

RAMAN AND XRD FIELD CHARACTERISATION OF SULFATE EFFLORESCENCES AT RIO TINTO (SPAIN) F. Rull¹, A. Sansano¹, P. Sobron¹, B. Lafuente¹, P. Sarrazin², M. Gailhanou³, D. Blake⁴, ¹Unidad Asociada UVA-CSIC, al Centro de Astrobiología, Universidad de Valladolid, 47006-Valladolid, SPAIN 2inXitu Inc., 2551 Casey Ave Ste A, Mountain View, CA 94043; ³Universite Paul Cezanne, Faculte des Sc. et Tech. de St Jerome 13397 Marseille, France.. ⁴NASA Ames Research Center, Moffett Field, CA 94035

Introduction: The Río Tinto mining district can be considered as the largest volcanogenic massive sulphide district worldwide and probably one of the oldest in the human history being in continuous operation from the Bronze Age to the XXth. An important characteristic of the Rio Tinto system is derived from the interaction between the river waters and the iron-rich sulphide minerals. This interaction is mediated by a significant acidophilic biogenic activity leading to an acidic aqueous media (pH is about 2.3 along its 100 km long course) from which a large amount of oxides hydroxides and sulphates are precipitate as the mineral products. The occurrence of sulfates on Mars, expected since the Viking Landers found sulphur in the Martian soil in 1976 and detected more precisely with the Miniaturised Mössbauer spectrometer located at the robotic arm of the MER rovers and OMEGA instrument onboard Mars Express proved that these minerals are an important part of the Martian surface mineralogy.

The possible relation between the formation processes of sulphates on Mars and in Rio Tinto has attracted the attention of the scientific community in the last years [1-2]. An important part of these studies is the precise identification of the mineral phases related with the bio-mineralization processes. Raman spectroscopy is a powerful tool for this task [3]. Raman is also a technique included as part of the “Pasteur” instruments payload inside the rover for “ExoMars” mission. This mission now scheduled for launch in 2016 is the first flagship mission the “Aurora” program developed by the European Space Agency (ESA).

In-situ analysis of samples at the Rio Tinto area using micro-Raman spectroscopy is an important step in the development of the Raman operation mode which is part of the instrument development. Nevertheless the use of a complementary technique for mineral identification as XRD can give unique information on the mineral phase identification.

Methodology

Raman spectra were performed in-situ without any sample preparation at different places of the Rio Tinto area from the source to several kms away and at the Peña del Hierro gossan (Fig.1). The Raman spectrometer used was a portable i-Raman from *B&W TEC Inc.* The spectrometer was adapted to work in the field

conditions and the optical head was attached to a mechanical device simulating the rover’s arm to approach the samples. The excitation used was a 532nm wavelength laser with about 15mW power on the sample and a spot diameter of 100µm. Spectral resolution was ~5cm⁻¹. The XRD diffractometer was a Terra field instrument, a commercial spin-off of the MSL CheMin XRD/XRF. It combines a miniature X-ray tube (Co) and a direct detection CCD into transmission geometry to produce XRD and XRF data with no moving parts. The instrument requires sample collection, preparation (crushing to <150um) and delivery into a small sample cell that is vibrated during analysis for improved statistics. Analyses were performed in the field after manual collection and preparation of samples, over integration times of about 20min. (Fig. 2)



Figure 1. Raman optical head taking spectra on the mineral precipitates at the Rio Tinto source



Figure 2. Terra portable XRD/XRF instrument deployed at the same location.

Results

Figure 3 and 4 show the Raman and XRD spectra obtained at the Rio Tinto source on samples 1, 2, and

3. Epsomite, Copiapite and Rozenite sulfates were clearly identified. Figure 5 shows the Raman results obtained at the El Loco “outcrop” (see Figure 6) in which different alteration minerals product of the interaction with the acidic water from the river are observed. Figure 7 shows the XRD results obtained after crushing part of the area observed by Raman.

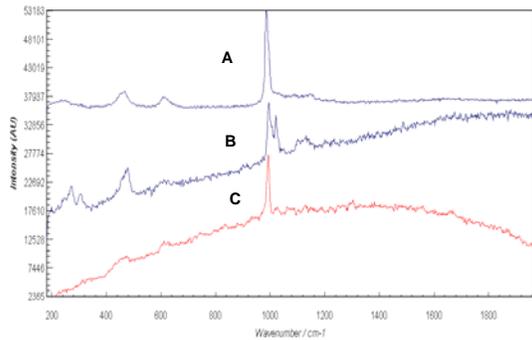


Figure 3. Raman spectra obtained at the source of Rio Tinto on evaporite minerals. A: Epsomite+Hexahydrite; B: Copiapite; C: Rozenite.

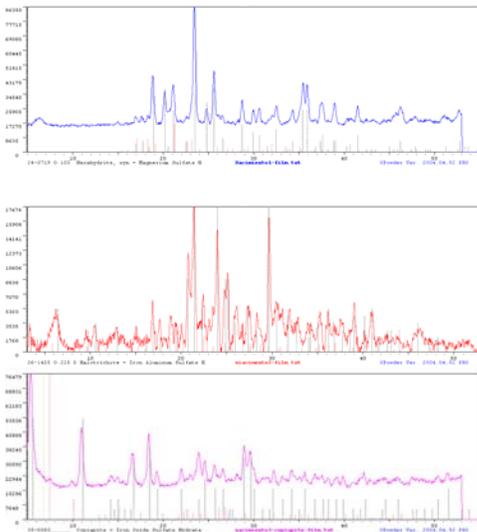


Figure 4: XRD results of sample 1, 2 and 3: Hexahydrite, halotrichite, and copiapite.

These results stress the complementarities and differences between the two techniques working at the field in the same area. Micro-Raman spectroscopy can identify precisely the phases at the selected spots at the mineral grain scale given also their spatial distribution. Some of these phases can be missed by XRD if they are present at low concentrations. On the contrary XRD can give a general picture of the mineralogy of the whole sample, including phases that Raman can not identify if a limited number of spots are used or some of the samples show fluorescence. Therefore the

combination of both can be considered a powerful mineralogical tool for field analysis and planetary surface exploration.

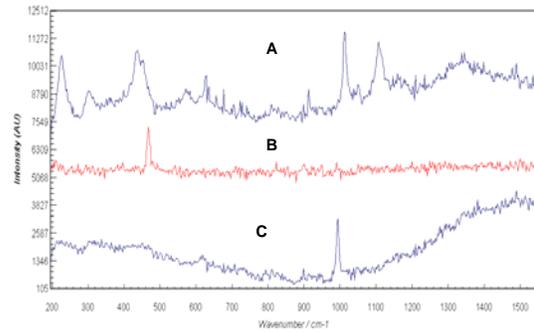


Figure 5. Raman spectra obtained at the “outcrop” El Loco. A: Jarosite with Haematite; B: Quartz; C: Rozenite.

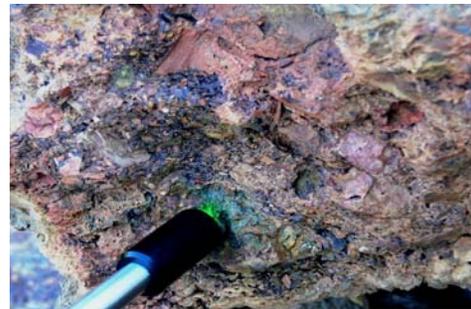


Figure 6. El Loco “outcrop” and the different spots analysed by Raman spectroscopy.

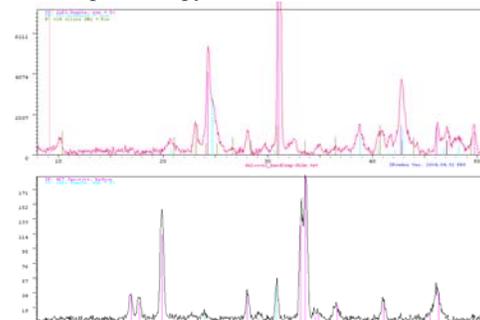


Figure 7: XRD analysis of a bulk sample of El Loco “outcrop” (quartz, goethite, and illite) –top- and of the surface deposit on the riverbed (hydronian jarosite with traces of quartz) –bottom.

References: [1] D.Fernandez-Remolar et al. (2004) Planet. Space. Sci. 52, 239. [2] D. Fernandez-Remolar et al. (2005) *EPSL* 240, 149-167. [3] P. So-bron et al. (2008), *Spectrochim. Acta A*, 71, 1678

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