show how the encrusted material differs from the rest of the NWA 6963 Martian meteorite (Figure 2d).



**FIGURE 1** Generation of images by micro-CT of material embedded in the Martian NWA 6963. (a) Reconstructed three-dimensional image by stacking several two-dimensional images similar to images (b), (c), and (d) that were generated during the acquisition process



**FIGURE 2** Composition of comparative images made by micro-CT of the material encrusted in the Martian meteorite NWA 6963. The image (a) is a 3D model generated by the reconstruction method that illustrates the density of materials, where the scale is increasing from blue to yellow. The image (b) configures the porosity analysis of the analyzed material volume. The image (c) shows the same porosity analysis but leaving only the material of higher density. The image (d) is the generated 3D model in which the encrusted material differs from the rest of the meteorite and served as one of the comparative analysis bases with images (a), (b), and (c)



**FIGURE 3** A typical X-ray fluorescence spectra chemical elements of Martian meteorite NWA 6963 obtained from XRF spectrometer (model: ARTAX 200, made: Bruker, Germany)

### 3.2 | Chemical composition

The qualitative determination of the chemical elements present in the NWA 6963 Martian was done in a

nondestructive way, that is, it did not result in the characterization of the sample or in the possible loss of some future information, if it is analyzed again. Essentially, the analysis performed was based on simple and well-known physical principles that chemical elements emit characteristic radiations when subjected to an appropriate characteristic excitation and that is specific for each atom of the periodic table, thus not having the possibility of having two atoms with the same characteristics.

The analysis of the chemical composition of the NWA 6963 Martian meteorite generated initially through the first local beam spot in a specific region detected Si, Ca, Ti, Cr, Mn, Fe, and Zn elements. Later, when conducting the meteor sweep NWA 6963, other elements such as K, Ni, Cu, Sr, Y, and Zr were also detected. Among the detected elements, Ti, Mn, Cu, Zn, Sr, and Zr are considered in meteorites by the literature as moderately and highly volatile trace elements.<sup>[25]</sup> Moreover, the chemical composition of the NWA 6963 Martian meteorite is remarkable because it has been detected the yttrium element, which is considered a rare earth element and is usually found in meteorites of carbonaceous chondrites.<sup>[26]</sup> In general, yttrium, in terrestrial rocks, is found

associated with minerals such as xenotime, which is a rare earth phosphate mineral, whose main component is yttrium orthophosphate ( $\text{YPO}_4$ ).<sup>[27,28]</sup> Essentially, these rare earth minerals are generally found in association with alkaline igneous complexes in pegmatites associated with alkaline magmas or associated with carbonatite intrusions. Finally, we call attention to the detection of the elements Ca, K, and Sr on the surface of the region in which the peculiar structure well embedded in the NWA 6963 Martian meteorite is embedded. Although these compounds are commonly found in chemical analysis of fossils and microfossils in archeology and paleontology.<sup>[29–31]</sup> However, it is important to emphasize that Ca is an element that here on Earth can be linked to minerals such as calcite. Calcite is a calcium carbonate, and its formation comes mainly from biochemogenic processes or forms through chemogenic processes when in aqueous media and presence of water.<sup>[32]</sup> Furthermore, by combining the possible presence of xenotime, that is, associated with carbonatite intrusions, there appears to be consistency in suggesting a likely combination of calcite and xenotime as part of the NWA 6963 meteorite structural composition, as the mantle-derived melted carbonatites may be carriers of rare lands. In addition, xenotime may also be associated with apatite, and in this case, the relationship between these minerals would be associated with hydrothermal fluid environments bound to alkaline magmatism that contain a variety of minerals of rare earths.<sup>[33]</sup> All of these information are of extreme relevance to astrobiology, because according to Blumberg,<sup>[34]</sup> astrobiology aims to investigate not only the origin and evolution of life on Earth but also the distribution and future of life in the universe, and these results as it suggests the possibility that in the Mars' past, there were habitable conditions in which life could have been established.

## 4 | CONCLUSION

Essentially, we seek to develop in this research a methodology capable of analyzing the meteorite NWA 6963 from Mars, through the performance of nondestructive techniques with the objective of characterizing a standard model of preliminary analysis and with that, to demonstrate the possible information, discoveries, and results that could be obtained through the of this methodology.

We concluded that the micro-CT has a huge potential to be considered in the future as one of the essential techniques preliminary analysis of fragments of meteorites. Within this standard model we are looking for, perhaps the micro-CT should be the first to be used in preliminary

meteorite analyzes. Fundamentally, for being a nondestructive technique and also for having provided us with innumerable information of extreme relevance, which without it, we would not have accessibility in this work. Thus, through the imaging results from micro-CT, we were able to detect structures encrusted in the NWA 6963 Martian meteorite, one of them possessing differentiated characteristics due to its material being well organized and structured. Furthermore, this technique has generated important information about the density, porosity, and how the internal structure of the object found in the meteorite is distributed.

We also concluded that the X-ray fluorescence technique was employed, although other complementary techniques were needed to provide more complete information on the chemical composition present in the encrusted material and also to provide more accurate and detailed information on the chemical components present in the NWA 6963 meteorite. It was able to generate results of the chemical present in the sample, also without causing any kind of de-characterization of the meteoric material or the encrusted material. In this way, XRF may also have to be seen as one of the essential techniques for preliminary meteorite analysis.

Finally, we believe that this research has a character of originality because it is an analysis of a new and newly discovered meteorite, as well as being a work that demonstrates to have relevance and implications for a relatively new area, that is, astrobiology, besides contributing to the geoscientific understanding of the planet Mars. However, deeper analysis and the use of additional techniques will be required to obtain more specific information about its chemical composition and structural and molecular arrangement of the encrusted material, including whether there is any relationship of this material with the elements Ca, Sr, K, and the others detected. In addition, to understand as the rare element, the minor, moderately, and highly volatile trace elements detected are related to the history of the NWA 6963 Martian meteorite and especially the possible relations with the history of the planet Mars.

## ACKNOWLEDGEMENTS

We acknowledge Nuclear Instrumentation Laboratory (LIN) COPPE, UFRJ, mainly the chief of department Dr. Ricardo Tadeu for the support with micro-CT for our research. Furthermore, we also acknowledge Joaquim Assis for the support with ARTAX for our XRF research. In addition, the authorship acknowledge and thanks for CAPES student scholarship without which none of this research would have been possible. In addition, the authorship acknowledge and thanks

for CAPES student scholarship without which none of this research would have been possible. Finally, the authorship acknowledge everyone that did part of this hard work to be real.

## COMPETING FINANCIAL INTERESTS

The authors declare no competing financial interests.

## ORCID

Bruno L. do Nascimento-Dias  <http://orcid.org/0000-0002-3632-9073>

Davi F. de Oliveira  <http://orcid.org/0000-0003-2038-1480>

Alessandra S. Machado  <http://orcid.org/0000-0002-7973-9611>

Ricardo T. Lopes  <http://orcid.org/0000-0003-1398-0151>

## REFERENCES

- [1] G. Dreibus, H. Wanke, *Phil. Trans. R. Soc. Lond.* **1988**, 325, 545.
- [2] L. L. Nyquist, D. D. Bogard, J. L. Wooden, H. Wiesmann, C.-Y. Shih, B. M. Bansal, G. McKay, *Meteoritics* **1979**, 14, 502.
- [3] F. Nimmo, K. Tanaka, *Earth planet Sci.* **2004**, 33.
- [4] D. J. Milton, P. S. DeCarli, *Science* **1963**, 140(p), 670.
- [5] F. Begemann, *Rep. Prog. Phys.*, Vol. **1980**, 43.
- [6] V. S. Safronov, E. L. Ruskol, Formation and evolution of planets, in *Planetary systems: Formation, evolution and detection*, (Eds: B. F. Burke, J. H. Rahe, E. E. Roettger), Kluwer, Dordrecht **1994** 13.
- [7] B. Gladman, *Icarus* **1997**, 130, 228.
- [8] B. J. Gladman, J. A. Burns, M. Duncan, P. Lee, H. F. Levison, *Science* **1996**, 271, 1378.
- [9] Y. Fei, C. M. Bertka, The interior of Mars science, 308, 1120 **2005**. <https://doi.org/10.1126/science.111053>
- [10] R. Selin, J. Gross, J. Filibert, Water fluorine and chlorine fugacity ratios of the Martian interior derived from apatite in gabbroic shergottite NWA 6963, 45<sup>th</sup> lunar and planetary science conference **2014**
- [11] M. Humayun, K. Kurosawa, T. Usui, *Nature* **2013**, <https://doi.org/10.1038/nature12764>.
- [12] S. C. Solomon, O. Aharonson, J. M. Aurnou, W. B. Banerdt, M. H. Carr, A. J. Dombard, H. V. Frey, M. P. Golombek, S. A. Hauck II, J. W. Head III, B. M. Jakosky, C. L. Johnson, P. J. McGovern, G. A. Neumann, R. J. Phillips, D. E. Smith, M. T. Zuber, *Science* **2005**, 307, 1214, <https://doi.org/10.1126/science.1101812>.
- [13] L. E. Nyquist, D. D. Bogard, C. Y. Shih, A. Greshake, D. Stöffler, O. Eugster, *Chronology and Evolution of Mars* **2001**, 96, 105.
- [14] D. S. McKay, E. K. Gibson Jr, K. L. Thomas-Keprta, H. Vali, *Science* **1996**, 273, 924.
- [15] E. K. Gibson Jr, D. S. McKay, K. L. Thomas-Keprta, S. J. Wentworth, F. Westall, A. Steele, C. S. Romanek, M. S. Bell, J. Toporski, *Precambrian Res.* **2001**, 106, 15.
- [16] G. Horneck, C. Mileikowsky, H. J. Melosh, J. W. Wilson, F. A. Cucinotta, B. Gladman, Viable transfer of microorganisms in the Solar System and beyond, in *Astrobiology: The quest for the conditions of life*, (Eds: G. Horneck, C. Baumstark-Khan), Springer, Berlin **2002** 57.
- [17] C. Mileikowsky, *Icarus* **2000**, 145, 391.
- [18] Meteoritical Bulletin. *Meteoritics & Planetary Science.* **2017**
- [19] Meteoritical Bulletin. Iniciativa: The Meteoritical society. Disponível em <<http://www.lpi.usra.edu/meteor/metbull.php>> last access: 05 de march de 2017.
- [20] G. Bernasconi, A. Tajani, **1996**. Quantitative X-ray analysis system (QXAS) software, package: Documentation version 1.2, International Atomic Energy Agency, Vienna.
- [21] P. Van Espen, H. Nullens, F. Adams, *Nucl. Instrum. Methods* **1977**, 142, 243.
- [22] B. Vekemans, K. Janssens, L. Vincze, F. Adams, P. Van Espen, *X-Ray Spectrom.* **1994**, 23, 278.
- [23] W. D. Carlson, T. Rowe, R. A. Ketcham, M. W. Colbert, *Applications of X-ray computed tomography in petrology, meteoritics and palaeontology*, Geological Society, London, Special **2003** Publications 215.
- [24] F. Mees, R. Swennen, M. Van Geet, P. Jacobs, *Applications of X-ray computed tomography in the geosciences*, Geological Society, London, Special **2003**.
- [25] S. F. Wolf, J. R. Compton, C. J. L. Gagnon, *Talanta* **2012**, 100, 276.
- [26] W. V. Boynton, Cosmochemistry of the rare earth elements: meteorite studies, in *Rare earth element geochemistry*, Elsevier **1983**.
- [27] P. Rey, H. Wakita, R. A. Schmitt, *Analytica Chim. Acta* **1970**, 51, 163.
- [28] R. A. Schmitt, R. H. Smith, J. E. Lasch, A. W. Mosen, D. A. Olehy, J. Vasilevskis, *Geochim. Cosmochim. Acta* **1963**, 27, 577.
- [29] M. Olivares, N. Etxebarria, G. Arana, K. Castro, X. Murelaga, A. Berreteaga, *X-Ray Spectrom.* **2008**, 37, 293.
- [30] R. A. Wogelius, P. L. Manning, H. E. Barden, N. P. Edwards, S. M. Webb, W. I. Sellers, K. G. Taylor, P. L. Larson, P. Dodson, H. You, L. Da-qing, U. Bergmann, *Science* **2011**, 333, 1622.
- [31] G. Pigaa, A. Santos-Cubedo, S. M. Sola, A. Brunetti, A. Malgosa, S. Enzo, *Jour. of Arch. Sci.* **2009**, 36, 1857.
- [32] K. L. Thomas-keprta, S. J. Clemett, D. S. Mckay, E. K. Gibson, S. J. Wentworth, *Geochim. Cosmochim. Acta* **2009**, 73(21), 6631.
- [33] Y. Liu, C. Ma, J. R. Beckett, Y. Chen, Y. Guan, *Earth Planet. Sci. Lett.* **2016**, 451, 251.
- [34] B. S. Blumberg, *Astrobiology* **2003**, 3(3), 463.

**How to cite this article:** do Nascimento-Dias BL, de Oliveira DF, Machado AS, Araújo OMO, Lopes RT, dos Anjos MJ. Utilization of nondestructive techniques for analysis of the Martian meteorite NWA 6963 and its implications for astrobiology. *X-Ray Spectrometry*. 2017;1-6. <https://doi.org/10.1002/xrs.2815>