

IDENTIFICATION OF HYDRATED SULFATES COLLECTED IN THE NORTHERN RIO TINTO VALLEY BY REFLECTANCE AND RAMAN SPECTROSCOPY. S. M. Chemtob¹, R. E. Arvidson¹, D. C. Fernández-Remolar², R. Amils², R.V. Morris³, D. W. Ming³, O. Prieto-Ballesteros², J. F. Mustard⁴, L. Hutchison⁴, T. C. Stein¹, C. E. Donovan¹, G. M. Fairchild¹, L. R. Friedlander¹, N. M. Karas¹, M. N. Klasen¹, M. P. Mendenhall¹, E. M. Robinson¹, S. E. Steinhardt¹, and L. R. Weber¹. ¹Dept. of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130, ²Centro de Astrobiología, Torrejón de Ardoz, Spain, ³NASA Johnson Space Center, Houston, TX 77058, ⁴Dept. of Geological Sciences, Brown University, Providence, RI 02912

Introduction: OMEGA recently identified spectral signatures of kieserite, gypsum, and other polyhydrated sulfates at multiple locations on the surface of Mars [1,2]. The presence of sulfates was confirmed through *in situ* spectroscopy by MER Opportunity [3]. An approach to validate these interpretations is to collect corresponding spectral data from sulfate-rich terrestrial analog sites. The northern Rio Tinto Valley near Nerva, Spain, is a good Martian analog locale because it features extensive seasonal sulfate mineralization driven by highly acidic waters [4]. We report on mineralogical compositions identified by field VNIR spectroscopy and laboratory Raman spectroscopy.



Figure 1. The MWG grid site. Distance to bridge is about 20 m.

Methods: Our team visited multiple sites in the Rio Tinto Valley in the province of Andalucía, including sites named Anabel's Garden (ABG) and Mrs. White's Garden (MWG), in Feb. and Sept. 2005. Both sites featured extensive sulfate mineralization grading away from the center of the river. Approximately 330 VNIR (0.4 – 2.5 μm) spectra, representing both endmember phases and transects, and accompanying color images were acquired using a portable spectrometer. At the MWG site, spectra were collected at 2 m intervals across a 20 x 10 m grid to capture phase variation with increasing distance from the river (Fig. 1). Approximately 70 spectra from 2-20 μm were also collected in the field using a FTIR spectrometer. Results from the FTIR data will be reported

separately. In addition, solid and liquid samples were collected from ABG and MWG and analyzed in the lab by laser Raman spectroscopy.

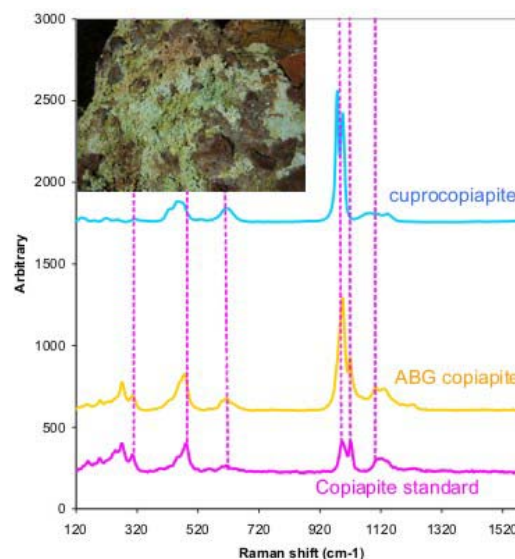


Figure 2. Raman spectra of copiapite and corresponding image of sample. Note the peak shift in the cuprocopiapite spectrum and the blue color of the popcorn-like deposits.

Results: As determined by analysis of VNIR and Raman spectra, the most ubiquitous phases present at both ABG and MWG are copiapite-group minerals ($\text{AFe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$, where $\text{A} = \text{Mg}^{2+}, \text{Fe}^{2+}, \text{Cu}^{2+}, \text{Al}_{2/3}^{3+}, \text{or } \text{Fe}_{2/3}^{3+}$). Copiapite-group minerals precipitated most commonly at ABG and MWG with a popcorn texture and a yellow color, but was observed to have bluish and greenish crystals as well (Fig. 2). The yellow copiapite crystals match our Raman standard exactly. Blue copiapite crystals have the same spectral form, but the primary doublet at 998 and 1018 cm^{-1} is offset to 978 and 997 cm^{-1} . This offset, combined with the color, suggests the presence of cuprocopiapite, in which copper replaces the ferrous iron (Fig. 2). Cuprocopiapite was found at MWG close to a tailings pile from early 20th century mining, indicating anthropogenic contamination.

ABG exhibited a much greater abundance of gypsum relative to MWG. The gypsum crystals are bladed with good crystal habit and commonly precipitate in association with a red-brown crust. Raman spectra of samples match exactly our Raman gypsum standard (Fig. 3). VNIR spectra match the gypsum standard, but additional absorptions at 0.43 and 0.50 μm correspond to jarosite and schwertmannite the likely mineralogical composition of the underlying crust. In addition to forming efflorescent crusts, gypsum forms the sand that fills the center of the river, indicating that gypsum is insoluble in this system. Copiapite-group minerals dominate >1 m away from the center of the river.

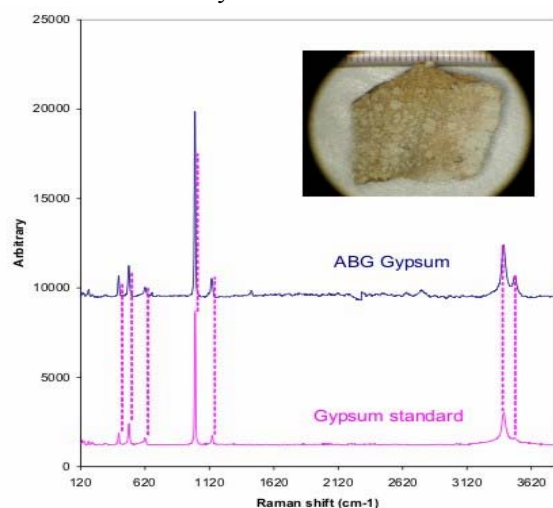


Figure 3. Raman spectra of gypsum and corresponding image.

The presence of jarosite at both MWG and ABG has been confirmed by Raman spectra. The spectra do not match the K-jarosite standard exactly, but have the same spectral form (Fig. 4). Hydronium jarosite has been previously identified at ABG via XRD and Moessbauer spectroscopy [5]. VNIR spectra show positive identification of jarosite and schwertmannite, and a phase containing (Si,Al)-OH (2.20 μm spectral feature), for samples similar to that shown in Fig. 4. At ABG jarosite appears to coat the bottom and sides of the stream bed where no efflorescents grow and to underlie gypsum and copiapite where they do grow. At MWG, jarosite and schwertmannite form a red stain that coats the rocks on which the efflorescents form, and is in some cases associated with copiapite.

VNIR spectra of mud at MWG are also consistent with phases that contain (Si,Al)-OH. Raman spectra of the dried mud indicate that the surface of some mud samples is covered by anatase.

The titanium oxide probably precipitated in conjunction with acid sulfate processes.

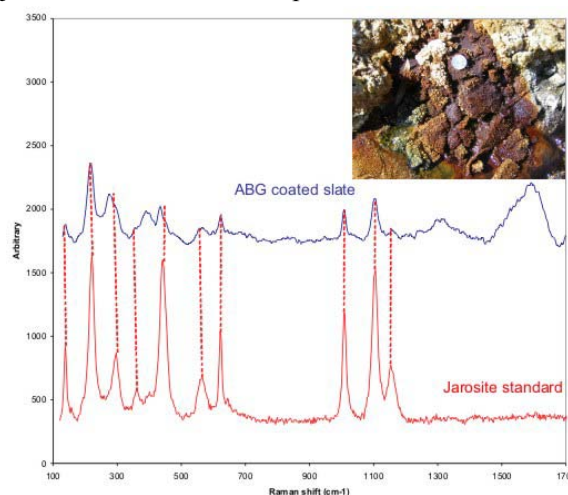


Figure 4. Raman spectra of jarosite and corresponding image. Unmatched peaks in sample spectrum may correspond to other Fe^{3+} -sulfates or iron oxides.

Interpretation: Results from field VNIR spectra and laboratory Raman spectra were remarkably consistent. Both indicate that the geochemical systems at ABG and MWG are dominated by copiapite-group minerals, gypsum, jarosite, and schwertmannite. Differences in mineralogical composition between the two sites likely result from different headwater chemistries. The pH of river water at MWG was measured as 2.08 ± 0.05 , and pH of water at ABG has been previously measured as 2.86 [5]. Water at the Rio Tinto headwaters that feed MWG are comparatively depleted in calcium relative to the ABG spring, possibly indicating why gypsum is not present at MWG. For a full discussion of the geochemical environment of formation, see [4,6]. Future work will identify minor phases present and will assess mineralogical dependence on distance from the river center, using field spectra and images, together with laboratory-based analyses of returned samples.

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References: [1] Gendrin et al. (2005) *Science*, 307, 1587-1591. [2] Arvidson et al. (2005), *Science*, 307, 1591-1594. [3] Klingelhöfer et al. (2004) *Science*, 306, 1740-1745. [4] Fernández-Remolar et al. (2005), *EPSL*, 240, 149-167. [5] Fernandez-Remolar et al. (2002) *LPSC XXXIII*, #1226. [6] Fernandez-Remolar et al. (2006) *LPSC XXXVII*, co-submitted.