

RAMAN SPECTROSCOPY, A POWERFUL TOOL FOR THE CHARACTERIZATION OF HYDRATED SULFATES AND ACIDIC WATER IN RIO TINTO (SPAIN) P. Sobron, A. Sansano, A. Sanz, T. Acosta, B. Lafuente, F. Rull, F. Sobron, J. Medina, Unidad Asociada Universidad de Valladolid-CSIC a través del Centro de Astrobiología. Paso Prado de Magdalena s/n. 47011 Valladolid, Spain (psobron@iq.uva.es)

Introduction: The discovery of ferric hydroxides/oxyhydroxides, jarosites (iron-bearing sulfates thought to have formed via aqueous activity) and other sulfate-bearing minerals in the Meridiani region provides strong evidence that liquid water once flowed on the Martian surface [1-4]. It is suggested that sulfate deposits enriched in iron and mixed iron oxyhydroxide were precipitated from meltwaters, thought to have been acidic yet hydrothermalism and volcanism could have played a role shaping the Meridiani surface conditions as well. Terrestrial acidic and sulfate-rich sites such as Rio Tinto and El Jaroso in Spain, Iron Mountain in California, and some lakes in Western Australia are exceptional sites for the study of acidic waters, its associated precipitates and efflorescent salts, and sulfate-forming processes in general. The characterization of the hydrogeochemistry of these sites is crucial in order to describe all of the different processes and settings of iron and sulfate deposition on Earth. As these localities host mineralogical signals detected on Meridiani, the comparison may help to understand how the Meridiani minerals formed.

Raman spectroscopy is regarded as a powerful characterization technique for the sulfate systems due to its intrinsic features: it requires little or no sample preparation prior to spectra collection, and allows real-time identification of species in acidic waters and associated precipitates and very rapid quantification of their abundance, among others. Furthermore, recent advances in optics, lasers and detector systems allow for the development of compact field Raman instruments for in-situ analyses. This fact, together with the capabilities of the Raman spectroscopy for the unambiguous characterization of mineral phases and potential biosignatures, make the Raman technique an outstanding tool for the exploration of sulfate-rich areas, and most likely for the Martian surface and subsurface. A landmark for the technique is the selection of a contact combined Raman-LIBS spectrometer as a fundamental instrument within the upcoming European Space Agency (ESA) ExoMars mission (2016).

In this work we report the Raman spectroscopy of some aqueous solutions and associated precipitates (found in coexistence in most cases) of Rio Tinto (SW Spain). Spectral fingerprints from various forms of iron sulfates have been found in the minerals and as such are used for their identification. The relative abundances of sulfate and bisulfate ions and water have

been derived from the Raman spectra of stream waters. The *in-situ* Raman spectroscopy of the acidic stream waters and related mineralogy is also reported.

Experimental:

Samples:

Efflorescent salts from acidic surface stream waters were collected from several sampling spots near the site considered as the source of the river, Peña de Hierro (Spanish for iron mountain). Water samples display yellowish-to-reddish colors whereas solid samples show white, yellow, orange and dark red colors as shown in Fig. 1.

Raman instrumentation:

Raman spectra of the aqueous samples were collected in the laboratory at a constant temperature of 20 °C with a con-focal Raman microscope (WiTec alpha300 R) in the spectral range 75-3900 cm^{-1} . The spectral resolution was 1 cm^{-1} . The 532.4 nm line of a frequency doubled Nd:YAG laser was used as excitation source. Solid samples were placed on a 3D-motion stage of a Nikon Eclipse microscope, equipped with 5 \times , 20 \times and 50 \times objective lenses. The microscope is connected to a Kaiser HoloSpec f/1.8i spectrograph. A CCD attached to the spectrograph was used to collect the Raman spectra. The 632.8 nm line from a He-Ne laser was used excitation source. The spectra were recorded within the region 200-3800 cm^{-1} with a spectral resolution of 4 cm^{-1} . In the field, Raman spectra were recorded, without any sample preparation, using a field portable B&W Tek *i*-Raman spectrometer equipped with a laser at 532 nm.

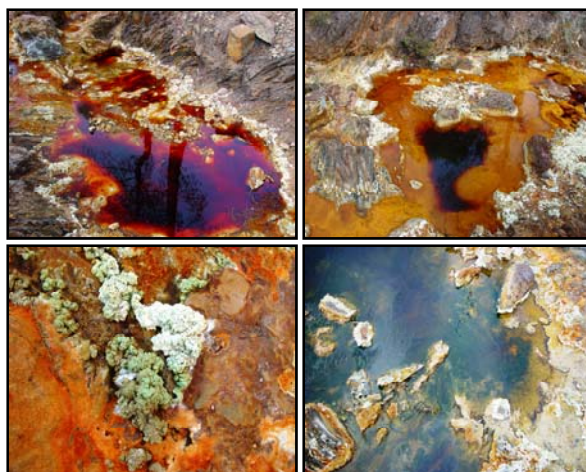


Fig. 1

Results: The laboratory Raman spectra of both water and solid samples are plotted in Fig. 2. Variable amounts of sulfate and bisulfate are found in the aqueous samples, suggesting changes in the acidity of the solutions. The sulfate/water relative abundance has been estimated from the derived relative intensities of the associated bands: 982, 1044 and 1640 cm^{-1} for sulfate, bisulfate and water, respectively (Table 1). Solid samples are identified as gypsum and as mixtures of hydrated iron(II)/iron(III) oxides belonging to the copiapite-group and jarosite-group.

Fig. 3 shows some of the Raman spectra collected at the Rio Tinto source (solid lines). The spectra have been offset for clarity and some spectra from reference materials have been overlaid for comparison purposes (dashed lines). The spectrum RTNcs01, showing two pairs of intense bands at approximately 995/1108 cm^{-1} and 1021/1132 cm^{-1} , is consistent with the presence of copiapite in the sample. The spectra RTNcs02 and 03 do not show the two pairs. It is well known that the ν_1 symmetric stretching band of sulphate ion (around 982 cm^{-1}) in ferrous iron shifts with hydration state of the salt. The presence of three and two bands in the spectra RTNcs02 and 03 in the 970-1020 cm^{-1} region, respectively, may be indicative of a mixture of hydrated iron(II) sulfates, likely following a sequence of dehydration from the evaporated salt. Whereas spectrum RTNcs02 shows fingerprints of melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) and szomolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$), only the two latter are present in spectrum RTNcs03. The spectrum RTNcs04 shows a single band centered approximately at 983 cm^{-1} . Rather than iron sulfate, the position of this band is more consistent with the presence magnesium sulfate in the sample, most likely epsomite.

Conclusion: Off-site and on-site Raman spectroscopy has been used as a means of characterizing the hydrogeochemistry of Rio Tinto area. Variable amounts of sulfate and bisulfate ions have been measured in the streams waters close to the source of the river. Gypsum and ferrous and ferric sulfates have been detected in the efflorescences. A portable Raman spectrometer has been used for in-situ analysis of Rio Tinto stream waters and mineralogy thus justify the importance of Raman spectroscopy as a potential tool for the characterization of Rio Tinto hydrogeochemistry and hence of any environment relevant for planetary exploration.

References: [1] Klingelhöfer et al. (2004) *Science*, 306, 1740. [2] Clark et al. (2005) *Earth Planet. Sci. Lett.*, 240, 73. [3] Rieder R et al. (2004) *Science*, 306, 1746. [4] Lane et al. (2004) *Geophys. Res. Lett.*, 31, L19702, doi:10.1029/2004GL021231

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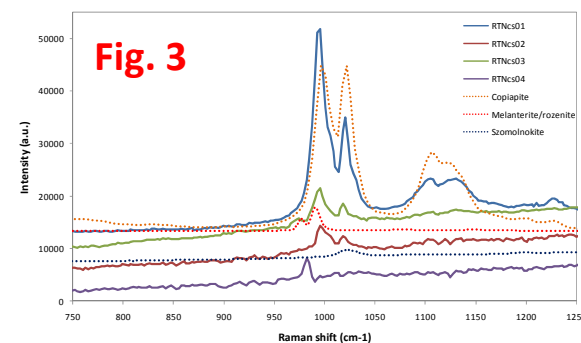
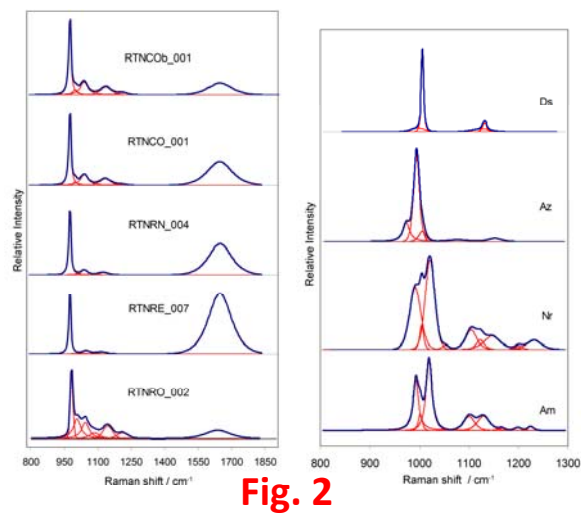


Table 1

Sample	Band relative intensity		
	982 cm^{-1}	1044 cm^{-1}	1640 cm^{-1}
RTNCOB	6.25	1.13	1.00
RTNCO	2.94	0.44	1.00
RTNRI	2.04	0.16	1.00
RTNRE	0.97	0.05	1.00
RTNRO	11.11	3	1.00