

RAMAN ANALYSIS OF SULFATE SEQUENCE OF PRECIPITATION FROM IRON-RICH WATERS OF RIO TINTO RIVER. A. Sansano¹, P. Sobron¹, B. Lafuente¹, J. Medina¹ and F. Rull¹, ¹Unidad Asociada Universidad de Valladolid-CSIC a través del Centro de Astrobiología. Valladolid. SPAIN. (asansanoc@gmail.com).

Introduction: Rio Tinto area is considered a referent as an extremophilic scenery of iron rich and acidic water conditions for life [1]. Physic-chemical equilibriums taking place along of its watercourse during a year produce a repertory of mineral species related with the main chemical species in solution (sulphates and iron). Raman spectroscopy is a powerful technique that allows studying these species with great accuracy and without any perturbation [2]. A detailed investigation of the process of precipitation needs both the in-situ analysis of natural samples at the field [3] and experimental simulation at the laboratory. This last subject is considered of great importance to monitor the different mineral species produced by a definite chemical composition of the acidic aqueous solutions and their sequence of precipitation.

Raman spectroscopy is regarded as a powerful characterization technique for the characterization of 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 [3]. 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 make the Raman technique an outstanding tool for the exploration of sulfate-rich areas. A compact Raman/LIBS instrument is regarded as the highest priority instrument for mineral analysis within the ExoMars mission roadmap.

Raman study in-situ: Raman spectra were collected on-site without simple preparation using a field portable B&W Tek i-Raman spectrometer equipped with a laser at 532 nm (Figure 1).

Figure 2 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 sulfate

(around 982 cm⁻¹) in ferrous iron shifts with hydration state of the salt.



Figure 1: Raman probe working in-situ on a mineral efflorescence.

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 (FeSO₄•7H₂O), rozenite (FeSO₄•4H₂O) and szomolnokite (FeSO₄•H₂O), 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.

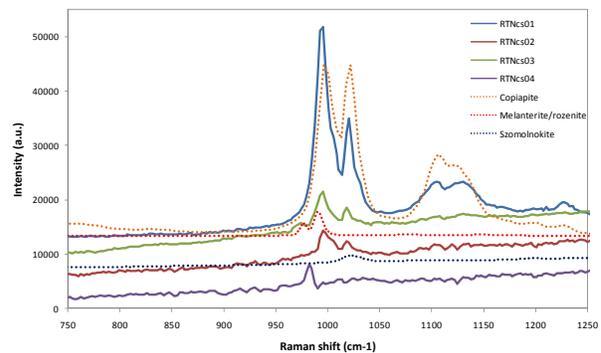


Figure 2: Raman in-situ spectra of the samples on Rio Tinto source.

Laboratory simulation of evaporative processes in Rio Tinto: We have developed a series of containers that mimic the geometrical and thermal constrains

of some of the ponds and springs more frequently found in the Rio Tinto area. The system geometrical, like river banks as well as the temperature and evaporation rate provides controlled environment were sequential evaporation-deposition can be investigated in detail. The aim of this work is to characterize the products from the evaporation of the acidic water from Rio Tinto (pH ~2) and the establishment of detailed precipitation models (sequences) for each of the mineral phases found. Such models are really a definition of the range of environmental stability for each mineral, i.e., a classification of the minerals as a function of their precipitation order, or increasing solubility in a given aqueous system. (Figure 3).



Figure 3: View of the evaporitic results of the simulation system.

After 40 days of evaporation under constant temperature and humidity we obtained a series of mineral species related with those obtained in-situ at the field site (Figure 2). We have identified copiapite ($\text{Fe}_5(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$) (RT206) together with ferri-copiapite and rozenite (RT406). Also, in a less extent coquimbite ($\text{Fe}_3(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (mixed in RT304) and romerite $\text{Fe}_3(\text{SO}_4)_4 \cdot 14(\text{H}_2\text{O})$ (RT407).

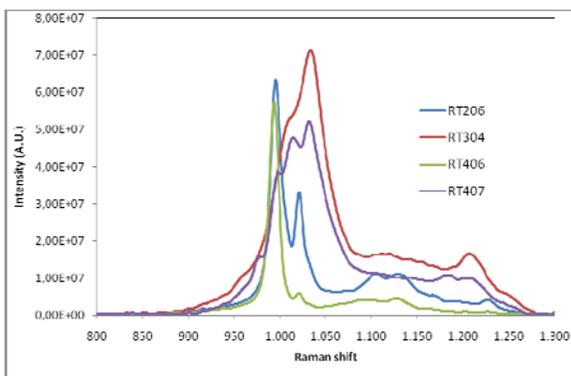


Figure 4. Samples of the species found in the simulation system.

Future work and implications to Mars exploration: Raman spectroscopy proves to be a powerful tool for the in-situ analysis of mineral species at the field and in laboratory. The results obtained at the simulation, together system for acidic water evaporation are consistent with the in-situ work, those obtained at the Rio Tinto river banks. The same mineral species are precipitated and their spatial distribution is in some cases also consistent represents a first approach to the evaporitic and precipitation mechanisms that take place in the Rio Tinto Mars analog. Models of the environmental stability of the minerals found both in the laboratory and the field are under development. The reverse application of these evaporation/precipitation models to the current Martian iron sulfate mineral phases might help obtaining a complete picture of the acidic waters that once flooded the planet's surface via describing phase relations in those waters.

References: [1] Amils R., et al. Planetary and Space Science, 2007. Vol. 55, Pag. 370. [2] Edwards H.G.M., et al. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2007 Vol.68 pag. 1133. [3] Sobron P. et al. (2008) Spectrochim. Acta A, 71, 1678.

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