RAMAN PROFILING OF CARBONATES LAYERS FROM HYDROTHERMAL ANALOGS OF MARS

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Introduction

In the remote exploration of the surface of Mars, a wide variety of evaporitic salts were found at Martian surface using remote sensing with the near-infrared imaging spectrometers OMEGA of Mars Express and CRISM of Mars Reconnaissance Orbiter. Also, rovers and landers confirmed the presence of, mainly hydrated sulfates and also carbonates[1]. Furthermore, carbonates were detected in Martian meteorites as ALH84001. These materials are closely related with hydrous environments or hydrothermal systems and in addition, in relationship with the potential habitability of Mars. AMASE (Arctic Mars Analog Svalbard Expedition) has been working from 1997 in the study of sites on the Svalbard islands, a very special Mars analog place with several scenarios with different geologies. In particular, the Bockfjord Volcanic Complex (BVC), with a special combination of volcanoes and permafrost, is a unique place on Earth with carbonate deposits similar to carbonates found in the Martian meteorite ALH84001[2]. In this work, we use Raman Spectroscopy as tool for analysis of these materials in relationship with the develop of the Raman Laser Spectrometer[3] that our group lead for the payload of Exomars mission of ESA, to be launched to Mars in 2018. Raman spectroscopy allows us a powerful spatial resolution using spots in the micro range without damage or special preparation of the sample.

Samples

During 2009 and 2010 campaigns, several breccia samples were collected. Samples from this localization, BVC, should be formed eruptions ca. 1 Ma ago behind the permafrost as subglacial eruptions. That activity brings to surface rich magnesium-carbonates fluids that formed those deposits and carbonate globules[4].

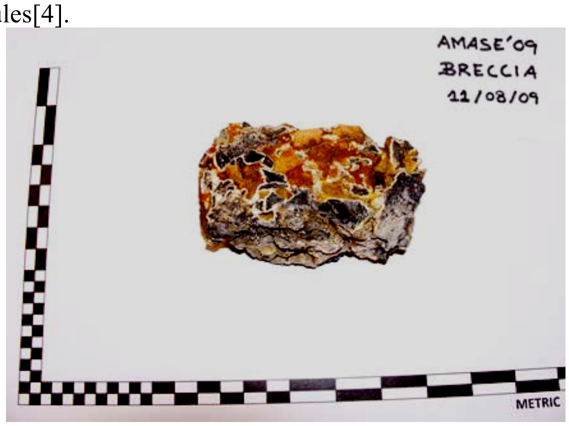

Figure 1: Breccia Sample

These carbonate deposits including dolomite- magnesite globules similar to the found in ALH84001 [5][6].

Methodology

The laboratory mineralogical characterization of the samples was performed by micro-Raman spectroscopy, using a microscope Nikon Eclipse E600 coupled to a spectrometer KOSI Holospec f/1.8i illuminated by a laser REO LSRP-3501, He-Ne 632.8 nm. The detection was performed with a CCD Andor DV420AOE-130. For the analysis, an automatic mode was selected and the spectra collected were processed using MATLAB.

After a survey done following the color variation, several profiles were done trailing line crossing these layers. The profiles were made with a constant step between the plots analyzed.

As we are going to analyze carbonates, we are looking for the specific fingerprints of carbonates active in Raman spectroscopy as the symmetric stretching mode, ν_1, from 1050 to 1190 cm^{-1}. Also the antisymmetric bending vibration, ν_4, occurs near 700cm^{-1} and the lattice external modes consist of ionic translations and librations (restricted rotations) in the low wavenumber region (100–300 cm^{-1})[7].

Results

For a first overview, a survey was performed looking to the color variations. On this survey, Dolomite and Magnesite were detected mainly. Also in several plots, Aragonite and Ankerite were identified.

With the profiling, we found how these species are distributed, the homogeneity and the transitions of the cationic compositions.

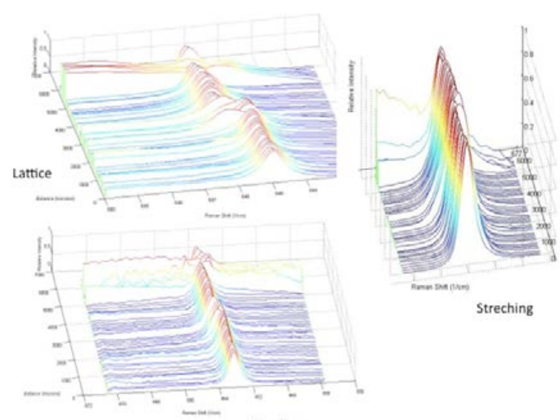

Figure 2:3D plotting of the spectral zones along the profile.

For the analysis of the cationic variations, the bending and the lattice modes are more sensitive than the stretching mode. This one gives us information about the degree of cristalinity with the analysis of its width.

Here we present the results of one of the profiles:

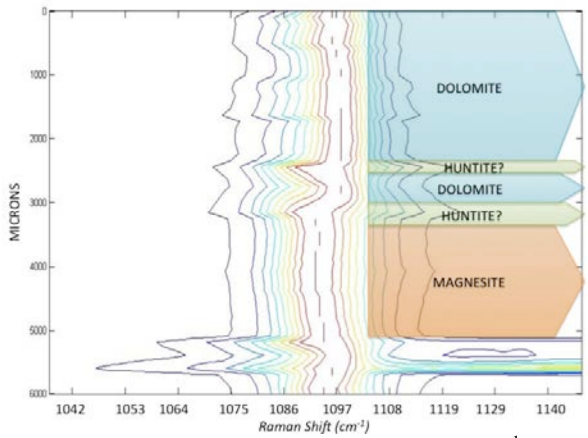

Figure 3: Stretching zone 1050-1090 cm^{-1}

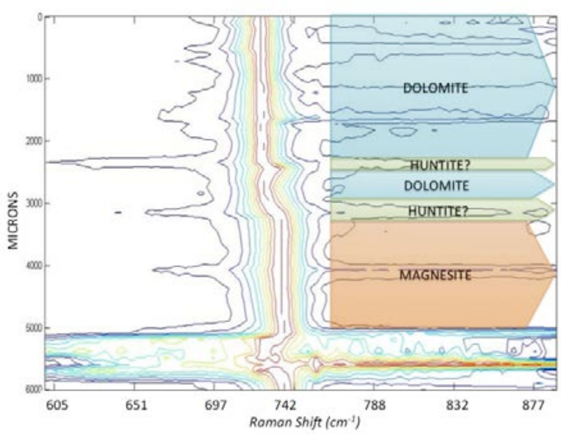

Figure 4: Bending zone around 700 cm^{-1}

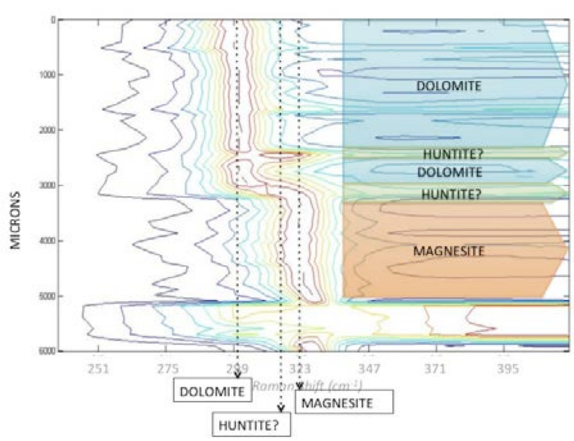

Figure 5: Lattice zone 200-350 cm^{-1}

We could identify on the profiles the sequence from Dolomite *($MgCa(CO_3)_2$)* to Magnesite *($MgCO_3$)* on the carbonate layers. Also we found two discontinuities that could be Huntite *($Mg_3Ca(CO_3)_4$)* zones. Huntite is a Mg-Ca carbonate richer in Mg than Dolomite.

Conclusions

The results are consistent with other studies related with these kind of carbonates[8] about the mineral species occurrence.

One interesting point is the occurrence of Huntite as transition from Dolomite and Magnesite. In the first episode, could be from an enrichment of the hydrothermal solution in calcium or a variation on the P-T conditions of the solution. The second episode seems to be the continuity of the decrease of the calcium content of the solution. A more detailed study of all these relationships is in progress.

The use of Raman micro-spectroscopy becomes very useful in the spatial resolution of this kind of transitions and for the interpretation of these analog structures of carbonates. This increase the relevance of the use of this technique in Exomars and in future planetary Raman instruments.

Acknowledgements

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