

# Raman study of mineralogical precipitation sequence of Rio Tinto “Mars analog”

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## Abstract

Rio Tinto (Spain) has been proposed as potential Earth analog [1] for the geological and astrobiological exploration of Mars. In this context of Mars exploration, and considering the geomorphological and sedimentological features of the selected landing sites [2], an important point to consider is the ratios of mineralization/alteration due to hydration-dehydration processes.

To carry out this objective a spectroscopic Raman study of a wide range of samples collected from Rio Tinto was performed. On the other hand it has carried out the simulation of the phenomenon of precipitation in the laboratory using small droplets of synthetic and natural water from Rio Tinto.

## 1. Introduction

The occurrence of sulphates has been observed on Mars using orbiter spectrometry and the two MER vehicles on the surface. These results show that sulphates are of prime importance in the geological evolution of Mars.



Figure 1: Red acidic water of Rio Tinto

Rio Tinto “potential Mars analog” is considered a modern model of formation of sulphates (see figure 1). In order to study the precipitation sequence of this zone, we focus in the study of the efflorescences. These efflorescences appear in the banks of Rio

Tinto as consequence of evaporation-precipitation processes.

These minerals belong to Copiapite-group that are based upon the formula  $AFe^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$ , where A:  $Mg^{2+}$ ,  $Cu^{2+}$ ,  $Al_{2/3}^{3+}$  or  $Fe_{2/3}^{3+}$ ; and other sulphates like Rozenite, Coquimbite etc [3].

## 2. Experimental and samples

For the analysis we used a Kaiser Raman spectrometer HoloSpec illuminated with a 632.8 nm laser. Detection was performed with an Andor CCD of 1024x256 pixels and a Raman head probe. This device is a portable model similar to those used in the field that is coupled by fiber optics to a Nikon Eclipse E600 microscope.

A sampling procediment was followed to represent the efflorescences at Rio Tinto. This sampling was carried out in the framework of a scientific campaign in 2007. Also in-situ analysis using simultaneously Raman, IR, XRD, LIBS and Mössbauer techniques was performed [4-6].

The evaporation-precipitation processes were simulated in the laboratory using two systems: macro and micro-scale. These experiments allow establish the precipitation sequences.

**Macro-scale experiments** were carried out in a recipient (evaporation-precipitation simulator) with a surface with slope approaching the river banks and infrared lamps to reproduce the daily changes in temperature and accelerate the evaporation. The introduced samples were irradiated eight hour at the controlling that the temperature was under than 45°C. Efflorescences resulting of this experiment were collected at different position from the recipient and characterized by Raman Spectroscopy.

**Micro-scale experiments** were performed putting several droplets of Rio Tinto's water with a syringe in a glass substrate. These droplets were characterized daily by Raman Spectroscopy.

### 3. Results

From efflorescences collected from Rio Tinto we obtain a high variety of sulphates that comply with the scheme proposed by Fernandez-Remolar [7]. The Raman spectra of this group of sulphates are shown in figure 2.

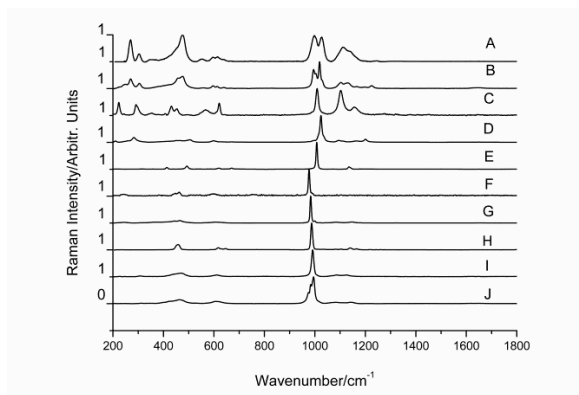


Figure 2: Raman spectra of Copiapite (A), Ferricopiapite (B), Jarosite (C), Coquimbite (D), Gypsum (E), Melanterite (F), Epsomite (G), Baryte (H), Rozenite (I) and Halotrichite (J) obtained from efflorescences of Rio Tinto.

The next table shows the precipitation sequences:

Experiment macro scale	Experiment micro scale
Coquimbite	Ferricopiapite
Ferricopiapite	Coquimbite
Copiapite	Copiapite
Rozenite	Magnesiocopiapite
Szomolnokite	Hematite
Magnesiocopiapite	Rozenite
	Szomolnokite
	Rhombochase
	Metavoltine

Table 1: precipitation sequence derived from experiments carried out in macro and micro scale.

### 4. Conclusions

The analysis carried out in-situ and in the laboratory of samples collected, provides the compositional information but the precipitation sequence cannot be established.

The acidic waters are used for the synthesis of the minerals that we found in the banks of the river. And to determine the order of precipitation procedure analysis in micro and macro scale.

At macro-scale, several minerals co-precipitate at the same time and this fact makes the determination of the sequence difficult. Nevertheless, at micro-scale the mineral formations can be detected when they appear.

The analysis of the droplets is a method very interesting to observe in a fast reliable way the evaporation and precipitation process for aqueous solutions.

### 5. References

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