DISTRIBUTION OF IRON AND TITANIUM OXIDES IN THE MILLER RANGE MIL 090030 MARTIAN METEORITE USING MICRO-RAMAN IMAGE AND SEM/EDS. L. Coloma*[1], J. Aramendia[1], I. Población[1], J. Huidobro[1], J.M. Madariaga[1]*, C. García-Florentino[1], K. Castro[1], G. Arana[1], [1]Dep. Anal. Chem., University of the Basque Country (UPV/EHU), 48940 Leioa, Spain (lcoloma001@ikasle.ehu.eus , juanmanuel.madariaga@ehu.eus)

Introduction: In Martian meteorites, different types of iron and titanium oxides have been detected, the most common ones being magnetite [Fe_3O_4], titanomagnetite [$Fe(Fe,Ti)_2O_4$], ilmenite [$FeTiO_3$] and hematite [Fe_2O_3]. All these minerals form part of the TiO_2-FeO-$1/2Fe_2O_3$ phase diagram in two different proportions of the solid solutions, magnetite-ulvospinel [$TiFe_2O_4$] and hematite-ilmenite. Titanomagnetite is found between magnetite and ulvospinel [1]. In some meteorites, these oxides were found forming a singular structure similar to a skeleton. Usually, these phases were analysed by optical techniques, for example backscattered electron (BSE). Using this type of analytical techniques, it is said that the oxide structure is formed by titanomagnetite [2]. However, using non-destructive molecular techniques, like Raman spectroscopy, the spatial distribution of the iron and titanium oxides can be observed in the skeleton structures found in the meteorites. To realize this aim, the meteorite Miller Range 090030 (MIL 090030) was analysed using micro-Raman spectroscopy and Scanning Electron Microscopy with Energy Dispersive Spectroscopy detection (SEM-EDS).

Instrumentation and methodology:

Micro Raman spectroscopy. This work was performed using the Renishaw inVia confocal micro-Raman spectrometer (Renishaw, UK). All the analyses were carried out with the 532 nm excitation diose laser (Renishaw UK RL532C50 with a nominal 300-mW output power). The instrument is equipped with a CCD detector cooled by Peltier effect, with a Leica DMLM microscope (Bradford, UK), implementing an XYZ stage control toolbar and with a micro camera. For this work, the Raman image was acquired using the HR StreamLine Imager device coupled to the Raman spectrometer. Samples were analysed using 5% of laser power, 1800 l/mm (vis) grating, 10 s of exposure time, 100x objective, 2 accumulations and a step of 0.8. The wavenumber range was from 100 to 4000 cm^{-1}.

After data acquisition, the Raman spectra were treated with the Wire software to subtract the baseline and to remove the cosmic rays. Finally, the center of each band was extracted for each spectrum by using a curve fitting (50% Lorentzian-Gaussian) option of the Wire software.

Scanning Electron microscopy coupled to Energy Dispersive Spectrometer (SEM/EDS). The SEM/EDS instrument is an is an EVO 40 (Carl Zeiss NTS GmbH, Germany) Scanning Electron Microscope (SEM) that uses an X-Max Energy-Dispersive X-Ray (EDS) spectroscopy detector (Oxford Instruments, UK). The SEM images are acquired at high vacuum employing an acceleration voltage of 20 kV, 1 nA of amperage, 15 mm of working distance and objective between 500x and 15000x were used. The EDS is used for elemental mapping, and the analyses were performed using an 15 mm working distance, a 35 take-off angle. For the SEM/EDS data collection the program INCA suite 4.13 (Microanalysis Suite, UK) is used. This software allows performing chemical maps of all elements present in the scanning image simultaneously. The plots appear in black and white, where the former represents the absence of an element and the latter its presence. Besides, there is the possibility to obtain false color images of the analyzed surface where the energies of each element are represented in different colors over the SEM image for a better view of the chemical maps.

Results and discussion: In the MIL 090030 Martian meteorite, the four oxides mentioned were detected. The High Resolution Raman image in a skeleton structure showed the spatial distribution of minerals: ilmenite was located in the most inner parts of the skeleton, titanomagnetite was found surrounding ilmenite grains and magnetite was detected surrounding titanomagnetite. This distribution can be seen in Figure 1.

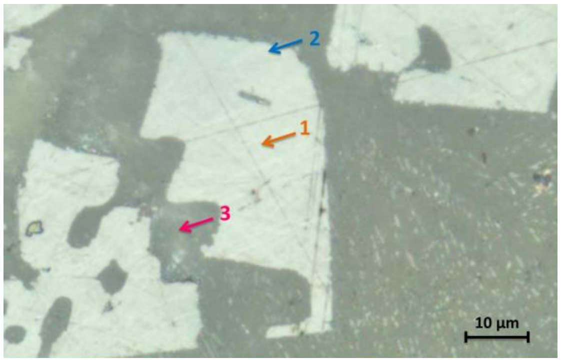

Figure 1. Skeleton structure found in the MIL 090030 Martian meteorite. With different colours the points where the measurements were made are shown.

Figures 2-4 display the Raman spectra collected at the different points showed in Figure 1. For clarity, different colors are also used to differentiate among detected compositions at each point.

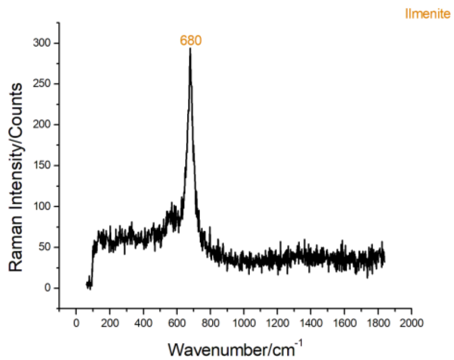

Figure 2. Raman spectrum of ilmenite (in orange). This spectrum was measurement in point 1 of Figure 1.

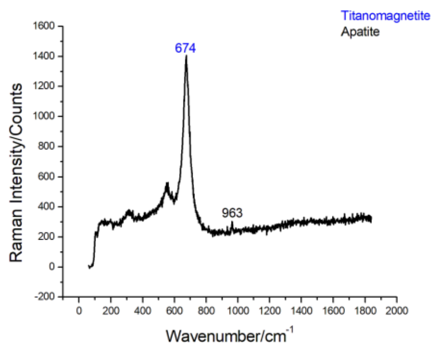

Figure 3. Raman spectrum of titanomagnetite (in blue) and apatite (in black). This spectrum was measurement in point 2 of Figure 1.

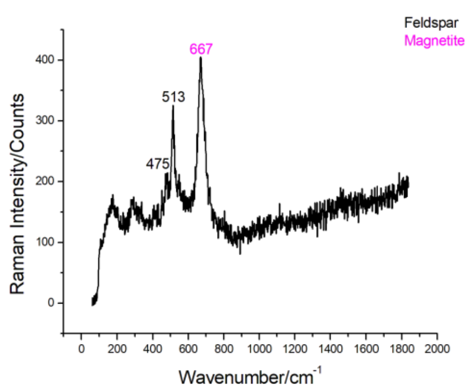

Figure 4. Raman spectrum of magnetite (in pink) with feldspar (in black). This spectrum was measurement in point 3 of Figure 1.

In this distribution, a rise of titanium from the outside of the skeleton to the inside can be seen, due to ilmenite being the oxide with more proportion of titanium whereas magnetite does not have this element. Titanomagnetite has a different proportion of Fe/Ti. This variation in the proportion of titanium was confirmed by SEM-EDS.

The spatial distribution observed suggests the following explanation for the formation of these skeletons. Firstly, titanomagnetite was formed by a crystallization of magmas with titanium. Secondly, titanomagnetite was oxidized to form ilmenite and magnetite, as shown in reaction 1:

$$6Fe_2TiO_4 + O_2 \leftrightarrow 6FeTiO_3 + 2Fe_3O_4 \qquad (1)$$

Ilmenite formed in reaction 1 could not remain in a solid solution and it was segregated in small grains surrounded by titanomagnetite. Magnetite from reaction 1 was precipitated surrounding titanomagnetite [1].

Conclusion: This work demonstrates the importance of using non-destructive molecular techniques (mainly spectroscopic image, i.e. High Resolution Raman Image) to determine the distribution of different minerals in the meteorite.

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References:

[1] Hughes H. R.S. and Andersen J. (2020) *Encyclopedia of Geology, 2*. [2] Sautter V. et al. (2006) *Earth & Planet. Sci. Lett., 252,* 45-55.