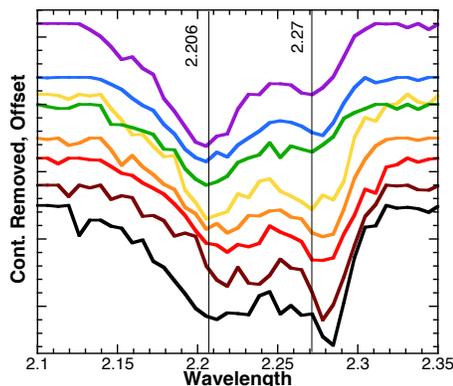
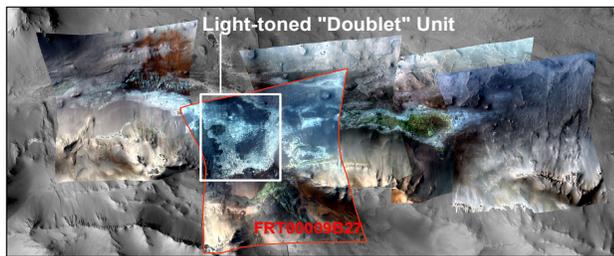


**ORBITAL EVIDENCE FOR CLAY AND ACIDIC SULFATE ASSEMBLAGES ON MARS AND MINERALOGICAL ANALOGS FROM RIO TINTO, SPAIN.** H. H. Kaplan<sup>1</sup>, R. E. Milliken<sup>1</sup>, D. C. Fernandez-Remolar<sup>2</sup>, A. H. Knoll<sup>3</sup>, and R. Amils<sup>2</sup>. <sup>1</sup>Brown University, Box 1846, Providence, RI 02912 ([Hannah.Kaplan@brown.edu](mailto:Hannah.Kaplan@brown.edu)), <sup>2</sup>Centro de Astrobiología (INTA-CSIC), Ctra Ajalvir km 4, Torrejon de Ardoz, 28850, Spain, <sup>3</sup>Harvard University, Cambridge, MA 02138.

**Introduction:** Sulfate and clay minerals have both been identified at many locations across the surface of Mars using visible-near infrared reflectance spectra acquired with the CRISM and OMEGA spectrometers [1]. Meridiani-like deposits with hematite and jarosite may exist in Valles Marineris [2] and nearby regions also host stratified clay deposits [3]. Of particular interest are CRISM observations of units in Valles Marineris that exhibit absorptions at  $\sim 2.207$  and  $2.269 \mu\text{m}$  [4,5] [Fig. 1], features that are not easy to reconcile with a single hydrated mineral phase. Hypotheses for what this spectral “doublet” feature represents include a mixture of gypsum and jarosite, opaline silica mixed with clays, some combination of Al-smectites, Fe/Mg-smectites and jarosite, and acid alteration of Fe/Mg-smectite to Al-ferric clay [4].



**Fig 1:** CRISM image FRT9B27 provides coverage of a light-toned unit in Ius Chasma, Valles Marineris, which shows the doublet variation. Absorption features do not co-vary, implying these spectra represent a mixture of two or more components.

Environments with detrital clays and authigenic acidic sulfates (e.g., jarosite) have been documented at the headwaters of the Rio Tinto near Nerva, Spain [6]. In addition, airborne (HyMap) reflectance spectra acquired over certain locations at Rio Tinto exhibit a doublet absorption similar to what is observed in the CRISM data. Spectra of these regions were examined in situ and samples were collected and characterized in

detail using laboratory techniques (reflectance spectra and XRD). Here we present evidence that these spectral signatures are consistent with mixtures of jarosite and Al-bearing clays and that the Rio Tinto samples are possible mineralogical analogs for the equivalent Martian spectral signatures.

**Methods: Field Observations:** A field campaign was conducted in May 2014 in and around Nerva, Spain. Samples and reflectance spectra were collected from five main localities that range from modern sites with active precipitation of ferric sulfates to the clay and goethite rich Neogene-aged Old Terrace site. The ages and mineralogy of the successive terraces, which become depleted in sulfates and other ions with exposure to meteoritic and neutral solutions, are discussed in detail by [6]. Field reflectance spectra were acquired with an ASD FieldSpec3 from  $0.35$  to  $2.5 \mu\text{m}$  and representative hand samples were collected for further laboratory analysis.

**Laboratory Measurements:** Reflectance spectra, chemistry, and mineralogy of the Rio Tinto samples were measured at Brown University. Spectra of hand samples, chips, and  $<45 \mu\text{m}$  powders were measured with the same ASD FieldSpec3 using a QTH light source. The powders were also measured from  $2.5$  to  $25 \mu\text{m}$  with a Nicolet iS50 FTIR. Spectra were continuum-removed from  $2.1$  to  $2.35 \mu\text{m}$  to isolate the doublet absorptions prior to analysis of the position, width and depth of these features.

The same powders were analyzed with a Bruker D2 Phaser XRD to identify mineralogy. For a select set of samples, quantitative mineralogy was determined with a Reitveld refinement using Diffrac.Suite software, Topas. Quantitative assessments are accepted with a root-mean-squared error less than 10%, though the majority of analyses have RMS error less than 5%. Sulfur content was analyzed using a NC2100 elemental analyzer, which helps constrain the XRD analyses by providing an independent assessment of the amount of sulfate (or sulfide) expected in each sample.

**Remote Sensing Observations:** CRISM image cubes were corrected for atmospheric gases and all pixels within each image were ratioed to the spectrum from a spectrally bland region within the same image. Band depth maps were created for the entire image cube (10 CRISM images to date) using continuum-removed spectra to isolate the doublet feature. Amplitudes from

Gaussian fits to the doublet features were also mapped. Similar analyses were carried out for the HyMap data.

**Results: Rio Tinto Results:** The doublet absorption near 2.2  $\mu\text{m}$  appears in HyMap, field, and lab spectra. Lab spectra for 12 of the powders exhibit two distinct absorption features of variable strength in the wavelength region of interest. Spectra of one sample with a varnished exterior shows the characteristic doublet spectrum at the hand sample scale, but spectra of the powdered portion of the same sample do not show a doublet. Spectra for most of the other samples, however, show a doublet absorption at all scales (whole, chip, powder) as well as in the corresponding field spectra.

XRD of these 12 powders suggests that the spectral features arise from jarosite and Al-bearing clay. All powders contain >1% of jarosite and muscovite/illite. Varying proportions of these two components correspond with changes in band depth of the individual absorptions that comprise the doublet [Fig. 2]. The shorter wavelength absorption ( $\sim 2.207 \mu\text{m}$ ) becomes stronger as the amount of illite/muscovite increases, consistent with increased Al-OH vibrations, whereas the 2.269  $\mu\text{m}$  feature becomes stronger with increasing jarosite.

Field spectra, hand sample spectra, and XRD results are consistent with the transitions in mineralogy seen by [6]. Samples whose spectra exhibit the doublet are all collected from younger units (modernly precipitating streambeds or Holocene-aged young terrace). It is likely that the clay component represents detrital clastic material from the surrounding watershed, whereas the jarosite is produced authigenically in these locations.

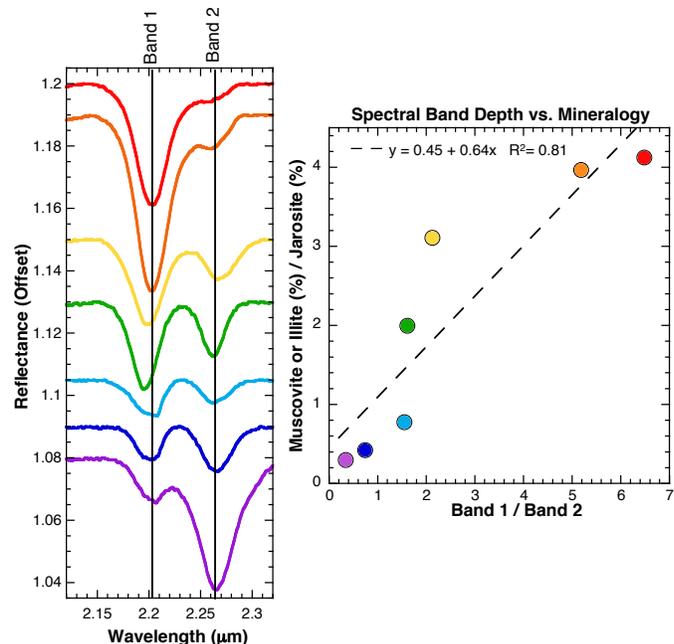
**CRISM Results:** Variations in the strength of the individual components of the doublet feature are apparent within a single CRISM image (e.g., Fig. 1). The observation that these features do not vary together suggests more than one phase is likely responsible for the spectral feature and the proportion of these phases is spatially variable. The width and positions of the CRISM absorptions are comparable to those in the Rio Tinto spectra, but the former exhibit less variation in band strength than the latter. We find that the spectral doublet is often associated with light-toned units in Valles Marineris, similar to what was found by [5], along with evidence of clays and sulfates.

**Implications for the Martian Surface:** The spectral doublet is consistent with the presence of Al-clay and sulfate-bearing deposits on Mars that are mixed at a spatial scale below that of CRISM (i.e., <18 m). Comparison of CRISM spectra to those acquired for select locations at Rio Tinto indicate the latter may provide mineralogical analogs for what has been observed on Mars. If correct, then the strength of the two

absorptions as observed in CRISM data would give clues to the relative proportions of jarosite and Al-bearing clay within the Martian deposits.

If Rio Tinto is a process analog as well as a spectral/mineralogical analog, then we may be seeing younger, precipitated sulfates mixed with older, detrital clays. If the potential Al-clay component in the Valles Marineris deposits represents detrital material, possibly sourced from Al-clay on the surrounding plateau [7], and the inferred jarosite is authigenic, then variations in the CRISM spectra may provide information about relative variations in clastic flux and local aqueous geochemistry (e.g., pH, solute concentration). Additional study of the Martian deposits, including detailed geologic mapping and refined spectral analysis, is needed to test this hypothesis. This is the focus of our ongoing work and will ultimately help us to better constrain the role of water-rock interaction and implications for habitability on post-Noachian Mars

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**Fig 2:** Relative band strengths of the two absorption features are correlated to the relative amounts of jarosite and illite/muscovite in the Rio Tinto samples (subset of samples with doublets). As the amount of jarosite increases, the absorption at longer wavelengths ( $\sim 2.269 \mu\text{m}$ ) strengthens, effectively tying spectral response to composition.