

RAMAN AND MÖSSBAUER SPECTROSCOPIC CHARACTERISATION OF SULFATE MINERALS FROM THE MARS ANALOGUE SITES AT RIO TINTO AND JAROSO RAVINE, SPAIN. F. Rull¹, I. Fleischer², J. Martinez-Frias¹, A. Sanz¹, C. Upadhyay² and G. Klingelhöfer², ¹ Unidad Asociada UVA-CSIC al Centro de Astrobiología, Valladolid, Spain (rull@fmc.uva.es), ²Institut für Anorganische und Analytische Chemie, Johannes-Gutenberg-Universität, Mainz, Germany (klingel@mail.uni-mainz.de).

Introduction: The occurrence of sulfates on Mars has been expected since the Viking Landers found sulfur in the Martian soil in 1976 but the host minerals were never identified. The amazing discoveries of the MER rovers and OMEGA instrument onboard Mars Express have shown that sulfates are an important component of the Martian surface mineralogy. Along the 11 km traverse of the rover Opportunity in Meridiani Planum, jarosite was detected by the Miniaturised Mössbauer spectrometer [1-3]. The identification of sulfates and in particular jarosite provides strong mineralogical evidence that water once flowed through these rocks. The European “ExoMars” rover, which is scheduled for launch in 2013, will carry both a Moessbauer spectrometer and a Raman-LIBS spectrometer. The combination of these techniques will provide definite mineralogical and chemical identification of a great number of surface minerals and in particular of sulfates on Mars. Identification of sulfates with Raman and Moessbauer spectroscopy using samples from potential Martian analogues is an important step in the development of the techniques and the methodology for the mission. In this case two important potential Martian analogues situated in Spain were studied, Rio Tinto and Jaroso Ravine.

General description of the sites and samples:

The Río Tinto is situated in the SW part of Spain. This river drains pyrite mines situated in the Iberian Pyrite belt which have been in operation since the Bronze Age and probably constitutes the oldest continuously operating mining activity in the world. An important characteristic of the river is its near constant acidic pH (about 2.3) along its 100 km long course. Rio Tinto is considered a modern model of formation of sulfates, linked to significant acidophilic biogenic activity. Sulfates mainly come from aqueous alteration of iron-rich sulfide minerals of the Iberian Pyrite Belt [4]. 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 [5].

Evaporate samples from Rio Tinto were collected from the surface close to the river source at different periods of the year between 2005 and 2006 (Fig-1). Samples from Jaroso were also collected at the surface, in this case, paying special attention to Jarosite.



Figure 1: Rio Tinto at the source near Peña del Hierro and precipitates observed at the surface.

Raman spectroscopy was performed in the laboratory on the samples without any preparation using a portable Raman spectrometer from Kaiser Optical System. This spectrometer is coupled to a Raman probe head through optical fibers. Excitation was performed by a He-Ne laser at 633nm and a NeYAG doubled laser at 532nm. Spot diameters ranged between 20 and 50 μm and irradiance on the sample was kept below the threshold of thermal damage. The optical configurations as well as the working distance to sample, spot diameter and power on the sample were very close to those designed for the Raman-LIBS ExoMars instrument.

Mössbauer (MB) spectroscopy was performed on the natural surface of the samples without sample preparation with a MER-equivalent instrument. The spot diameter for MB measurements is 15 mm.

Raman Results: Samples from Jaroso selected at different locations in the ravine were identified in all the cases as pure Jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) (Fig 2). Identification of the cation nature from Raman spectra is quite difficult in this case. Nevertheless shifts on the low wavenumber region suggest the minerals were natro-jarosite. This result was confirmed by using LIBS and EDX techniques. Samples from Rio Tinto were also fully identified (Fig. 3-4). In many cases, even at the scale of the Raman spot they showed a mixture composition of sulfates or oxides (goethite,

hematite) and sulfates. Copiapite ($\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{SO}_4)(\text{OH})_2 \cdot 20\text{H}_2\text{O}$) was the most abundant mineral followed by coquimbite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$). Jarosite was scarcely found. In the sequence Melanterite, Rozenite, Szomolnoquite [6], only the 7th and 4th hydrated forms were clearly identified (Fig.5). Mg and Ca sulfates as kieserite and gypsum respectively were also identified.

Mössbauer results: Mössbauer spectra were obtained on the same samples investigated by Raman spectroscopy. For all doublet phases from Mössbauer spectra, values for quadrupole splitting (QS) were plotted against isomer shift (IS) (Figure 5). The sulfate minerals copiapite, rozenite and jarosite were identified. The parameters are in agreement with those reported in [7]. Some spectra contained additional sextet phases corresponding to the oxide minerals hematite and goethite. Fig. 6 shows an example Mössbauer spectrum.

Conclusions: In general, results obtained from Raman and Mössbauer spectra are in agreement. Differences may result from the different diameters of the field of view of both instruments, leading to measurements of different portions of the samples.

References: [1] Klingelhöfer et al., Science 306 (2004) 1740-1745, [2] Morris et al 2006 b, [3] Squyres et al Opportunity. [4] D.Fernandez-Remolar et al. (2004) Planet. Space. Sci. 52, 239. [5] J. Martinez Frias et al. Earth Planets Space (2004) 56, v-viii). [6] C.H. Chio et al. 2007, J. Raman Spectroscopy 38, 87. [7] D. Fernandez-Remolar et al. (2005) *EPSL* 240, 149-167.

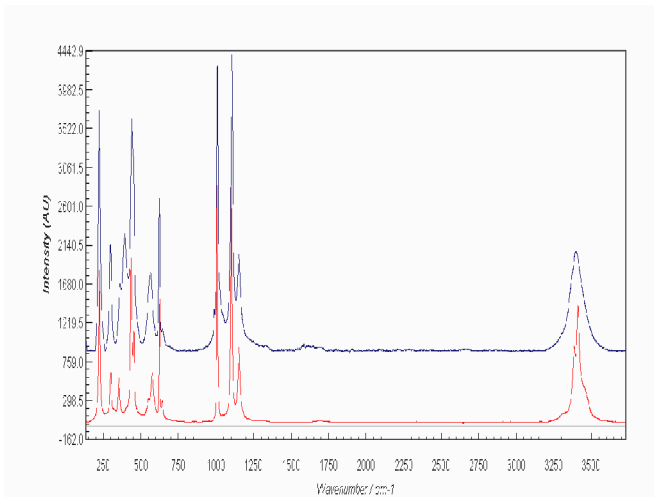


Figure 2 Raman spectra of Jarosite from the world type locality Jaroso Ravine (Spain) (upper spectrum). The spectrum from a small single crystal found in the same area is also displayed (bottom).

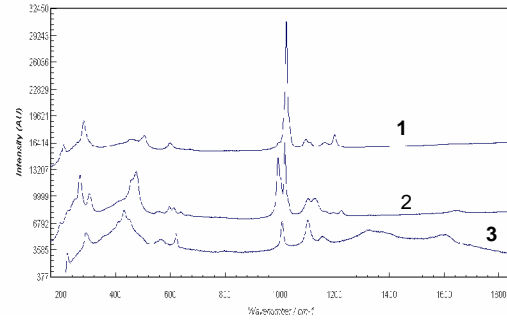


Figure 3 Raman spectra from Rio Tinto samples. 1-Coquimbite; 2-Copiapite; 3-Jarosite

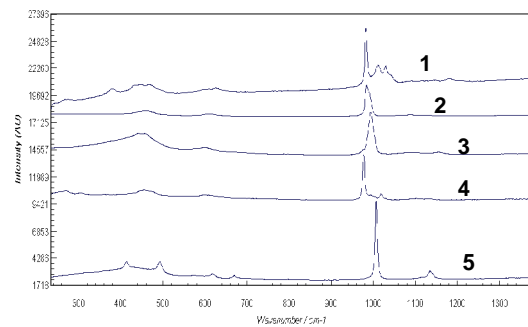


Figure.4 Raman spectra from Rio Tinto samples. 1-Kieserite and possible Rhomboclase. 2-Kieserite and Rozenite. 3-Rozenite. 4-Melanterite. 5-Gypsum

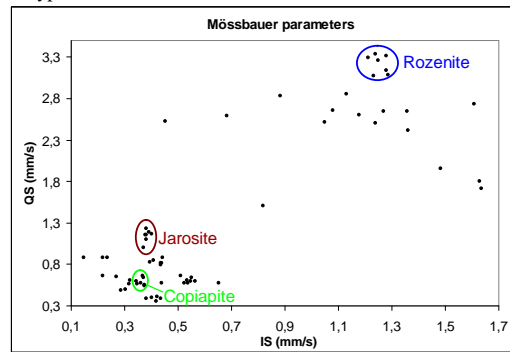


Figure 5: Mössbauer isomer shift (IS) vs. quadrupole splitting (QS) obtained on sulfate samples.

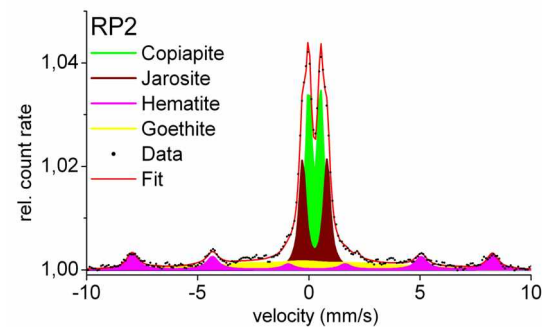


Figure 6: Mössbauer spectrum obtained on sample RP2, showing the minerals copiapite, jarosite, hematite and goethite.