

RAMAN AND LIBS: A DEFINITIVE COMBINATION FOR THE CHARACTERIZATION OF NATURAL SAMPLES FROM THE RIO TINTO MARS ANALOG. P. Sobron^{1,2}, A. Wang². ¹Unidad Asociada Universidad de Valladolid-Centro de Astrobiología CSIC-INTA. Paseo Prado de la Magdalena s/n. Valladolid-47011, Spain. (psobron@iq.uva.es), ² Dept. Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University, St. Louis, MO, 63130 USA (alianw@levee.wustl.edu).

Rio Tinto: Rio Tinto (SW Spain) environment is a sound example of acid mine drainage (AMD) environments, formed after large amounts of sulfides are exposed to water, air, and often microbes that catalyze the oxidation. As a consequence, waters that currently draining oxidized sulfide deposits and mine-waste sites have particularly high concentrations of dissolved sulfates and metals. Given the association of microorganisms such as *Acidithiobacillus ferrooxidans* with the aqueous oxidation of sulfides in Rio Tinto, the site is accepted by some as a geo/bio/mineralogical setting on our planet which offers comparable scenarios to those on Mars, and where technologies for Martian exploration can be defined and tested. Rio Tinto is being studied as an analog for acidic, sulfur-rich environments on Mars formed by oxidative weathering of metal sulfide ore deposits. However, hydrothermalism and volcanism could have played a role shaping the Meridiani (a region that host mineralogical signals comparable to those of Rio Tinto) surface conditions. As the Rio Tinto lithological setting has not been observed on Mars, the definition of Rio Tinto as a terrestrial Martian analog in terms of mineral paragenesis must be regarded with caution.

In this work, we use both Raman and LIBS techniques in contact mode to investigate several natural samples collected from Rio Tinto. The studied samples were visually identified in the field as sulfate-rich evaporation products from acidic stream waters (pH = 2.4) and collected within a 10 m radius from the GPS location 37°43.492N, 6°33.611W, in the Barranco del Loco

Raman, LIBS, and planetary exploration: The laser Raman and laser-induced breakdown spectroscopy (LIBS) techniques have been, and to certain extent still are, considered as laboratory techniques. Nevertheless, in recent years many Raman and LIBS systems have been specifically designed for field use and for planetary exploration, either in contact or remote deployments. In this context, the Raman/LIBS combined contact instrument has been ranked as a “Fundamental Instrument” for the ESA ExoMars mission. The LIBS technique has been successfully applied to remote sensing of distant targets [1], and a stand-off LIBS instrument (ChemCam) is included in the science payload of NASA’s Mars Science Laboratory.

Raman spectroscopy is based on the inelastic scattering of light. A small fraction of the incident photons

(10^{-6} to 10^{-9}) is wavelength-shifted in Raman scattering. The shift in wavelength depends on the chemical bonding responsible for the scattering. In other words, Raman photons exhibit distinct wavelengths for particular molecular species and its structure. Therefore, mineral composition and structure can be discerned from its figureprint Raman spectra.

LIBS spectroscopy can be produced from a variety of lasers but typically excimers or pulsed Nd:YAG lasers are used. The high intensity laser pulse interacting with the sample produces a plasma plume that evolves with time from the point impacted by incident laser pulse. The emission from the atoms and ions in the plasma is collected by a lens or fiber optics and analyzed by a spectrograph and a gated detector. The atomic spectral lines can be used to determine the composition and the elemental concentrations in the sample.

Both Raman and LIBS techniques are potential tools for detailed mineralogy and geochemistry investigation on planetary bodies including Mars, the Moon [2] and Venus [3] with landed missions. In addition to working in contact mode, stand-off Raman and LIBS instruments can conduct rapid analyses of targets at distances ranging 7 to 10 meters (current constrains for landing missions) identifying potential samples to be examined in further detail.

Advantage of Raman+LIBS in the investigation of sulfates: The fundamental stretching vibration modes of hydrous sulfates show a systematic Raman peak-position shift toward lower wavenumber when the hydration state increases [4]. Those Raman peak positions are affected by the mass and the ionic radius of the substitution cations in sulfates [5], e.g. jarosites (Na, K, Pb, Ag, NH₄ ...). These peak shifts are often minimal, and hence make their detection difficult when using low-resolution spectrometers (which would be the case for flight-like systems). On the other hand, LIBS can reveal the relative concentration of major (and sometimes trace) elements present in the sample. Thus, the use of LIBS together with Raman on the same sample will allow for a definitive mineral phase identification and precise chemical and elemental concentrations of sulfates. From the point of view of rover mission operation, a tactical operational advantage would be brought by a combined Raman-LIBS investigation: a rapid min/chem. evaluation of the target. A rapid Raman-LIBS evaluation will be extremely useful

for selecting samples to be eventually collected for sample return purposes or sample site to be drilled in the search for other species (e.g. organics).

Raman+LIBS study of Rio Tinto sulfates: The Raman spectra of a few samples from Rio Tinto are shown in Fig. 1. It is clear from a simple inspection that the spectrum contains signatures of sulfate groups along with structural water. The presence of multiple bands around 1000 cm^{-1} indicates that different sulfates are present. According to the positions of the symmetric and asymmetric stretching bands of sulfate (e.g. [4-6]), the samples can be identified as gypsum (loco3f), jarosite (loco6e) and copiapite (loco2a). However, the substitution cation in the jarosite might be either K, Na, Pb, NH_4 , and the copiapite could be ferricopiapite, Al-copiapite, Mg-copiapite, Cu-copiapite, etc, or a mixture of them, and the origin of the broad shoulder around 1034 cm^{-1} in the loco3f spectrum is unknown. Only by knowing more details in the elementary composition of these samples, their exact mineralogy and geochemistry nature can be determined.

Fig. 2 displays the LIBS spectra of these samples in different regions of interest. S is present in all the samples (lines at 543.3, 545.4, 547.4 and 551.0 nm, not shown). As expected, the loco3f shows lines characteristic of Ca, but Mg, Na and Fe lines are also found. Most likely the sample loco3 is mainly composed by gypsum with trace amounts Mg, Na, Fe sulfates which give rise to the broad Raman peak shoulder. Only N and Na lines are clearly observed in the loco6e LIBS spectrum, thus sample loco6 is identified as a mixture ammonio/natro-jarosite. Finally, strong Al and Mg lines arose in the loco2a spectrum, most likely from the coexistence of aluminum and magnesio-copiapites.

Conclusion: The Raman and LIBS techniques, when used independently, on natural samples are sometimes not enough for a complete characterization of compounds, but a combination of both provides the whole picture: molecular and structural information from Raman plus elemental composition and abundance from LIBS. Samples from a Mars sulfate analog site, Rio Tinto, have been fully characterized, and relative elemental concentration will be extracted.

We are currently building a new laboratory that will allow us to conduct a set of combined Raman/LIBS/MIR/NIR measurements on sulfates and other relevant minerals under simulated Mars environmental conditions in the context of the ExoMars mission. We are investigating the synergy to extract and combine the spectroscopy information for the characterization of planetary surface materials for Mars, and for the Moon and Venus.

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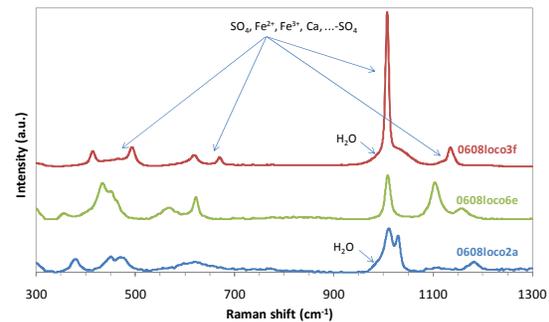


Fig. 1. Raman spectra of Rio Tinto samples

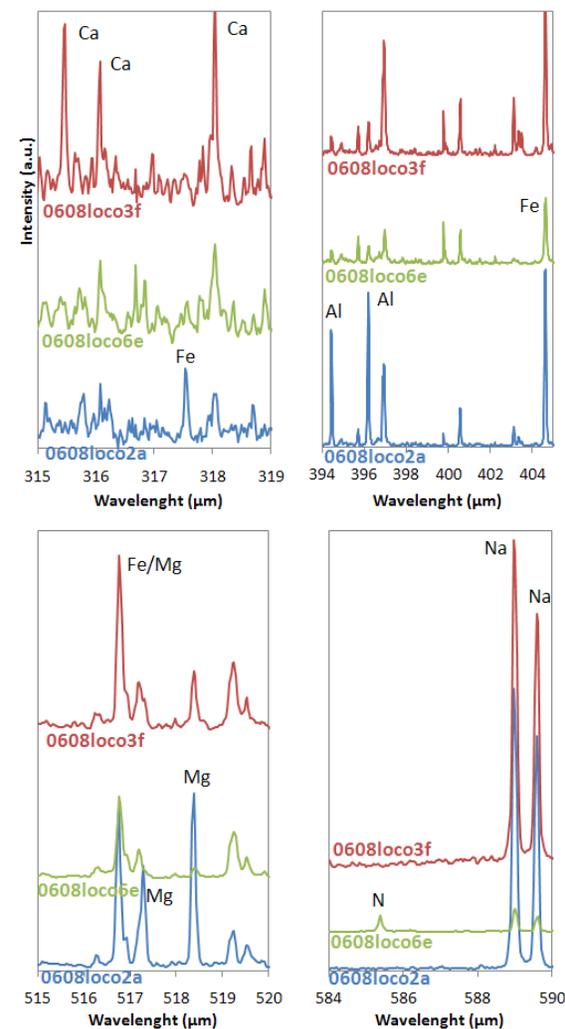


Fig. 2. LIBS spectra of Rio Tinto samples