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Analysing the astrobiological aspects through the comparison of pyroxenes detected in meteorites and Martian environments

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Abstract

Although pyroxenes are found abundantly in igneous rocks, this mineral group stands out for being one of the ferromagnesian mineral groups that constitute rocks of several different compositions. Hence, the purpose of this work is to demonstrate how these minerals may be relevant to Astrobiology. Essentially, through geochemical analyses of pyroxenes detected in Martian meteorites, it may be possible to find evidence of the existence of water in hydrothermal flows located in deep regions below the Martian surface. To this extent, it is also very important to highlight the whole collection of observational data from Mars, in which it is possible to notice that pyroxenes are found in a wide variety of geological environments. Therefore, based on Martian surface observations, meteorite analysis and experimental data, it is conceivable that, given the appropriate conditions, pyroxenes might be related to the formation and release of water molecules in the Martian environment.

Introduction

Minerals carry within their structure a great range of information regarding physical and chemical processes that have occurred during their formation (Nascimento-Dias *et al.*, 2018). In general, these processes are related to evolutionary environmental patterns of the region in which they are found. Hence minerals are indispensable tools for the understanding of the history and geological evolution of a planet. Among many mineral groups, the pyroxene group stands out for being one of the ferromagnesian minerals that constitute rocks of different compositions, despite being found more abundantly in igneous rocks (Deer *et al.*, 1992).

Given these circumstances this article aims to show how the study of the parageneses of the minerals from the chemical group of the pyroxenes, which are found in meteorites and in many Martian environments, might be relevant for Astrobiology. Analyses regarding the potential processes that might have shaped the formation, alteration and distribution of pyroxenes in Mars were made, as well as μRaman data were collected from Zagami, a Martian meteorite in which pyroxene was detected.

There is strong evidence to support the claim that a million years ago Mars was very similar to Earth in terms of environmental conditions (Sagan and Mullen, 1972; Nyquist *et al.*, 2001). Due to these geological similarities, NASA (National Aeronautics and Space Administration) began promoting many space missions in order to gain knowledge about the red planet. According to Klein (1978), the Viking I space probe was the first scientific instrument to successfully land on the Martian surface. Since then, the American agency and other international collaborators started promoting many more scientific explorations seeking information with regard to the atmosphere, geology, gravity, magnetosphere and temperature of Mars.

In the last 10 years, there has been a vast amount of activity related to the understanding and the exploration of Mars. Many rover missions (e.g. Spirity, Opportunity and Curiosity) were sent with the aim of exploring and clarifying the mineralogy and the geology of the Martian surface, and also the possible existence of water on the red planet. The data collected in these missions have been responsible for a lot of theoretical and experimental work regarding the stability fields and the alteration phases of sulphates and silicates in Mars (Papike *et al.*, 2009).

Furthermore, Hutchinson *et al.* (2014) investigated the viability of studying Martian meteorite samples through analytical techniques. The purpose of this idea is related to the arrangement of the new mission to Mars, whose space probe, ExoMarsRover 2021, is equipped with many sophisticated instruments for chemical, physical, biological and mineralogical analyses.

It is possible to say that comparative planetary science has, lately, been developing itself due to the data obtained by space probes and rovers that provide detailed information on the

Martian surface. This database provides, on a global scale, specific high-resolution spectrometric and photometric information on the atmospheric and mineralogical distribution. These results obtained through observational and *in situ* methods can be crossed and complemented by meteorite analyses through analytical techniques (Ehlmann and Edwards, 2014).

Although nowadays no liquid water has been detected on the surface of Mars, it may have been abundant in the past (Nascimento-Dias, 2018). This is thus a very important discussion for the investigation of the habitability conditions of Martian environments. Therefore, it is necessary to seek answers for the countless questions that arise regarding the role water may have played on the yet obscure past of Mars.

Materials and methods

μRaman

Raman is a high spatial resolution technique that provides, in a quick and non-invasive manner, information regarding molecular vibration modes of any organic or inorganic material, as long as its molecules are polarizable (Rodrigues and Galzerani, 2012; Nasdala *et al.*, 2004). Hence it is an analytical technique through which we are able to identify molecules constituted by the fundamental atoms of the system, such as in the structural composition of life, in which there is fundamentally Carbon (C), Hydrogen (H), Oxygen (O), Nitrogen (N), Phosphorus (P) and Sulphur (S), also known as 'CHONPS'. Besides, it is possible to identify the structural and mineralogical composition of the material.

In this work, a Renishaw inVia equipment connected to a Leica confocal microscope (5X, 20X and 50X objectives) available at Laboratório Brasileiro de Luz Synchrotron (LNLS/CNPEM) was used. This system is equipped with excitation lasers of 532, 633 and 785 nm, diffraction gratings of 1200 l mm^{-1}, CCD detector and special optics and software for rapid mapping system (Renishaw Streamline®). Also, it has a spectral resolution of 4 cm. The measures were taken with a 20X objective and a 785 nm excitation, which guaranteed a lower fluorescence flow of the sample. Data processing was made by using a Renishaw WiRE® 4.1 software.

It is important to state that the limitations of the analyses lie in potential fluorescence interference and Raman dispersion of the sample. These can create background noise on the spectrum, preventing the existence of Raman peaks or low-intensity peaks for some components.

Martian meteorite Zagami

The Zagami meteorite fell on 3 October 1962, about 1.2 km away from Zagami Rock, Katsina province, Nigeria (Graham *et al.*, 1985). In 1985, its 18 kg main mass was sent for analyses at Geological Survey of Nigeria, in Kaduna. However, in 1988, the meteorite dealer Robert Haag obtained a big piece of Zagami, which was chopped up and widely distributed.

This meteorite is classified as an achondrite, from the SNC group, (shergottites, nakhlites e chassignites). This group is known for the similarities between the isotopic composition of gases trapped in its meteorites and the Martian atmosphere composition, which indicate that they have Mars as a common origin. It is worth to mention that Zagami was the second meteorite found containing a significant quantity of Martian atmosphere gases trapped inside its minerals (Marti *et al.*, 1995).

Fig. 1. Zagami meteorite fragment.

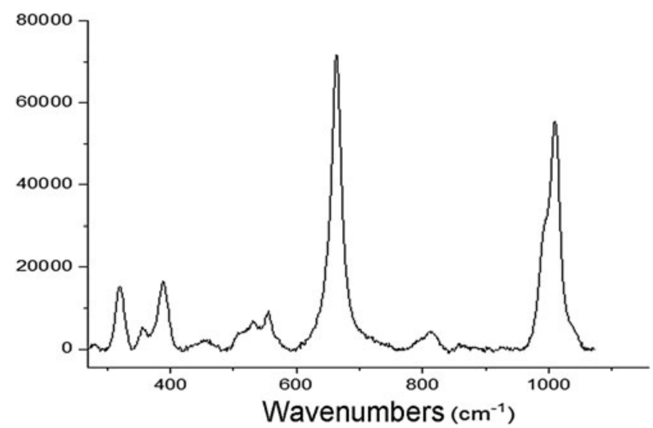

Fig. 2. Raman spectra of Zagami meteorite in this work.

The Zagami meteorite, in Fig. 1, is classified within the SNC group as a shergottite.

The fragment used in this work was provided by the Brazilian National Museum (UFRJ), which has confirmed that the sample corresponds to the mineralogy and description reported in the *Meteoritical Bulletin*(2017).

Results

Detection of pyroxenes in samples and Martian environments

The analysis of Zagami was made through the punctual variation of the monochromatic beam across important regions of the sample. In Fig. 2, the μRaman spectrum obtained at the Laboratório Nacional de Luz Síncrotron (LNLS) is presented. The Zagami spectrum peaks are composed by frequencies of 318, 363, 393, 536, 664, 821 and 1013 cm^{-1}.

Based on this result, it is possible to make a comparative analysis between the presented spectrum and the spectra (a) and (b) from Fig. 3. This comparison aims to identify the mineralogical composition of important regions of the sample.

It is worthy of notice that the features of the peaks from Fig. 2 match those from Fig. 3(b), such as those also obtained through Raman and presented by Wang *et al.* (1999). However, for a more accurate analysis, these frequencies typical of the pyroxene group describe precisely the spectrum of a specific mineral that belongs to this group, the clinopyroxene diopside [CaMgSi2O6].

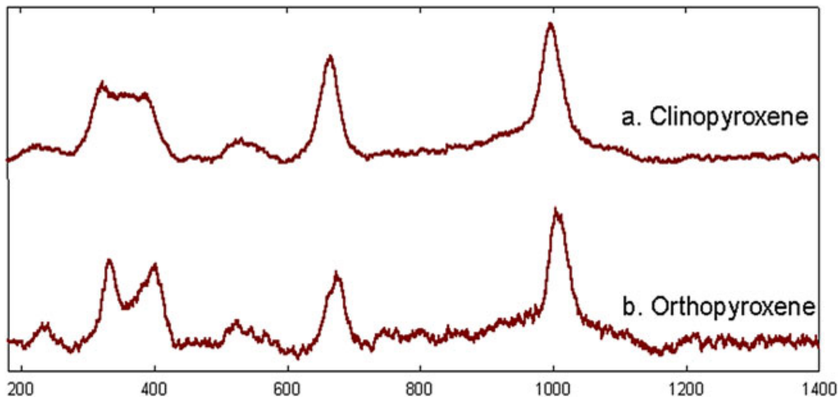

Fig. 3. Raman spectra of clinopyroxene and orthopyroxene minerals from the scientific literature.
Source: Wang *et al.* (1999).

This mineral in its pure form has peaks that are very similar to the ones from Table 1.

Table 1. Vibrational modes of diopside

Expected vibrational mode	
Raman deviation (in this work)	Raman deviation (diopside)
318 cm^{-1}	325 cm^{-1}
363 cm^{-1}	357 cm^{-1}
393 cm^{-1}	392 cm^{-1}
536 cm^{-1}	531 cm^{-1}
664 cm^{-1}	667 cm^{-1}
821 cm^{-1}	855 cm^{-1}
1013 cm^{-1}	1013 cm^{-1}

Discussion

Of all the aims of the exploratory missions to Mars, the search for evidence of water in hydrothermal flows is one of the main goals. According to Ellery *et al.* (2004), analytical techniques such as Raman are particularly important and can be used in mineralogical analyses of meteorite and of the Martian soil and in order to seek potential traces of fossilized biota of microorganisms in Mars. Thus the search for water can be conducted, for example, through geochemical analyses of pyroxenes detected in Martian meteorites using Raman (Tarcea *et al.*, 2008).

With respect to the pyroxenes, McSween *et al.* (2001) report that they might have been some of the first minerals to crystallize on Mars. Their parageneses is briefly described in Fig. 4.

Essentially, the homogeneous magnesium nuclei of these grains might have been originated in great depths far below the Martian surface and dragged up due to the intrusive material of the ascending magma. Although the content of magmatic water in the chemical analyses of Martian meteorites is relatively low, it is possible that significant quantities of water were provided to the Martian surface by volcanic outgassing (McSween *et al.*, 2001).

Still according to McSween *et al.* (2001), the inner nuclei of the pyroxene minerals of the shergottites are more enriched than the edges of these minerals. This may bring relevant implications for Astrobiology, because water could be present in pyroxenes at greater depths below the Martian surface. Besides, other facts that might be connected to the data found in meteorites are the high concentrations of orthopyroxenes found in the ancient and cratered terrains of the southern hemisphere of Mars.

Through the collection of observational data of Mars obtained by rovers and telescopes, it is noticeable that the pyroxenes are found in a great range of geological environments. Although they are mostly present on the cratered and ancient terrains of the southern hemisphere, it is possible to find some pyroxene in more recent environments, such as the northern hemisphere of Mars. Figure 5 shows the distribution of pyroxenes on the crust of Mars.

The presence of pyroxene on the recent and smooth regions of the northern hemisphere still demands an explanation. However, it might be that these minerals are a piece of the puzzle we ought to solve in order to understand the hemispheric dichotomy of Mars.

Furthermore, as stated by Bowen and Tuttle (1949), it is possible to observe the crystallization of pyroxenes under temperatures and water vapour pressure above 700°C and 5000 lb in^{-2} (345 bar). However, the process presents itself stable in the presence of water when the temperature is around 900°C. It can be described by the following reaction:

$$\underset{\text{(Talc)}}{(OH)_2Mg_3Si_4O_{10}} + \underset{\text{(Olivine)}}{Mg_2SiO_4} + \underset{\text{(Pyroxene)}}{5MgSiO_3} + \underset{\text{(Water)}}{H_2O} \tag{1}$$

Conclusion

The observations of the Martian surface morphology are frequently used to argue that an ocean has existed on Mars. However, potential geochemical evidence of water in the interior of the planet may also be found through the analysis of information contained in minerals such as pyroxenes. Thus, based on these observations, meteorite analysis, combined with the realization of experiments, it is possible to search for geochemical indications of water in the interior of the planet.

Given the adequate conditions, the pyroxenes might thus be related to the formation and the release of water molecules in the Martian environment. Therefore, these minerals can be seen as great sources for the investigation of the geochemical transformations that might have happened in Mars. Hence, as they are distributed along the Martian crust, it is possible to

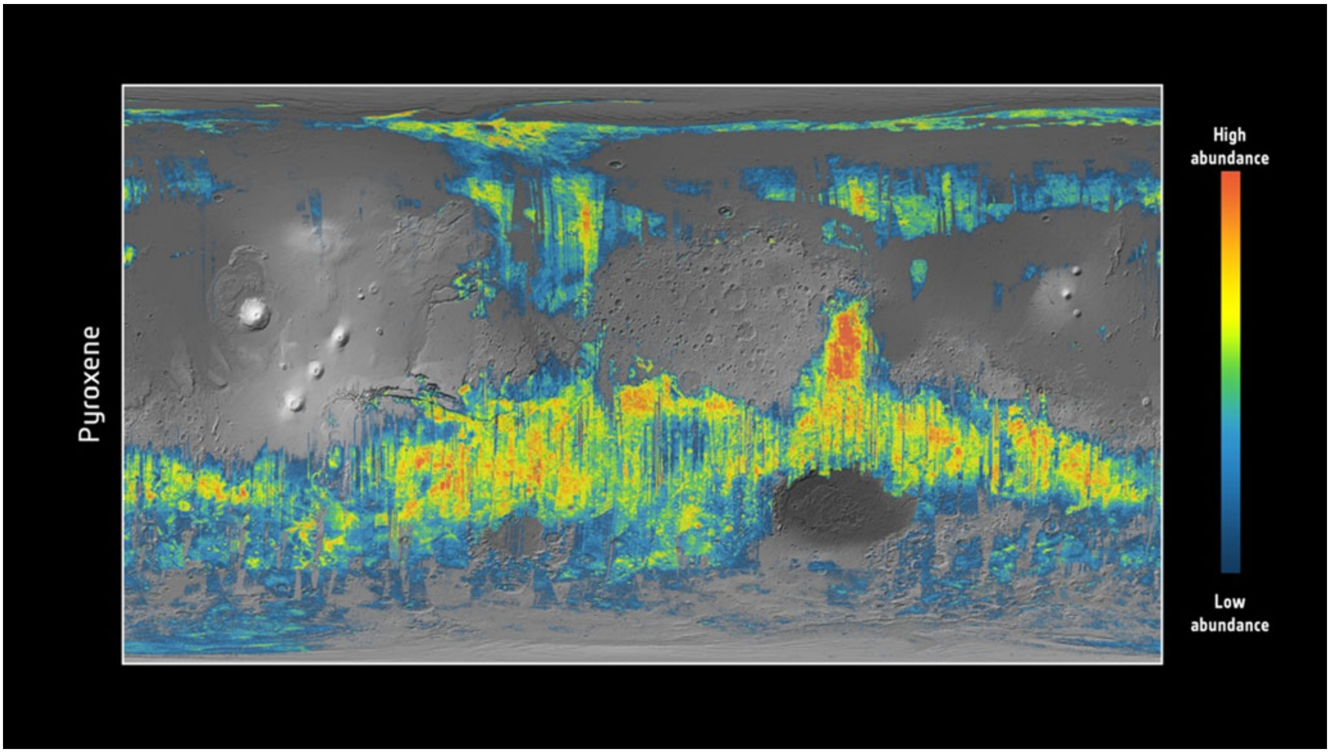

Fig. 4. Distribution of pyroxenes on the crust of Mars.
Source: Bibring (2005).

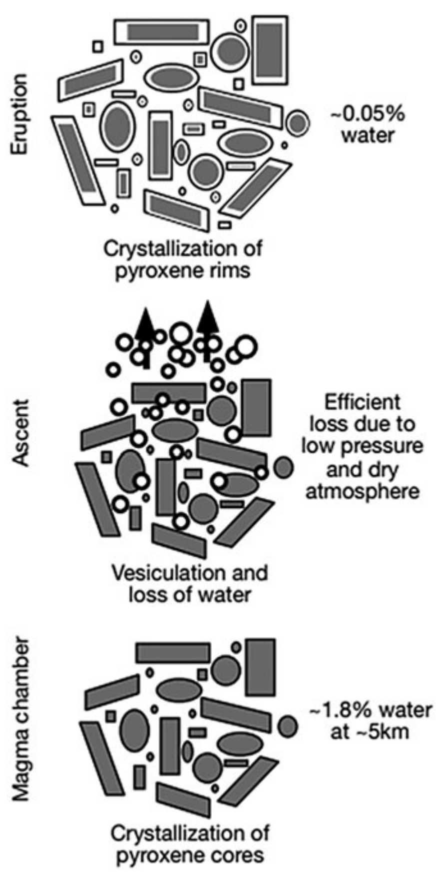

Fig. 5. Illustration of the process of crystallization of pyroxene during ascent and on eruption Fonte.
Source: McSween *et al.* (2001).

conclude that pyroxenes were likely related to the aqueous environments that might have existed during the evolution of the red planet.

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Conflict of interest. None.

References

Bibring JP, Langevin Y, Gendrin A, Gondet B, Poulet F, Berthé M, Soufflot A, Arvidson R, Mangold N, Mustard J, Drossart P and OMEGA team. (2005) Mars surface diversity as revealed by the OMEGA/Mars Express observations. *Science*, v. **307**, n. 5715, pp. 1576–1581

Bowen NL and Tuttle OF (1949) The system MgO–SiO2–H2O. *Geological Society of America Bulletin* **60**, 439–460.

Deer WA, Howie RA and Zussman J (1992) *An Introduction to the Rock Forming Minerals*, 2nd edn. Essex, UK: Longman.

Ehlmann BL and Edwards CS (2014) Mineralogy of the Martian surface. *Annual Review of Earth and Planetary Sciences*, v. **42**, pp. 291–315.

Ellery A, Wynn-Williams D, Parnell J, Edwards HGM and Dickensheets D (2004) The role of Raman spectroscopy as an astrobiological tool in the exploration of Mars. *Journal of Raman Spectroscopy* **35**, 441–457.

Graham LA, Bevan AWR and Hutchinson R. (1985) Catalogue of meteorites. With special reference to those represented in the collection of the British Museum (Natural History). London: British Museum, 1985, 4th ed., 1985.

Hutchinson IB, Parnell J, Edwards HGM, Jehlicka J, Marshall CP, Harris LV and Ingley R (2014) Potential for analysis of carbonaceous matter on Mars using Raman spectroscopy. *Planetary and Space Science*.

Klein HP (1978) The Viking biological experiments on Mars. *Icarus* **34**, 666–674.

Marti K *et al.* (1995) Signatures of the Martian atmosphere in glass of the Zagami meteorite. *Science* **267**, 1981.

McSween Jr HY, Grove TL, Lentz RC, Dann JC, Holzheid AH, Riciputi LR and Ryan JG (2001) Geochemical evidence for magmatic water within Mars from pyroxenes in the Shergotty meteorite. *Nature* **409**, 487.

Meteoritical Bulletin (2017) Meteoritics & Planetary Science.

Meteoritical Bullitin. Iniciative: The Meteoritical Society. Available at http://www.lpi.usra.edu/meteor/metbull.php (Accessed 05 de March de 2017).

Nascimento-Dias BL (2018) Combination between Ca, P and Y in the Martian Meteorite NWA 6963 could be used as a strategy to indicate liquid water reservoirs on ancient Mars? *International Journal of Astrobiology* 1–6.

Nascimento-Dias BL, Galante D, Oliveira D and Anjos M (2019) Probing the chemical and mineralogical characteristics of the Martian meteorite NWA 7397 through μRaman and μXRF non-destructively. *International Journal of Astrobiology* **18**, 73–78.

Nasdala LUTZ, Smith DC, Kaindl REINHARD and Ziemann MA (2004) Raman spectroscopy: analytical perspectives in mineralogical research. *Spectroscopic Methods in Mineralogy* **6**, 281–343.

Nyquist LE, Bogard DD, Shih C-Y, Greshake A, Stöffler D and Eugster O (2001) Ages and geologic histories of martian meteorites. *Chronology and Evolution of Mars* **96**, 105–164.

Papike JJ, Karner JM, Shearer CK and Burger PV (2009) Silicate mineralogy of martian meteorites. *Cosmochimica Acta* **73**, 7443–7485.

Rodrigues AG and Galzerani JC (2012) Infrared, Raman and photoluminescence spectroscopy: potentialities and complementarities. *Revista Brasileira de Ensino de Física* **34**, 1–9.

Sagan C and Mullen G (1972) Earth and Mars: evolution of atmospheres and surface temperatures. *Science* **177**, 52–56.

Tarcea N, Frosch T, Rösch P, Hilchenbach M, Stuffler T, Hofer S and Popp J (2008) Raman spectroscopy – a powerful tool for *in situ* planetary science. In *Strategies of Life Detection*. Boston, MA: Springer, pp. 281–292.

Wang A, Jolliff BL and Haskin LA (1999) Raman spectroscopic characterization of a Martian SNC meteorite: Zagami. *Journal of Geophysical Research: Planets* **104**(E4), 8509–8519.