LIBS/RAMAN INVESTIGATION OF MARS-RELATED SULFATES FROM IRON MOUNTAIN, CALIFORNIA.

P. Sobron[1] C. N. Alpers[2] and A. Wang[1]. [1]Dept. Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University, St. Louis, MO 63130. (psobron@levee.wustl.edu, alianw@levee.wustl.edu), [2]U.S. Geological Survey, Placer Hall, 6000 J Street, Sacramento, CA 95819.

Introduction: Some studies suggest that the sulfates on Mars are produced via aqueous oxidation of sulfides [1] that are known to be present there from analyses of Martian meteorites [2]. Before we target specific locations on Mars in the search for more information on Mars' hydrous past and even on the possibility for extant or extinct life, it is imperative that we characterize and understand analogous settings on Earth. We are currently investigating a terrestrial site that provides examples of sulfate deposits related to those observed on Mars. Iron Mountain, CA, contains hydrated iron sulfate minerals in unusually acidic waters formed via drainage from sulfide mining (pH as low as -3.6, combined metal concentrations as high as 200 g/L, and sulfate concentrations as high as 760 g/L). This extreme environment hosts mineral phases such as rhomboclase, copiapite group minerals, and jarosite group minerals [3], which have been already identified on Mars [4]. The site could therefore serve as an analog for sulfate formation on Mars.

As part of a comprehensive study of Iron Mountain minerals and mine waters using diverse techniques, we report here a combined LIBS (laser-induced breakdown spectroscopy) and Raman characterization of a set of mineral precipitates that were collected in a series of USGS campaigns (1990–92, 1998). These two spectroscopic techniques are particularly suited for this task, and have proven to be complementary for the analysis of the mineralogy of terrestrial sulfate samples [5]. On the other hand, these two techniques will be providing key information for the identification of minerals on the Martian surface and subsurface. A Raman contact instrument is slated for the upcoming ESA's ExoMars (2018) mission and a stand-off LIBS instrument (ChemCam) is included in the science payload of NASA's Mars Science Laboratory (2011).

Instrumental techniques: 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, i.e., Raman photons exhibit distinct wavelengths for a particular molecular species and its structure. Therefore, a mineral's composition and structure can be discerned from its fingerprint 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 the 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 equipped with a gated detector. The atomic spectral lines can be used to determine composition and elemental concentration.

Both Raman and LIBS techniques are potential tools for detailed mineralogy and geochemistry investigation on planetary bodies including Mars [6], the Moon [7], and Venus [8] 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 from 7 to 10 meters (current constrains for practical landing missions) identifying potential samples to be examined in further detail.

The advantages of combining both techniques for the analysis of a given sample are evident: LIBS can reveal the relative concentration of major (and often trace) elements present in a bulk sample, whereas Raman yields information on the individual mineral species and their chemical and structural nature. Thus the data from both allow a definitive mineral phase identification with precise chemical characterization of all major, minor, and some trace mineral species. In the context of a planetary surface exploration, the combined investigation may provide a rapid mineralogical/chemical evaluation of the target that will be very useful for selecting samples to be eventually collected for sample return purposes or sample sites to be drilled in the search for other species (e.g., organics).

Tools for spectral processing: We have developed a Raman and LIBS signal processing package (RLSPP) to perform automated, rapid, and in-depth processing of both Raman and LIBS spectra that aims to eliminate, insofar as possible, the noise (i.e., to improve the signal-to-noise ratio (SNR)), remove the baseline (background signals) from the spectra, and to identify the molecular and elemental species present in the analyzed sample spots. In the case of LIBS spectra, the RLSPP is also able to derive the elemental concentration of the sample, thus providing very valuable information that, when examined together with the Raman information, allows an unambiguous classification of the rock type(s), including the minerals phases present.

Because of the different nature of the Raman and LIBS phenomena, their spectra must be processed accordingly. Raman spectra are processed through: (1) a set of automated Fourier-analysis-based band-fitting routines in order to remove noise and baseline; (2)

Fourier self-deconvolution and band-fitting routines to retrieve relevant band parameters; and (3) mineral search-match algorithms for identification of spectral fingerprints from a mineral database. Unlike Raman spectra, LIBS spectra are noise-corrected using a moving average criterion, whereas the baseline is constructed by spline interpolation. As with the Raman spectra, Fourier self-deconvolution and band-fitting routines allow retrieval of critical band parameters from the LIBS spectra, and element line search-match algorithms are used to identify the elements present and to quantify their relative concentration. The area of an atomic emission line that is assigned to a particular element is a parameter of paramount importance that is used to estimate the concentration (atomic fraction) of that element in the sample. This is done in the RLSPP by using a calibration function for each of the relevant elements derived from a series of independent measurements on certified reference samples.

Example of application: a sulfate sample from Iron Mountain: Figure 1 shows the Raman spectrum of a mineral precipitate exhibiting black/dark blue prismatic crystals. Three sets of bands centered around 250, 450 and 600 cm^{-1} can be oberserved. The latter two arise from the ν_2 and ν_4 vibrational modes of the sulfate tetrahedral oxyanions, respectively. The fact that multiple bands are observed in the ν_2 and ν_4 region indicates symmetry breakdown of sulfate tetrahedra, probably related to the presence of different cations in the structure. The two sets of bands between 978 and 1076 cm^{-1} and between 1100 and 1250 cm^{-1} in Fig. 1 are assigned to the ν_1 and ν_3 sulfate modes, respectively. The observation of multiple bands in the ν_1 and ν_3 sulfate vibration region confirms the previous suggestion of the presence of different cations associated with sulfate groups. The difficulty of performing accurate band analysis of closely overlapped bands is exemplified by this spectrum. In addition, the band positions are affected by the mass and ionic radius of the substituting cations. The Raman analysis tells us only that the analyzed spot contains a hydrated (from the high wavenumber region) polycationic sulfate.

On the other hand, Fe, K, Al, Mg, Zn, and O, among other elements, were identified by comparing the LIBS spectrum of the sample (Fig. 2) with an atomic emission reference database. The presence and relative abundance of these elements derived by the RLSPP, in combination with the Raman information, allow us to classify the sample as voltaite, $K_2(Fe^{2+}, Mg, Zn)_5(Fe^{3+},Al)_4(SO_4)_{12} \cdot 18H_2O$.

Summary: The LIBS and Raman methodology here presented for the investigation of natural sulfates prove that the combination of both techniques allows for definitive mineral phase identification and precise calculation of chemical and elemental concentrations.

References: [1] Squyres S.W. and A.H. Knoll, 2005 EPSL, 240, 1. [2] Greenwood J.P. et al., 2000, EPSL, 184, 23. [3] Alpers C.N. et al., 2008, GCA, 72, 12, S1, A17. [4] Klingelhöfer G.R. et al., 2004, Science, 306, 1740. [5] Sobron P. et al., 2009, LPSC XL, abs#2400. [6] Thompson, J.R. et al., 2006, JGR, 111, E05006 [7] Wang A. et al., 2007, LEAG, abs#3055. [8] Wang A., 2008, Venus Workshop, abs#2003.
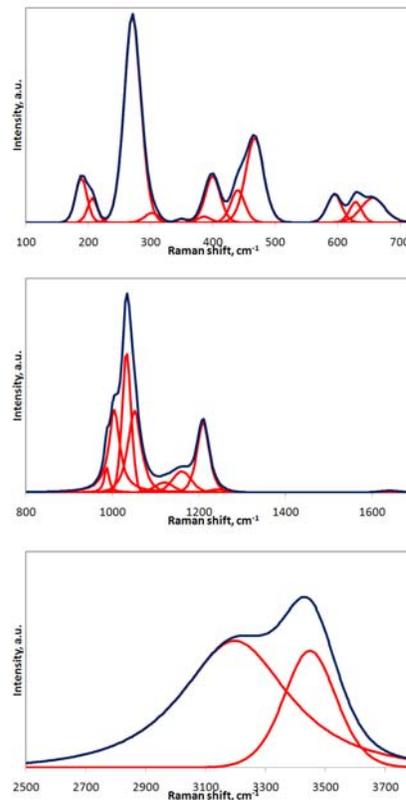

Figure 1 (top): Raman spectrum (3 regions) of an Iron Mountain sample with self-resolved and fitted bands.

Figure 2 (bottom): LIBS spectrum with automatic element identification