



RAMAN-LIBS AND MÖSSBAUER SPECTROSCOPIC STUDY OF ALTERATION MINERALS FROM THE MARS ANALOGUE JAROSO RAVINE (SPAIN)

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Abstract

The SE Mediterranean margin of Spain is an extremely interesting area of simultaneous interaction of tectonic, volcanic, evaporitic and mineralizing hydrothermal processes. These characteristics could be used as a potential model for Mars analog studies. And in particular for in-situ field analysis using prototypes of Mars exploration mission instruments or collecting samples for detailed laboratory analysis. In the present work results obtained using a combined suite of Raman, LIBS and Mössbauer spectrometers in the field and at the laboratory are presented and discussed. These results stressed the importance of use combined techniques for precise mineral identification and elemental chemical characterization of unknown samples at the field illustrating their potential for surface analysis in future planetary missions.

1. Introduction

The Jaroso Ravine (world locality of Jarosite) located in Sierra Almagrera (Almeria, Spain) is part of the "Jaroso Hydrothermal System". This system constitutes an ancient model of formation of supergenic sulfates associated with polymetallic (Fe,Pb,Ag) sulfides and sulfosalts which are genetically linked to the calc-alkaline shoshonitic

volcanism (Upper Miocene) of the SE Mediterranean margin of Spain [1]. The supergenic mineral alteration represent a very interesting way for studying some of the main possible Mars minerals formation processes. In Jaroso these processes can be separated in two stages. The first one associated with insoluble mineral precipitation (clays, oxi-hydroxide phases and alunites-jarosites) and the second associated with more soluble sulphate phases. Therefore, sulphates are a key by-product of these processes. Sulphates have been found on Mars using orbiter spectrometry (OMEGA on Mars Express and CRISM on Mars Reconnaissance Orbiter) [2] and surface spectroscopy. In particular Jarosite ((K,Na,H₃O)Fe₃(SO₄)₂(OH)₆) was unambiguously identified by Mössbauer spectrometer (MB) on Opportunity rover [3]. These results show that sulphates are of prime importance in the geological evolution of Mars.

1.1. Experimental

For the in-situ Mössbauer setup, a MIMOS II sensorhead was used equipped with ⁵⁷Co-sources (~30mCi). Spectra of good quality were obtained within less than two hours and at ambient temperatures of ~35°C. The spot diameter for a measurement is 15 mm. MIMOS II sensorheads were also used for laboratory measurements. The enhanced follow-up version of the spectrometer, MIMOS IIA, will be equipped with silicon-drift-detectors (SDD) instead of Si-PIN detectors, thus providing a significantly better signal-to-noise ratio. The instrument will also be able to measure X-ray fluorescence to determine elemental composition.

Raman spectra were obtained in-situ with a portable i-Raman from B&W TEC Inc, adapted to work under field conditions. The optical head was positioned in front of the samples using a mechanical device which allows mapping the surface at near the mineral grain scale. A baffle was used to minimise the solar light background. The excitation used was a 532nm wavelength laser with ~15mW power on the sample and a spot diameter of 100µm. Spectral resolution was 5cm⁻¹.

2. Results

Raman, LIBS and Mössbauer spectra were collected at several places in Jaroso ravine by direct in-situ analysis of samples and outcrops (fig1/fig.4).



Figure 1- Mössbauer, Raman and LIBS instruments displayed at an outcrop with clay minerals covered by jarosite and oxi-hydroxide deposits.

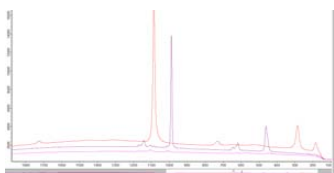


Figure 2. Raman spectra of some minerals detected in-situ. From top to bottom Calcite, Barite and Jarosite.

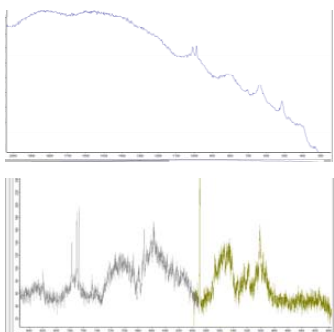


Figure 3. In-situ Raman (top) and LIBS (bottom) spectra of clay minerals at the outcrop in Figure 1.

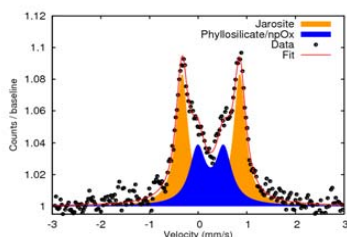


Figure 4. In-situ Mössbauer spectra of clay minerals at the outcrop in Figure 1.

6. Summary and Conclusions

Mössbauer- and Raman- spectroscopy provide complementary mineralogical information allowing near unique mineral identification: Raman spectroscopy is sensitive to a large number of minerals and organic phases, Mössbauer spectroscopy provides detailed information about Fe-bearing mineral phases, Fe oxidation states and the distribution of Fe among them. Both techniques are also complementary on analyzing surface samples: Raman spectroscopy is sensitive to the very surface of a sample, with a spot size small enough ($\sim 100 \mu\text{m}$) to perform measurements at the scale of single mineral grains. MIMOS II with a field of view of $\sim 1.5 \text{ cm}$ and sampling depth of $\sim 200 \mu\text{m}$, provides mineralogical context information about a larger volume and depth selective information about a sample by detecting backscattered 14.4keV keV and 6.4keV X-rays simultaneously [4]. Raman and Mössbauer spectroscopy have proven to be a extremely valuable combination to determine organic phases and Fe oxidation states to search for past or present traces of life on Mars.

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