Orbital evidence for clay and acidic sulfate assemblages on Mars based on mineralogical analogs from Rio Tinto, Spain

Hannah H. Kaplan, Ralph E. Milliken, David Fernández-Remolar, Ricardo Amils, Kevin Robertson, Andrew H. Knoll

Abstract

Outcrops of hydrated minerals are widespread across the surface of Mars, with clay minerals and sulfates being commonly identified phases. Orbitally-based reflectance spectra are often used to classify these hydrated components in terms of a single mineralogy, although most surfaces likely contain multiple minerals that have the potential to record local geochemical conditions and processes. Reflectance spectra for previously identified deposits in Ius and Melas Chasma within the Valles Marineris, Mars, exhibit an enigmatic feature with two distinct absorptions between 2.2 and 2.3 μm. This spectral ‘doublet’ feature is proposed to result from a mixture of hydrated minerals, although the identity of the minerals has remained ambiguous. Here we demonstrate that similar spectral doublet features are observed in airborne, field, and laboratory reflectance spectra of rock and sediment samples from Rio Tinto, Spain. Combined visible-near infrared reflectance spectra and X-ray diffraction measurements of these samples reveal that the doublet feature arises from a mixture of Al-phyllosilicate (illite or muscovite) and jarosite. Analyses of orbital data from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) shows that the martian spectral equivalents are also consistent with mixtures of Al-phyllosilicates and jarosite, where the Al-phyllosilicate may also include kaolinite and/or halloysite. A case study for a region within Ius Chasma demonstrates that the relative proportions of the Al-phyllosilicate(s) and jarosite vary within one stratigraphic unit as well as between stratigraphic units. The former observation suggests that the jarosite may be a diageneric (authigenic) product and thus indicative of local pH and redox conditions, whereas the latter observation may be consistent with variations in sediment flux and/or fluid chemistry during sediment deposition.

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be spectrally dominant even at the spatial resolution of instruments such as CRISM (e.g., ~18 m/pixel). Therefore, those regions on Mars whose reflectance spectra cannot clearly be attributed to a single dominant hydrated mineral are of particular interest as they may record different and more diverse geological processes than are typically recognized from CRISM data.

Reflectance spectra of deposits and strata within the Valles Marineris reveal a number of locations that fall within this category, and these are the focus of this study. Specifically, CRISM spectra of various deposits within Ius, Melas, and other chasmas exhibit an absorption feature with local minima centered at ~2.21 and ~2.27 μm (Metz et al., 2009; Roach et al., 2010; Weitz et al., 2011) (Fig. 1). The spectral shape and properties of this absorption feature, which we will refer to as a spectral ‘doublet’, does not match the spectrum of any single common mineral in existing spectral libraries, suggesting it likely cannot be attributed to a single type of clay, sulfate, or other common hydrated mineral.

Previous studies have hypothesized that this material represents a mixture of clays, sulfates (possibly including jarosite), and/or poorly crystalline phases (Roach et al., 2010; Tosca et al., 2008b; Noe Dobrea et al., 2011; Weitz et al., 2014), but the exact assemblage remains unknown. We have observed that similar spectral features occur in airborne, field, and lab spectra of rocks and sediments at Rio Tinto, Spain, which has been previously studied as a Mars analog due to the river’s acidity, iron hydrochemistry, and extensive iron oxide deposits (Fernández-Remolar et al., 2003). Indeed, it has been suggested that the ferric iron and sulfate mineralogy produced by the acidic waters may be analogous to conditions experienced in Terra Meridiani during the Hesperian (Fernández-Remolar et al., 2005), and similar conditions may also have occurred in portions of the Valles Marineris (e.g., Bibling et al., 2007).

In this study we integrate airborne, in situ, and lab measurements to characterize a suite of samples from different sites at Rio Tinto to understand the mineralogical origin of the ‘doublet’ spectral signature, and we then compare our findings to reflectance spectra acquired by the CRISM instrument for deposits in Valles Marineris, Mars. We demonstrate that the doublet absorptions observed in samples from Rio Tinto are comparable to the spectral signatures observed in Valles Marineris, that these are the result of Al-bearing phyllosilicates mixed with jarosite, and that similar mineral assemblages may be present on Mars. This indicates Rio Tinto contains materials that can serve as mineralogical and spectral analogs for the martian deposits, though the geological processes that lead to the formation of these assemblages on Earth and Mars need not be equivalent. Specifically, although jarosite and Al-phyllosilicates may co-occur in geologic units today on Mars, this association does not require their formation environments to have been the same in space and/or time. Both mineral types may be authigenic or detrital, and detailed geologic context is necessary to distinguish between these options and the associated implications for local paleoenvironmental conditions.

2. Background

2.1. Overview of clay and sulfate detections on Mars

The most commonly observed spectral signatures on Mars that have been interpreted as clay minerals are identified as Fe/Mg smectite, but mixed-layer clays, clorite, Al-smectite, mica, kaolinite, and serpentine have also been observed (Mustard et al., 2008;
Murchie et al., 2009; Ehmann et al., 2011; Carter et al., 2013). Aqueous alteration of basaltic protoliths both at the surface and in the subsurface have been invoked as the major source of these clay minerals, although subsequent erosion and eolian/fluvial transport has led to their occurrence in a number of different depositional environments. Intriguingly, these clay minerals, hereafter referred to simply as ‘clays’, occur predominantly in terrains that are Noachian (>3.6 Ga) in age (Bibring et al., 2006). The presence and apparent spatial and temporal distribution of these clays has been used to infer that early Mars was characterized by circum-neutral pH, low salinity, and possibly habitable conditions (Ehmann et al., 2011). More recently, in situ observations of clay-bearing mudstones in Gale Crater by the Curiosity rover are also supportive of a habitable environment, possibly during the Hesperian (Grotzinger et al., 2014, 2015; Vaniman et al., 2014; Bristow et al., 2015).

In contrast, sulfate detections on Mars typically occur in younger Hesperian terrains and may be indicative of a decreased hydrological cycle (Bibring et al., 2006). Decreased water availability, coupled with increasing salinity, may indicate near-surface conditions inhospitable to most life (e.g., Tosca et al., 2008a). Though many sulfate salts (e.g., Ca, Na, and Mg-sulfates) can form under a wide range of pH conditions, it is worth noting that Al$^{3+}$ and Fe$^{3+}$-sulfates are indicative of low-pH fluids. As such, understanding the distribution and geologic setting of these minerals on Mars has important implications for deciphering ancient aqueous chemistry, whether it be indicative of surface waters, groundwater, or diagenetic fluids.

Jarosite, a ferric sulfate that forms under acidic conditions and that was first detected on Mars by the Opportunity Rover in Meridiani Planum (Squyres et al., 2004), has received considerable attention in this context. Integrated payload observations by the rover reveal that jarosite is likely associated with Mg and Ca-sulfates at this location, all of which occur in eolian sandstones that have been interpreted as reworked dune and playa sediments (Grotzinger et al., 2005). The Curiosity rover has also detected small amounts of jarosite in clay-bearing laminated mudstones in Gale Crater (Cavanagh et al., 2015), though the origin of this phase (e.g., detrital or authigenic) in these deposits is not yet well constrained.

Orbital observations of jarosite and other possible ferric sulfates have also been reported in the Mawrth Vallis, Aram Chaos, Noctis Labyrinthus, and Valles Marineris regions of Mars (Bibring et al., 2007; Milliken et al., 2008; Farrand et al., 2009; Metz et al., 2009; Lichtenberg et al., 2010; Weitz et al., 2011; Thrott et al., 2012; Noe Dobrea et al., 2011). Of the Valles Marineris detections, possible submarine fan deposits in Melas Chasma and strata exposed on the surrounding plains are notable in that ferric sulfates are found in proximity to other hydrated minerals such as opaline silica, providing additional constraints on local aqueous geochemistry (Milliken et al., 2008; Metz et al., 2009). These rover- and orbiter-based observations indicate ferric sulfates may be common alteration or diagenetic phases on Mars, as discussed by Burns (1987, 1993), and understanding their occurrence can provide insight into local, regional, or global redox conditions.

2.2. CRISM Observations of the spectral ‘doublet’

CRISM spectra of martian deposits that exhibit the ‘doublet’ feature mentioned above are characterized by absorption maxima (reflectance minima) occurring at wavelengths of 2.205–2.218 and 2.265–2.278 μm. These spectral features have been noted previously in a number of CRISM-based studies, particularly for deposits within Valles Marineris, and in some of these studies the material has been referred to as a hydrated silicate (e.g., Roach et al., 2010). However, many minerals, including gypsum, jarosite, nontronite, and silica, exhibit absorptions in this wavelength range, and it is possible that the spectral doublet represents a mixture of two or more hydrated minerals (Fig. 1). The main doublet feature is consistent with vibrational absorptions due to the presence of cation-OH bonds, although the position and shape of absorptions within the feature lead to ambiguity in determining the specific cation(s). The shorter wavelength absorption (∼2.21 μm) may be consistent with Si- or Al-OH bonds, whereas the longer wavelength feature (∼2.27 μm) may be indicative of Fe- or Mg-OH bonds. However, spectra of H$_2$O-bearing Ca-sulfates such as gypsum also exhibit absorptions in this wavelength region, despite the lack of structural Si, Al, Fe, Mg, or OH.

In addition, CRISM spectra that exhibit the doublet feature also exhibit an absorption at ∼1.9 μm due to the combination stretch-bend vibration mode of H$_2$O. A similar doublet absorption has also been observed in laboratory spectra of poorly crystalline Fe-silicate and sulfate mixtures (Tosca et al., 2008b) as well as acid-leached Fe-smectite (Madejova et al., 2009), suggesting the spectral signature may also be consistent with poorly crystalline or amorphous phases. Therefore, while it is likely that the spectral doublet feature is indicative of OH and/or H$_2$O-bearing phases, the specific mineral assignments remain ambiguous.

Roach et al. (2010) proposed four hypotheses to explain the doublet material: (1) a mixture of sulfates (in particular, sulfates structurally similar to gypsum and jarosite), (2) a mixture of opaline silica and Fe/Mg-smectite, (3) an Al-OH phase mixed with Fe/Mg-smectite and/or jarosite, and (4) acid-leached Fe/Mg-smectite or neof ormation of poorly crystalline clays. Subsequent study by Weitz et al. (2014) supported the latter two hypotheses based on an analysis of CRISM spectra for the Melas Chasma region, demonstrating that the spectral doublet is associated with “light-toned draping deposits” (termed LD in Weitz et al., 2014) that locally form some of the highest stratigraphic units. These LD deposits extend through portions of Melas Chasma and drape over pre-existing topography, suggesting an airfall origin. Weitz et al. (2014) interpreted this LD unit to have been deposited after the Late Hesperian valleys that incise the walls of the chasma, but stratigraphic position alone cannot be used to determine whether the hydrated phase(s) associated with the spectral doublet in this unit represent transported sediments or authigenic products.

Roach et al. (2010) described a similar thin light-toned unit in Ius Chasma that drapes pre-existing topography, but the stratigraphic and possible genetic relationships between this unit and those in Melas have not yet been established. Roach et al. (2010) interpreted the light-toned unit to have been emplaced on top of Fe/Mg-smectite and sulfate-bearing strata either during or after a period of acidic aqueous alteration when sulfates formed from evaporating brines. Another study by Weitz et al. (2011), of Noctis Labyrinthus, identified the doublet material in a ∼20-m-thick massive light-toned unit that outcrops near the top of a stratified light-toned deposit (see Weitz et al., 2011 Fig. 2). It was suggested that this deposit was also formed under acidic conditions, and the doublet-bearing unit was interpreted to pre-date deposition of Fe/Mg-smectite and sulfates in the same region (Weitz et al., 2011). Although the doublet-bearing materials in Valles Marineris are often associated with units that drape pre-existing topography, including the canyon wallrock, Metz et al. (2010) provided evidence for deformation features in some of the deposits, suggesting they may have originated higher up the canyon walls than indicated by their current topographic position. Finally, CRISM data for Mawrth Vallis also show evidence for doublet-bearing materials in the vicinity of Fe/Mg-smectites and Al-phyllosilicates (Noe Dobrea et al., 2011; Bishop et al., 2013).

To summarize, doublet-bearing units are present in stratigraphic sections that contain hydrated minerals suggestive of complicated and extended periods of water–rock interaction and/or sediment transport. Fe/Mg-smectites and sulfates are often found
in nearby units and in most cases these occur in strata emplaced prior to the doublet-bearing units. An exception is Noctis Labyrinthus, where the doublet material occurs in a unit that lies stratigraphically below an Fe/Mg smectite-bearing outcrop.

We note that jarosite, which typically forms under conditions of pH < 4, is also identified in several of the regions that also exhibit the spectral doublet (Milliken et al., 2008, Metz et al., 2009, Noe Dobrea et al., 2011). Although the jarosite deposits are not necessarily in rocks that are stratigraphically adjacent to the doublet materials, the presence of this mineral in these regions may provide insight into local aqueous geochemistry. Jarosite deposits on Mars may have formed where acidic sulfate-bearing water ponded and subsequently evaporated (Tosca and McLennan, 2006), though it is also possible for jarosite to form through weathering of basalt (e.g., Elwood Madden et al., 2004). Alternatively, acidic conditions that lead to jarosite formation may be induced by local or regional oxidation of Fe²⁺-bearing fluids, possibly via the emergence of groundwater and interaction with the oxidizing martian atmosphere (Hurowitz et al., 2009). An important aspect of any of these scenarios is that the presence of authigenic jarosite records information about local pH as well as redox conditions.

### 2.3. Overview of field region at Rio Tinto, Spain

The headwaters of the Rio Tinto near Nerva, Spain are acidic (mean pH of 2.3) and rich in ferric iron and other heavy metals. Three terraces of the Rio Tinto are exposed in the river valley with the youngest terrace closest in elevation to the modern day channel and the intermediate and oldest terraces located stratigraphically above it (see Fig. 2). The youngest of these (called the lower or young terrace) is Holocene in age (750–1500 years) and composed of poorly sorted conglomerates overlain by cross-bedded sandstones. Both types of deposits are consistent with formation by mass wasting and sediment accumulation in the active channel, a process that also occurs in the modern river. The Pleistocene-aged (~35 Kyr) intermediate terrace is exposed 100 m above the
lower terrace and consists of poorly sorted clasts of country rock within a goethite-bearing matrix; this terrace is distinct from the other river terraces as it lacks the sedimentary facies corresponding to channel and backwater deposits seen in both the young and old terraces. Finally, the Late Pliocene-aged (2 My) upper or old terrace is exposed in a ≥10 m thick outcrop at Alto de la Mesa. The outcrop at Alto de la Mesa consists of a lag conglomerate overlain by sandstones and iron oxide precipitates, reflecting similar types of channel deposits as those seen in the lower terrace. Further description of the terraces and radiometric age constraints are reported in Fernández-Remolar and Knoll (2008).

The mineralogy of the modern river system and its terraces is dominated by ferric oxides and ferric sulfates. A number of previous studies have investigated variations in the mineralogical assemblages in the river terraces using X-ray diffraction (XRD), visible–near infrared (VIS-NIR) reflectance spectroscopy, and Raman spectroscopy (Fernández-Remolar et al., 2005; Roach et al., 2006; Chemtob et al., 2006; Sobron et al., 2009, 2014). The reader is directed to Fernández-Remolar et al. (2005) for a more thorough discussion on the mineralogy and mineral-forming processes of the Rio Tinto. Those authors found that seasonal precipitation of Ca- and Fe-sulfates occurs near the source region of the river, with the Fe-sulfates jarosite (in particular hydronium jarosite), schwertmannite, and copiapite making up much of the mineral assemblage, along with nanophase iron oxide and nanophase goethite. Only the most stable minerals (iron oxides, goethite, jarosite) survive through the wet season, during which meteoric water dissolves many of the precipitates and aids in cementation of the terrace deposits. Jarosite is less abundant and often absent in the older deposits, likely due to its long-term instability under wet conditions, and these units instead contain more stable Fe-oxides such as goethite and hematite. Therefore, the persistence of jarosite may indicate a low degree of water–rock interaction or low water-to-rock ratios since its precipitation. Country rock in this region is composed of quartz, chlorite, and pyrite, which act as a source of solutes for the precipitates as well as a source of detritus for the terrace conglomerates.

In addition to sulfates and Fe-oxides, phyllosilicates (2M1 illite, chlorite, kaolinite, and smectites) are also present throughout the Rio Tinto system and are thought to form by alteration of the volcanic sedimentary bedrock near the source of the acidic river system (see Fernández-Remolar et al., 2011 for details). At Rio Tinto, phyllosilicates typically accumulate at times of maximum waterflow during the wet season when deposition of detrital sediment is dominant over chemical sedimentation, but they can also be found in environments where conditions are outside those typical for clay formation, such as the low-pH source streams. The diversity and stability of these phyllosilicates depends on the hydrology, source rock composition and geochemical processes occurring in the river, all of which must be accounted for when interpreting the deposits (Fernández-Remolar et al., 2011). Likewise, jarosite is neither stable nor formed in all of Rio Tinto’s hydrogeochemical environments (Fernández-Remolar et al., 2005 and discussed below).

3. Methods

3.1. Hyperspectral imaging data

3.1.1. HyMap data analysis

For remote observations of Rio Tinto we used aerial HyMap scenes that covered the headwaters of the river, nearby mining activity, and urban areas. These data were acquired by Integrated Spectronics on Aug 14, 2004 and are the same as the fully processed and analyzed data used by Roach et al. (2006). The reader is directed to that publication for a detailed description of how these data were calibrated, atmospherically corrected, and processed.
compare band depths between spectra (Clark and Roush, 1984). Band depth is defined as $I - [R_b(\lambda) R_c(\lambda)]$, where $R_b$ represents the observed reflectance value at wavelength $\lambda$, and $R_c$ represents the calculated reflectance of the spectral continuum fit at the same wavelength. Band depth maps were created for each CRISM image to provide a more in-depth analysis of the spatial distribution of the spectral doublet feature.

Gaussian curves were also fit to the continuum-removed doublet absorptions and the resulting Gaussian amplitudes and center positions were mapped for each CRISM image. Gaussian modeling of absorptions is commonly used for remote sensing data to assess band strength in the presence of noise or to remove the influence of adjacent or partially overlapping absorption features on the absorption of interest (Clark and Roush, 1984; Sunshine and Pieters, 1993). Noise in the CRISM images, for instance, may introduce apparent changes in band position/strength if these calculations are based on the observed absolute reflectance values on a pixel-by-pixel basis. This can introduce uncertainties in the band depth maps, which we attempt to mitigate by examining the amplitudes and positions of Gaussian fits.

To determine the background noise in an image prior to Gaussian fitting, a histogram of the standard deviations within each image was examined for a flat, absorption-free portion of the spectrum (1.70–1.85 $\mu$m), an example of which is presented in Fig. 4. Here it is clear that the standard deviations in the ratio spectra are predominantly < 0.005, thus any absorption feature (band depth) in the ratio spectra that is larger than this value is above the typical level of ‘noise’ in the CRISM image. Two CRISM ratio spectra exhibiting the doublet feature and their corresponding Gaussian fits are also presented in Fig. 4, where it is clear that the doublet absorptions are much stronger than the typical channel-to-channel variation in reflectance. Pixels that exceed the 0.005 threshold are fit with two Gaussian curves, one for each absorption in the doublet (see example in Fig. 4).

3.2. Field measurements

Fieldwork was conducted at multiple locations in the vicinity of Rio Tinto, Spain in early May of 2014. Rock and/or soil specimens were collected and field spectra were acquired at each of five primary sites (Table 1). These locations included the modern streambed environment and two successively older terraces that have been affected to different degrees by diagenetic processes (Fig. 2). Previous studies have shown that the materials at these sites exhibit different mineral assemblages (Fernández-Remolar et al., 2005; Fernández-Remolar and Knoll, 2008), allowing us to examine whether spectral reflectance properties can be linked to post-depositional processes in these types of environments.

Samples collected were collected from the Rio Tinto source region (Anabel’s Garden, Rich Spring, and Source Spring sites), a series of small streams with actively forming efflorescent and crust-forming precipitates (e.g. copiapite, jarosite, gypsum). A number of samples were also collected from an actively mined terrace directly above Anabel’s Garden that showed evidence for the spectral doublet absorption in the airborne HyMap data. Another field site, Berrocal, is also located directly on the Rio Tinto approximately 20 km downriver from the mining operations. At this location, there is a mix of detrital sediment and authigenic precipitates. We also examined older deposits at Barranco de los Locos, a site that is part of the Holocene-aged lower terrace in which the lower unit is a ferruginous conglomerate and is overlain by sandstone (Fernández-Remolar et al., 2005). Finally, for comparison to the modern environment we examined an older (early Quaternary) terrace exposed at Alto de la Mesa. Detailed descriptions of these sites, their ages, and local geology can be found in previous publications (e.g., Fernández-Remolar et al., 2005; Fernández-Remolar and Knoll, 2008; and references therein).

A portable VIS-NIR spectrometer (ASD FieldSpec 3®) was used to acquire reflectance spectra in situ from 0.35 to 2.5 $\mu$m.
Table 1
A full list of samples collected at the modern streambed, lower and upper terraces at Rio Tinto. All samples are rocks unless otherwise noted. Each sample is measured with the ASD, FTIR, and XRD in the laboratory. Samples with a spectral doublet and those that have been analyzed with a Rietveld refinement are noted.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Location</th>
<th>Terrace</th>
<th>Spectral doublet</th>
<th>Rietveld refinement</th>
</tr>
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<tbody>
<tr>
<td>RT1</td>
<td>Berrocal</td>
<td>Modern</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT2</td>
<td>Berrocal</td>
<td>Modern</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT3</td>
<td>Berrocal</td>
<td>Modern</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT4 (mud, loose)</td>
<td></td>
<td>Modern</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT5</td>
<td>Anabel’s Garden, Upper Road</td>
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<td></td>
</tr>
<tr>
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<td>Anabel’s Garden, Upper Road</td>
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<td></td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
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<td></td>
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<tr>
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<td></td>
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<tr>
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<td></td>
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<td>RT34</td>
<td>Gossan outcrop</td>
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Reflectance spectra were acquired for a variety of materials passively (relying on ambient sunlight) and/or actively (relying on a contact probe with internal illumination). All measurements were made using a Spectralon® panel as the reflectance standard. Passive measurements that rely on solar illumination and reflectance are more directly analogous to airborne data such as HyMap. A more detailed description of the ASD measurements is provided in the supplemental material.

Rock and sediment samples were collected to capture the spectral diversity of deposits at each location and were based in part on interesting absorption features observed in the HyMap and field reflectance spectra (see Table 1 for full list). To the extent possible, samples were collected at the different sites to be representative of the mineralogy expected at HyMap and CRISM spatial scales (e.g., the dominant mineral assemblages at scales of ~8–18 m/pixel, respectively), focusing on regions whose spectra exhibited evidence for compositional diversity. Of specific interest were regions with spectral or field-based evidence for Fe-oxides, Fe-sulfates, and clay minerals. A number of locations contained materials whose reflectance spectra exhibited the doublet absorption feature described above, and a variety of these materials were collected for detailed laboratory characterization. Though many other samples and spectra were collected during the field campaign, the samples, field measurements, and HyMap data whose spectra exhibit these distinct doublet absorptions were chosen as the focus for the present study. A more complete treatment of how field-based spectral observations and diversity at Rio Tinto relate to aerial and orbital-scale observations is presented in Roach et al. (2006).

3.3. Laboratory measurements

3.3.1. Sample preparation

All laboratory analyses were conducted in the Department of Earth, Environmental and Planetary Sciences at Brown University. A number of small chips (~2.5 cm) were removed from each hand sample and a second portion of each was ground by hand in an agate mortar and pestle. The resulting powders were ground such that the material could pass through a ~45 μm mesh sieve. Grind and sieving serves the dual purpose of homogenizing the sample and reducing particle size-dependent absorption/scattering processes. Where possible, separate powders were prepared for different portions of a single sample to assess heterogeneity (e.g., rock varnish, dark or light components, areas with different degrees of weathering) and for comparison to the whole rock powders. Some hydrated mineral phases are expected to be unstable even over short time frames, and these are not included in our dataset.

3.3.2. Reflectance measurements

Reflectance spectra of the hand samples, chips, and powders were measured in the laboratory using the same ASD FieldSpec3 instrument over a wavelength range of 0.35–2.5 μm. The measurement spot size was adjusted to encompass the entire sample in order to provide a better assessment of the bulk spectral properties of each hand, chip, and powder sample rather than averaging spectra of individual components. We note that the chips and powder samples were placed in ~10 mm diameter sample holders for
measurement, thus the measurement spot size for these samples is equivalent.

All of the rock powders sieved to < 45 μm were also measured with a Nicolet iS50 FTIR from 1.75 to 25 μm. The FTIR was equipped with a Praying Mantis diffuse reflectance attachment from Harrick Scientific and diffuse gold from Labsphere was used as a reflectance standard. These measurements used a KBr beamsplitter and DTGS detector, and each final spectrum was an average of 50 scans. Absolute reflectance values from the FTIR are highly dependent on any slight differences in height between the sample and gold standard, thus all FTIR spectra were scaled to match the ASD values at 1.7 μm. These spliced spectra provide full VIS-NIR-mid-IR wavelength coverage, and because all samples were measured under identical conditions, the observed relative differences between samples are reliable.

All reflectance spectra (field and lab) were processed using the same methods, and continuum-removed spectra and band depths were calculated using the same procedures as described above for the CRISM data (i.e., an upper convex hull method was used to define the continuum slope). We analyzed the continuum-removed spectra using Matlab to find the local minima (which is equivalent to the maximum band depth) within the ~2.1–2.35 μm wavelength region. If the continuum-removed spectrum is determined to exhibit absorptions near ~2.2 μm and ~2.26 μm, then this so-called doublet feature is further analyzed to determine the total width, center position, and depth of the individual absorptions.

3.3.3. X-ray diffraction measurements

The < 45 μm sieved powders were measured with a Bruker D2 Phaser XRD system (see supplemental material for details) to determine qualitative and quantitative mineralogy. Samples whose corresponding reflectance spectra exhibited the 2.2 μm doublet (n = 8) were studied in detail, as were a subset of samples from multiple locations whose spectra did not exhibit the doublet (n = 3) in order to test our hypothesis that a distinct mineral assemblage gives rise to the doublet feature (Table 2). Powder diffraction patterns were typically acquired over a range of 2–90° 2θ, 0.02° step size, with a total integration time of up to ~12 h (6.5 s/step).

XRD patterns were analyzed with two programs, DIFFRAC.SUITE™ EVA for full pattern phase identification and DIFFRAC.SUITE™ TOPAS for quantitative Rietveld refinement, where the latter is similar to the method described in Bish and Howard (1988). An overview of the mineralogy at Rio Tinto is provided in Fernández-Romolar et al. (2005), which we used as a guideline for choosing reasonable starting components for the qualitative mineral assessment. Modal mineralogy estimated from Rietveld refinement relied on the structural and instrumental parameters to model the XRD patterns. Structure files describing the crystallographic structure of relevant minerals used in the refinement are listed in the supplementary table.

These mineral structures were added and removed from the model iteratively until a reasonable fit to the observed pattern was obtained. TOPAS automatically normalizes the model results such that mineral abundances will always add to 100%. The quality of the refinement is determined by the weighted profile R-factor (Rwp), which considers the root mean square error (RMSE) for each scaled intensity value (peak and background). Although a smaller Rwp generally indicates a better model, it is possible to overfit the data with this method and discretion is used to ensure the resulting model is geologically realistic. We also calculated the areas for the muscovite 001 (~9° 2θ) and jarosite 101 (~15° 2θ) peaks. Though this method does not provide quantitative estimates like the Rietveld method, it does provide an independent estimate of how the relative abundances of the two minerals vary between samples without the uncertainties associated with modeling the full XRD pattern.

4. Results

4.1. Overview of Rio Tinto field observations

Previous work has shown that mineralogical and spectral differences exist between the old and young terraces (Fernández-Romolar et al. 2005; Sobron et al. 2014), and we observe congruous spectral differences in our samples from these locations. Field spectra of samples from the source region exhibit absorptions consistent with the presence of gypsum, jarosite, and copiapite (Fig. 5). Hydrated iron-bearing phases are also common in these field spectra, including absorptions consistent with the presence of schwertmannite and copiapite, which are identified in spectra from the Rich Spring and Source Spring locations. The field spectra from Berrocal (not shown) have very similar identifying absorptions that are typical of the precipitates, phyllosilicates and iron hydroxides found in the source region spectra. Spectra exhibiting the doublet absorption are found in sand bar sediments from Berrocal, representing rocks/sediments that have not been influenced by mining activities.

Most of the Fe- and Ca-sulfate precipitates are absent at the young terrace site, Barranco de los Locos. Jarosite, Al-phyllosilicate (muscovite/illite), and goethite are the primary minerals identified in our field spectra at this location. VIS-NIR spectra from the old terrace site, Alto de la Mesa, exhibit the lowest mineral diversity and are dominated by iron oxides. Most spectra from Alto de la Mesa are consistent with the presence of goethite, though some indicate the presence of kaolinite or chlorite. Sulfate absorptions are not apparent in spectra of materials from the old terrace, and the doublet feature is also not observed in these spectra.
spectra for a number of samples that were taken from a mine road terrace above Anabel’s garden display the doublet absorption. Other samples from this site are spectrally consistent with goethite and hematite. Finally, samples from some of the mining terraces are spectrally consistent with chlorite, kaolinite, and muscovite, likely reflecting country rock components.

4.2. Laboratory measurements

4.2.1. X-ray diffraction

Based on an initial qualitative assessment of the XRD patterns and observed spectral diversity, eleven samples were chosen for further quantitative Rietveld refinement. Eight of the samples have spectra that exhibit the spectral doublet and contain between 3–38% jarosite and 4–50% illite or muscovite (Table 2). The other volumetrically important mineral in these samples is quartz, which does not have absorptions at VIS-NIR wavelengths, so the samples are spectrally dominated by Fe-sulfate and Al-bearing clay minerals. K-jarosite is a better fit in the Rietveld refinement than either hydroniumjarosite or natrojarosite. Though the mineral assemblage is largely the same, the relative proportion of jarosite and Al-clay is quite variable between samples (Fig. 6), and these values are presented in Table 2. Three samples that do not show evidence for the doublet feature in corresponding reflectance spectra were also examined. The XRD patterns for these samples are consistent with a mineral assemblage dominated by hematite, goethite, kaolinite, chlorite and quartz, but no jarosite, in agreement with the findings of Fernández-Remolar et al., (2005) for this locale (Table 2). One

Fig. 5. Example spectra from the field and laboratory for the A) modernly precipitating streambed at Rio Tinto (source region, which includes Source Spring, Richi Spring, and Anabel’s Garden) and B) the ~2 myr old terrace at Alto de la Mesa. These spectra show the transition from very hydrated, sulfate minerals to ferric oxides through time (with some clays possibly associated with mining activity). All of the mineralogies identified in hand samples are also found in the field spectra, but only a limited number of each is shown for the sake of clarity. In C), absorptions in powdered samples that show a doublet are specifically compared to jarosite spectral endmembers. Again, a very similar doublet signature is seen in both field and hand samples, but is not shown for clarity. Endmember mineral spectra from RELAB and USGS are shown for reference (RELAB: RM-JFM-036, RM-JFM-035, CC-JFM-013A, JB-JLB-752, JB-JLB-753, JB-JLB-757, JB-CMP-047, JB-CMP-054, CC-JFM-017-B, JB-CMP-25-B; USGS: B293-1, GDS2 Zeolite W1R1Bb).
sample from the young terrace, Barranco de los Locos sample RT23, is modeled to contain ~33% jarosite and ~39% gypsum but no Al-clay (Table 2), and its reflectance spectrum is dominated by gypsum at wavelengths > 1.3 μm (Fig. 5). In summary, the major secondary phases in these samples are jarosite, illite or muscovite, and Fe-oxides such as goethite and hematite. Although smectitic clays are an integral part of the alteration mineral assemblages on Mars, the Rio Tinto samples examined for this study show no clear evidence for the presence of smectitic clays.

4.2.2. Reflectance spectra

As with the field spectra, the laboratory spectra indicate variations in mineral assemblage with age. In samples from the modern streambeds (samples from Anabel’s Garden and Source Spring) gypsum is the primary mineral identified in two samples (RT18, RT23), with jarosite also being present in RT23 (see Fig. 5). Other samples from these sites have spectra with strong OH and H₂O bands at ~1.4 and ~1.9 μm as well as absorptions consistent with copiapite, schwertmannite, or possibly monohydrated sulfates (Fig. 5). These hydrated samples were not measured with XRD because these minerals change hydration states readily under laboratory conditions, so these spectral mineral identifications cannot be confirmed. However, other XRD studies of Rio Tinto samples have found evidence for a variety of sulfates, including epsomite, copiapite, and coquimbite (Fernández-Remolar et al., 2005), and it is likely that a range of hydrated sulfates are also present in our samples.

The spectral shapes of samples from the young terrace are distinct from those of Anabel’s Garden and Source Spring, with the former having weaker hydration absorptions and a strong spectral slope near 1 μm. In fact, the major difference in spectra of all the young terrace samples lie in the region between 2.2 and 2.3 μm; spectra of some samples show a doublet in this region whereas others have only an ~2.21 or 2.27 μm absorption. Samples collected from the old terrace deposit are spectrally consistent with clays such as kaolinite and chlorite as well as Fe-oxides such as hematite (Fig. 5). Gossan samples all show spectral evidence of goethite. As with the field spectra, lab measurements of the older samples typically lack spectral evidence for sulfates and are instead indicative of Fe-oxides and/or phyllosilicates. Samples from the mining terrace have spectra that exhibit the spectral doublet or that are representative of the same type of minerals discussed for the other sites, including chlorite and Fe-oxides (goethite and hematite). However, given that the specific geologic context of these samples is unknown, especially compared to the well-defined mineralogical and age progression of the river terraces, it is difficult to comment on the processes that have affected this group of samples.

To summarize thus far, laboratory spectra with the doublet absorption correspond to samples collected from the modern stream sites (Anabel’s Garden, Source Spring), the young terrace (Barranco de los Locos), and from a mining terrace site near Anabel’s Garden (Table 2). There are many minerals that have spectral features near 2.26 μm, but we attribute the 2.26 μm feature in the doublet to jarosite because of the combined presence of absorptions at wavelength positions that are attributed to jarosite (1.48, 1.86, 1.9, 2.26 μm), as well as evidence from XRD mineralogical analysis. The doublet feature is conspicuously absent in spectra of samples collected at the old terrace, all of which lack jarosite. Reflectance spectra of the ~45 μm powders of samples exhibiting the doublet show strong, broad electronic transition absorptions at wavelengths of ~1 μm due to the presence of iron (Fig. 6). There are also narrower vibrational absorption features at 1.4 and 1.48 μm due to OH, though the 1.48 μm feature is weak.
or absent in samples that show a very strong 2.21 μm short wavelength band in the doublet feature. Likewise, a broader absorption at ~1.9–1.95 μm due to OH/H₂O and a narrower absorption at 1.86 μm from OH/H₂O are also weaker in samples with a stronger ~2.21 μm feature. In contrast, the ~2.21 μm absorption in the doublet feature is related to the presence of Al-phyllosilicates (illite or muscovite). A vibrational absorption near 2.35 μm is present in some samples and is also consistent with the presence of Al–OH in illite or muscovite.

Spectra of rock chips and hand samples were also acquired and, in most cases, the samples whose powder spectra exhibited the doublet feature also exhibit the feature for these larger physical forms (see example for sample RT19 in Fig. 7). However, sample RT10 is an exception in that a spectrum of the orange-colored varnished face of the hand sample shows the doublet feature whereas the unvarnished side of the hand sample, a chip, and the powder spectra are dominated by the 2.21 μm feature (Fig. 7). This indicates the varnish may be enriched in jarosite, and although such coatings or varnishes may be only several micrometers thick, they may contribute significantly to aerial and orbital spectral observations.

Only the bulk powder versions of the samples were measured using both reflectance spectroscopy and XRD; thus, we compare only the powder spectra directly with the mineralogy determined by XRD. There is a strong correlation between the strength of the longer wavelength absorption in the doublet feature and the abundance of jarosite for the samples examined here (Fig. 8). There is also a strong relationship between the relative band strengths and the relative amounts of jarosite and Al-clay in the samples, as determined using either the Rietveld modal estimates or the XRD peak area. The relationship between Al-clay and the strength of the shorter wavelength absorption has a lower R² value than in the other plots, but we suggest this is due to the size of the dataset, where a relatively small amount of scatter (in this case one data point with anomalously high estimated Al-clay wt.%) has a strong control on the fit. These observations indicate that the doublet feature observed in spectra of some samples from Rio Tinto is related to the mixing of Al-phyllosilicate (illite or muscovite) with jarosite, and that the strengths of the absorptions within the doublet feature are directly related to the relative proportion of these phases.

4.3. HyMap and CRISM observations

4.3.1. HyMap results

The HyMap PCA false-color map presented in Fig. 3 highlights pixels whose spectra exhibit the doublet feature in dark red. Absorption maxima (reflectance minima) for these pixels occur at ~2.20–2.22 and 2.26–2.28, a range that is broader than observed in Mars CRISM data, and that could be a result of differences in spectral resolution, since HyMap only has 6 bands in this wavelength region compared to CRISM’s 13 bands. The doublet feature is evident in HyMap spectra corresponding to the Anabel’s Garden location, where it is possible to track changes in the relative strength of the absorptions across a ~500 m transect in the HyMap image (Fig. 3). The feature is also present in numerous pixels corresponding to mining terraces, although it was not possible to independently examine most of these locations during the field study. Bedrock, detritus, and soil at the young, intermediate, and old terrace sites discussed above are not always apparent in the HyMap data due to the presence of vegetation. However, chlorite, kaolinite, gypsum, and Al-clay are identifiable in the HyMap spectra, and Roach et al. (2006) provide a thorough analysis of iron oxides and hydrated or hydroxylated iron-sulfates in these airborne data. In this study we have only relied on the HyMap data to provide an airborne comparison (at lower spatial and spectral resolution) of the doublet-bearing materials with the spectra acquired in the lab and in situ using the ASD FieldSpec3. In this context, the HyMap data confirm that spectra of certain surface materials exhibit the doublet feature even at a meters-per-pixel spatial scale and lower spectral resolution, consistent with the higher spatial and spectral resolution field and laboratory data.

4.3.2. CRISM results

The spectral doublet feature is evident in a number of CRISM images in the Valles Marineris, with particularly good examples in Melas and Ius Chasma (e.g. Roach et al., 2010; Weitz et al., 2014). Our Gaussian fit analysis of three of these CRISM images show that the absorption band centers and relative strengths (Gaussian amplitudes) associated with the doublet materials are only moderately variable (Fig. 9). The centers of the Gaussian fits for the three CRISM images and the HyMap image are listed in Table 3. The typical 2σ deviation on the band positions in
the CRISM images is $\sim 0.015 \mu m$ and the band centers fall near 2.2060 and 2.2682 $\mu m$ on average. However, the wavelength varies across the spatial dimension of the CRISM detector (spectral smile) by $\sim 0.010 \mu m$, which may explain much of the width of the histograms in Fig. 9. To examine this effect we analyzed a $50 \times 50$ pixel region restricted to the center of each image where the spectral smile is minimal. Histograms for these subsets reveal a decrease in standard deviation as well as a shift in mean band center in all three cases (Table 3, Fig. 4). The difference in band centers between the full image and the central subset is statistically significant ($p < 0.05$) in every case.

Therefore, we conclude that the band centers of the doublet spectral feature are relatively constant and occur at wavelengths of $\sim 2.21$ and $\sim 2.265$–$2.270 \mu m$. It should be noted that Weitz et al. (2014) identified another spectral doublet occurrence with a long wavelength absorption closer to $\sim 2.28 \mu m$, and the inclusion of pixels with this feature in our analysis would create additional spread in the histograms in Fig. 9c. Given that we did not analyze each pixel in each image individually, it is possible that this longer wavelength doublet is present, but it is certainly not a dominant spectral signature, which is evident in the histograms and investigation of spectra from individual pixels and ROIs.

While the wavelength positions of the two absorptions appear to be fixed, their relative strengths are variable and are not directly correlated (Fig. 9d). Though this result is qualitatively similar to what is observed in field, lab and HyMap spectra of materials from Rio Tinto, the range in relative amplitudes of the two absorptions is typically much smaller in the CRISM data than for the terrestrial examples. That is, spectra of some materials from Rio Tinto are clearly dominated by the $\sim 2.21$ or the $\sim 2.27 \mu m$ feature, with the other feature being very weak or absent. In contrast, nearly all CRISM spectra for the regions examined here exhibit both features and in many instances both features are of equal strength and, while variability does exist, it is less intense than the variability in strengths observed in the Rio Tinto spectra.

The relative band strengths, which is the Gaussian amplitude of the $2.21 \mu m$ absorption divided by the amplitude of the $2.27 \mu m$ absorption, for the three CRISM images is $1.1925 \pm 1.47$ ($2\sigma$), $1.2714 \pm 1.35$ ($2\sigma$), and $1.2207 \pm 1.28$ ($2\sigma$). These averages suggest that the band strength of the shorter wavelength absorption is often slightly stronger than the longer wavelength absorption. However, the standard deviation of the distribution is large enough that it is clear the two absorptions do not co-vary. That is, the two absorptions that comprise the doublet feature in CRISM spectra are independent of one another and thus represent two or more distinct phases. Both tails of the distributions in Fig. 9d are affected by “bad” pixel values (typically a spike in the value for a single CRISM channel in one column of the image that will influence the Gaussian fits). This is particularly obvious as a bulge in the distribution as the Band 1/Band 2 amplitude ratio approaches
Fig. 9. Examples of doublet-bearing materials on Mars as observed in MRO CRISM images. (A) MOLA hillshade image showing the location of three study regions in Ius and Melas Chasma within the Valles Marineris. Zoom-in regions below show locations of CRISM images FRT0009B27, FRT0000A396, and FRT0000AD3D in context with nearby CRISM images (overlain on HiRISE and CTX images). Doublet-bearing units in CRISM images B27 and AD3D are light toned and tend to drape pre-existing topography; CRISM image A396 shows that the doublet-bearing material corresponds to a blocky, brecciated unit. (B) Examples of spectral variation within the doublet-bearing units, ranging from a stronger 2.205 \( \mu \text{m} \) absorption to a stronger 2.269 \( \mu \text{m} \) absorption. (C) Histograms showing positions of the 2.205 \( \mu \text{m} \) (blue) and 2.269 \( \mu \text{m} \) (red) band positions for every doublet-bearing pixel in each of the three images and (D) histograms showing the relative strength of the two absorption features (Band 1 = \( \sim 2.205 \mu \text{m} \); Band 2 = \( \sim 2.269 \mu \text{m} \)). Values in (C) and (D) are based on Gaussian fits as described in the text. Data for each column in (B), (C), and (D) correspond to the CRISM FRT images labeled and highlighted in red in (A). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.4. A case study: doublet-bearing materials in Ius Chasma, Mars

This study is focused on the spectral characteristics of materials found on Mars and how they relate to those in Rio Tinto as seen in field, airborne, and lab data, with the goal of assessing whether or not the latter may be appropriate mineralogical analogs. However,
to fully understand the processes and environmental conditions associated with the deposits on Mars, and whether or not Rio Tinto is an appropriate process analog, it will be necessary to conduct detailed mapping studies that place the martian examples in their proper geologic context. We conducted a small-scale examination of MRO HiRISE and CTX images of the doublet-bearing materials in Valles Marineris to get a sense of the stratigraphic position of these deposits with respect to surrounding strata.

As discussed by Roach et al. (2010), some occurrences of the materials with the doublet absorption are in proximity to Fe/Mg clay-bearing strata. However, in many cases the contacts between units are obscured and bedding is not apparent, making it difficult to determine the relative stratigraphic position of these units. Despite these complications, it is clear that the doublet absorptions are commonly associated with light-toned units that drape pre-existing topography and span a range in elevation (e.g., Fig. 10a) or as deposits within the topographically lower portions of the chasma (e.g., Fig. 10b). In some locations the doublet unit surrounds the clay-bearing units, whereas in others the clay-bearing unit is located higher up the canyon wall. The doublet material also occurs as matrix in megabreccia deposits (Roach et al., 2010), an example of which can be seen in CRISM image FRT0000A396 in Fig. 9. We now discuss a case study for one region in Ius Chasma where several doublet-bearing units are in proximity to Mg/Fe clay-bearing strata, focusing on the relative stratigraphic position of these units in order to assess the relationship between the observed mineral assemblages in a more detailed geologic context.

The relative strength of absorptions in the doublet feature were mapped for several CRISM observations in Ius Chasma and overlain on HiRISE and CTX images (Fig. 11). This map reveals both the full extent of the doublet-bearing units and allows for further discrimination of spectral properties within and between the different units. Each colored pixel meets the criteria of having band depth $>0.005$ at both 2.205 and 2.269 μm. Where the ratio of band depths (BD 2.205/2.269 μm) is small, we interpret the unit to be enriched in the $\sim2.27$ μm phase, and a higher ratio represents the opposite, in a strictly relative sense. In some locations (Fig. 11c) there is a full transition between these cases within a single unit. In this example, the unit is heavily brecciated and lacks clear stratification. This example fits within a larger regional trend where the doublet-bearing units with the strongest $\sim2.27$ μm absorption are in the south, and seemingly higher up the walls of the chasma, which then transitions to a topographically lower region where the doublet has an absorption with two bands of equal strength, and finally to the north where the $\sim2.21$ μm absorption becomes stronger in the floor units (see the red-to-green-to-blue northerly progression in Fig. 11b). In this example it is clear that the doublet-bearing unit is quite heterogeneous with regard to the strength of the two absorptions, suggesting the relative abundances of the phases responsible for these absorptions are also highly variable within this single geologic unit.

A second example reveals changes in composition that are consistent with geomorphologic changes and that conform to geologic contacts. Three doublet-bearing units ("bright", "light", and "moderate"-toned) and a darker, stratified, Mg/Fe clay-rich unit are shown in Fig. 11d, with close-up HiRISE views of the contacts between these units presented in Fig. 12. The Mg/Fe clay unit has tilted strata (dipping approximately north/northwest, see Fig. 12b) and spectra for these units do not meet the criteria for being “doublet bearing” (with the exception of a few pixels that have high band ratios and therefore higher amounts of the $\sim2.21$ μm component). These stratified Mg/Fe clay units are superposed by a light-toned doublet-bearing unit. The significant difference in bedding geometry and the sharp nature of the contact suggests there is an angular unconformity between these units, with the clay strata predating the doublet-bearing unit (Fig. 12b). This light-toned doublet unit has a relative band strength ratio of $\sim1$, meaning the absorptions within the doublet are of equal strength (however, this does not necessarily imply that there must be equal amounts of each component). Overlying this unit is a second doublet-bearing unit that is moderate in tone but that exhibits similar morphological characteristics as the light-toned unit (Fig. 12c). At full HiRISE resolution it is apparent that both the light and moderate-toned units are stratified. The moderate-toned unit has a band strength ratio between 1.2 and 1.8, indicating the shorter wavelength ($\sim2.21$ μm) absorption is stronger.

The third unit in this region corresponds to pixels with band ratios $<0.9$, consistent with it being enriched in the longer wavelength ($\sim2.27$ μm) component relative to the other doublet-bearing units in this location. This unit is the brightest in grayscale.
HiRISE and CTX images and is overlain by the light-toned unit (Fig. 12d). In this location there is no direct contact between the dark-toned Mg/Fe clay strata and this bright unit, thus the relative stratigraphic order cannot be determined. However, in nearby locations it appears that this bright-toned unit that is characterized by a stronger ≈2.27 μm band is also stratigraphically above the Mg/Fe clay-bearing unit, though these individual outcrops are too small to identify compositionally with CRISM. Therefore, the apparent increasing stratigraphic order is: Mg/Fe clay strata—(angular unconformity)—bright unit—light unit—moderate unit. The associated mineralogy above the unconformity appears to decrease in the longer wavelength (≈2.27 μm) component and increase in the shorter wavelength (≈2.21 μm) component upsection, at least in a relative sense.

Together, these two examples indicate that the relationships between the minerals responsible for the doublet feature and the local stratigraphy are diverse. In the first example there appears to be spectral variation, and thus relative changes in mineral abundance, within a single geologic unit. In the second case the dominant spectral variations appear to conform to stratigraphic
boundaries, indicating differences in relative mineral abundance as a function of geologic unit and stratigraphic position.

5. Discussion

5.1. Mineralogy

The CRISM spectral doublet feature is similar to features observed in airborne, field, and laboratory spectra of materials in and around Rio Tinto, Spain. As discussed above, XRD analysis of select Rio Tinto samples demonstrates that this spectral doublet arises from a mixture of Al-bearing phyllosilicates and jarosite. By analogy, CRISM spectra exhibiting the doublet feature may also arise from a mixture of Al-phyllosilicates and jarosite, one of the possibilities discussed by Roach et al. (2010) and Weitz et al. (2014). This interpretation is supported because (1) the two absorptions that comprise the doublet feature vary independently, suggesting at least two phases are present, (2) the absorption features within the martian doublet examples occur at the same wavelength positions as observed in the Rio Tinto spectra and are consistent with Al-OH and Fe-OH vibrations, and (3) the doublet-bearing material occurs on Mars in the vicinity of other phyllosilicate and/or jarosite-bearing deposits. Therefore, we conclude that Al-phyllosilicate–jarosite mixtures in the Rio Tinto may serve as spectral analogs for the doublet materials found in the Valles Marineris and elsewhere on Mars. However, whether or not the Rio Tinto deposits may also serve as process analogs warrants further study, as discussed below.

Other suggestions for the doublet feature have included opaline silica and clay, mixtures of sulfates (e.g., gypsum and jarosite), and poorly crystalline Fe–SiO₄-bearing phases. Reflectance spectra of opaline silica do exhibit a broad absorption feature from 2.2 to 2.26 μm (Milliken et al., 2008), but it has been noted that this feature is typically too broad to match the doublet even when...
mixed with Fe-rich clay such as nontronite (Weitz et al., 2014). One of our Rio Tinto hand samples, RT23, provides a natural example of an intimate mixture of jarosite and gypsum in which there are similar proportions of both phases and no phyllosilicates (Fig. 5). The reflectance spectrum of this sample is clearly dominated by the H2O absorptions characteristic of gypsum and an absorption near 2.2–2.3 μm that is wider than observed for the typical doublet feature. In addition, although gypsum exhibits very narrow absorption features near ∼2.22 and ∼2.27 μm, these are rather weak and they are superposed on the much broader and stronger feature that spans the ∼2.08–2.3 μm region (see gypsum spectrum in Fig. 1). By contrast, the absorptions in the doublet feature do not appear to be superposed on any broader feature and each appears to be much stronger and more clearly defined than the narrow features observed at similar wavelengths in gypsum. In summary, it does not seem possible to recreate the shape of the doublet feature through a combination of only gypsum and jarosite, thus we consider the doublet feature to be most consistent with a mixture of an Al-phyllosilicate and jarosite. In our Rio Tinto samples the Al-phyllosilicate is dominated by illite or muscovite and is likely to be detrital, sourced from the surrounding country rock. In contrast, the jarosite, which in some samples occurs as a coating, is authigenic and a natural product of the Fe- and S-rich, oxidizing, acidic conditions that characterize the Rio Tinto system. The decrease in jarosite with progression in age suggests it is not stable over geologic time in the continued presence of water, particularly for circum-neutral and higher pH fluids. Indeed, we observe the doublet feature only in spectra that contain jarosite, which are primarily associated with the youngest deposits such as those at Anabel’s Garden and at the Source Spring. It is notable that in our Rio Tinto samples the spectral doublet feature can be directly attributed to relatively well-crystalline phases as there is no clear spectral or XRD evidence for hydroxylated poorly crystalline phases that may result from the acidic leaching of clay minerals. This is not to say that such processes do not occur in these locations, but rather to note that the presence of acid-leached clays or hydrated poorly crystalline precipitates are not required to explain the presence of the spectral doublet feature in the samples examined here.

The same may not be true of the doublet-bearing materials on Mars. There, acidic leaching of basaltic and/or pre-existing smectitic clays may be an important process for forming alteration minerals, including some sulfates such as jarosite (e.g., Tosca et al., 2004; Golden et al., 2005). As noted above, acid-leaching of clays has also been invoked to explain the presence of the spectral doublet feature on Mars (Tosca et al., 2008b; Roach et al., 2010; Doe Dobrea et al., 2011; Weitz et al., 2014), and the occurrence of jarosite in some locations is indicative of low-pH conditions, at least at a local scale. It is possible to make a poorly crystalline Fe–SiO2-bearing material through the acid leaching of nontronite, and reflectance spectra of such products can exhibit absorptions with band centers similar to those observed in the doublet feature (Madejova et al., 2009; Roach et al., 2010). In this scenario, the relative strengths of the absorptions may vary based on the degree of acid alteration. However, spectra of residues from the acid leaching of nontronite may be more consistent with Si-rich, opaline-like materials, and in these cases the full width of the resulting doublet feature is slightly wider than is observed in the martian examples (Tosca et al., 2008b; Altheide et al., 2010).

As a different example, reflectance spectra of Fe/Mg smectite-rich altered basalts from Mauna Kea, Hawaii that have undergone acid leaching exhibit a doublet feature that is thought to arise from the presence of jarosite and halloysite (Graff et al., 2012). In this instance the spectral doublet feature is the result of two distinct (presumably authigenic) mineral phases likely produced by dissolution/formation of pre-existing phases and not associated with a poorly-crystalline leached clay residue. The spectral characteristics of halloysite-jarosite mixtures, as presented in Graff et al. (2012), are more consistent with the doublet characteristics observed on Mars than are the spectral characteristics of a Si-rich leached clay residue. Spectra of the latter tend to exhibit absorptions in the ∼2.2–2.3 μm region that span a slightly broader wavelength range than the martian examples and for which the individual absorptions are not as narrow or well-defined as the martian examples. Halloysite and kaolinite are spectrally similar in the ∼2.2–2.3 μm region, thus halloysite-jarosite, kaolinite-jarosite, and montmorillonite/illite–jarosite mixtures could all be consistent with the martian doublet materials.

Perhaps akin to the observations by Graff et al. (2012), laboratory experiments by Tosca et al. (2008b) indicate that dissolution of basalt and addition of sulfur could lead to fluids that form precipitates under oxidizing conditions whose spectra also exhibit a doublet between 2.2 and 2.3 μm (see example spectrum in Roach et al., 2010). Though some of the precipitates generated during these experiments were X-ray amorphous, others exhibited XRD patterns consistent with neoformation of jarosite, Fe–oxides, and opaline silica (Tosca et al., 2008b). VIS-NIR reflectance spectra of these precipitates were also consistent with the presence of opaline silica, minor jarosite, and an Al–OH bearing phase, though the mineralogical host(s) of observed Al–OH bands at ∼2.21 μm was not directly evident in the XRD data and it/they may be below the XRD detection limit.

### 5.2. Formation processes: detrital and authigenic

From a process point of view the distinction between the scenarios described above may be somewhat semantic. The important point is simply the recognition that dissolution and alteration of basaltic materials on Mars, including cases where clay minerals may already be present, can lead to fluids capable of forming jarosite and Al-rich phyllosilicates. However, co-occurrence in the martian deposits does not necessarily imply that both jarosite and Al-phyllosilicates were formed at the same time, under the same conditions, or even in the same region. Either mineral could be detrital or authigenic in the doublet-bearing units, and detailed geo-logic context in conjunction with an assessment of the full mineral assemblage is needed to assess which scenario is most likely.

Given that halloysite, kaolinite, muscovite/illite, and montmorillonite all exhibit an absorption feature at ∼2.21 μm and that all have been identified on Mars from CRISM data (Ehlmann et al., 2009), it may be difficult to unambiguously determine which Al-bearing phyllosilicate is present in these purported mixtures using VIS-NIR reflectance spectroscopy alone. There is evidence in some of the martian spectra that the doublet feature may exhibit a shoulder on the short wavelength side of the ∼2.21 μm absorption, indicating a weak and narrow absorption may be present in the ∼2.15–2.21 μm region. If true, this could be more consistent with the presence of kaolinite or halloysite as the Al-bearing phyllosilicate as opposed to illite or muscovite or montmorillonite. The presence of jarosite would indicate low-pH conditions (at least locally), and previous studies have noted that kaolin minerals can be formed under acidic conditions (e.g., Fialips et al., 2000). On Mars, oxidation of fluids enriched in ferrous iron could lead to local (and transient) acidification, which could promote jarosite formation if sulfides are present or if sulfate is present in solution (e.g., Hurowitz et al., 2009, 2010).

The processes described above indicate the possibility that both the Al-phyllosilicates and jarosite are authigenic and thus indicative of local aqueous geochemical conditions. Though some Al-phyllosilicates can form under moderate to low-pH conditions, particularly kaolinite, an alternative possibility is that the Al-phyllosilicates in the martian doublet materials are detrital. In
this scenario the jarosite would be indicative of local aqueous conditions and the phyllosilicates would reflect eolian or aqueous sediment transport processes. If true, the doublet-bearing units in Valles Marineris may be similar to Rio Tinto in terms of mineralogy and process, in which case the relative proportions of Al-phyllosilicate and jarosite in a given deposit could reflect the relative contributions of sediment input and mineral precipitation, respectively. Recent experimental work by Dixon et al. (2015) demonstrated that jarosite dissolution is not strongly dependent on hydrologic conditions and that 1 mm jarosite particles are unlikely to survive for more than $10^3$–$10^4$ years even at low flow rates (~0.01 L/h). Therefore, while it is possible that the jarosite on Mars may be detrital, this is unlikely to be the case for long-lived fluvial transport systems, similar to the lack of jarosite observed in the older deposits at Rio Tinto. That stated, because we cannot constrain the particle size of the jarosite we cannot rule out eolian transport for this component.

A detailed ‘source to sink’ and stratigraphic study of the geologic setting of each of the doublet-bearing units on Mars is needed to help determine which ones may represent diagenetic/authigenic phases (do observed mineral boundaries cut across the stratigraphy?) versus those that may be detrital (do variations in mineralogy conform to stratigraphic boundaries?), which is beyond the scope of the current study. However, given the diversity in morphologic properties of the doublet-bearing units within Valles Marineris and the results of the case study described above, it is likely that multiple formation processes are responsible even though the spectral signatures are similar.

The massive brecciated deposit in Ius Chasma that shows a relative transition from more jarosite to more Al-phyllosilicate within a single geologic unit (first example in our case study, Fig. 11c) could be evidence of in situ alteration. Similarly, the thin draping units such as the one shown in Fig. 10a are difficult to explain by processes other than airfall deposition (e.g., Weitz et al., 2014), which would suggest a relatively fine grain size and thus make the original sediment more susceptible to chemical alteration if it has not been welded. In this case, the draping unit may be an airfall dust or volcanic ash deposit, either of which could contain sulfur, that was later altered by water, possibly in the form of thin films from melting snow or ice. Atmospheric sources of sulfur (e.g., from volcanic emissions) could also contribute to authigenic sulfate formation. Regardless of the source, local differences in iron and/or sulfur content of the original sediment would lead to different authigenic mineral assemblages, such as different amounts of Al-phyllosilicate and jarosite (Michalski et al., 2013).

The second example in our case study of Ius Chasma, where Mg/Fe clay-bearing strata are unconformably overlain by layers that differ in amounts of inferred jarosite and Al-phyllosilicate (Figs. 11 and 12), may be more consistent with changes in sediment flux and/or source region. The stratigraphic order of these units indicates the large Fe/Mg clay unit pre-dates deposition of the units with the doublet feature. Indeed, there is no clear genetic relationship between the Mg/Fe clay unit and the doublet units, suggesting the latter are inconsistent with in situ alteration or leaching of the former. One possible interpretation is that the different proportions of the Al-phyllosilicate component, which correspond to distinct stratigraphic units, represent changes in sediment flux and/or source region, perhaps where an increase in Al-phyllosilicate corresponds to a more highly weathered source region. Unlike the other example we presented for this region, the relative strength of the ~2.27 µm jarosite absorption also appears to conform to stratigraphic boundaries. This may indicate that the jarosite is also detrital, but an authigenic origin is possible as well since pore fluid flow or chemistry may be stratigraphically controlled.

If this sequence in Ius Chasma does in fact represent different relative amounts of authigenic jarosite and detrital Al-phyllosilicate, then we are potentially observing an upsection transition from precipitate (jarosite) dominated lithologies to ones dominated by clastic input. Such stratigraphic changes in mineralogy could be formed in a variety of environments, and without modal abundances for these minerals it is difficult to narrow the possible interpretations. However, possibilities include decreasing either the abundance of jarosite cement (which may or may not correspond to a change in absolute Al-phyllosilicate content), the availability of water, and/or Fe or S availability. Alternatively, a change in redox conditions, pH, or an increase in detrital input through time could also influence the relative proportions of jarosite and Al-phyllosilicate. Regardless, the observation that there are deposits suggestive of both in situ alteration and a combination of detrital influx of clay and precipitation of sulfate shows that multiple aqueous processes were likely responsible for formation of the doublet-bearing materials.

One of the most intriguing features of the doublet-bearing rocks at Rio Tinto is that the associated mineral assemblage is not preserved through geologic time in a terrestrial environment. Influx of fresh meteoric water removes sulfates, including jarosite, and results in a net increase in ferric oxides, predominantly goethite, through time (Elwood Madden et al., 2004; Golden et al., 2005). The transition from young sulfate-rich streambed deposits to older ferric oxide-rich terraces takes place in less than a million years, which is in agreement with jarosite dissolution rates reported by Dixon et al. (2015). That study also noted that jarosite dissolution rate is more likely to be controlled by mineral-surface reaction rates rather than hydrologic conditions. Assuming that the Valles Marineris deposits have been exposed on the surface since at least the Early Amazonian, the apparent persistence of jarosite indicates that interaction between the doublet materials and water (e.g., diagenetic overprinting) has been rather limited since the time of jarosite formation or deposition. Thus, while water is required for the formation of jarosite and phyllosilicates, and for some occurrences of the doublet materials water may have acted as a sediment transport agent, it is likely that post-deposition water-rock interaction has been significantly limited in these regions for hundreds of millions of years or longer.

In summary, it is important to keep in mind that the presence of a mineral or mineral assemblage in and of itself is not necessarily indicative of local aqueous geochemistry for a given outcrop or region. Mineral identifications, particularly those determined at spatial scales that are typical of orbital spectrometers (10 s of meter per pixel or greater), must be placed in proper context to determine how they relate to geologic processes and environmental conditions. Specifically, it is critical to determine which minerals may be detrital versus authigenic (to the extent possible) and to assess the textural relationships between different mineral phases. Do sulfates and/or phyllosilicates occur as cementing agents, vein fill, or clasts? For minerals that are indicative of specific chemical conditions, such as jarosite, does the abundance and/or presence of the phases require those conditions to be persistent or might they represent short-lived exceptions to very different background conditions? As it stands, addressing such questions typically requires detailed small-scale observations that are only achievable by rovers or humans, thus caution should be exercised when interpreting orbital observations in terms of specific geologic processes, particularly at small spatial scales.

6. Summary and conclusions

An enigmatic doublet feature in reflectance spectra has been observed alongside hydrated mineral deposits in a number of
regions on Mars. Previous studies have proposed that this spectral signature could arise from mixtures of hydrated minerals with known absorptions between 2.2 and 2.3 μm, including jarosite, gypsum, silica, Fe/Mg smectite, and Al-phyllosilicates. Possible spectral and mineralogical analogs from Rio Tinto are analyzed with a combination of laboratory, field, and aerial reflectance spectrometry and XRD analysis of the mineralogy and reveal that the doublet arises in rocks containing both illite or muscovite and jarosite. The martian doublet materials are also consistent with a mixture of Al-phyllosilicate and jarosite because (1) the wavelength positions of the martian doublet absorptions are similar to those observed in Rio Tinto data collected at lab, field, and airborne spatial scales, (2) the wavelength positions and widths of individual absorptions are consistent with the presence of Al-OH and Fe–OH-bearing minerals, and (3) the strengths of the two absorptions in the doublet vary independently, implying the spectra represent a mixture of two or more components. Likely Al-phyllosilicates for the martian examples include montmorillonite, illite, and kaolinite/halloysite.

Two scenarios are proposed for the creation of these clay-sulfate assemblages on Mars in the context of a case study of deposits in lus Chasma. In one example there are clear mineralogical changes (variations in relative proportions of jarosite and Al-phyllosilicate) within a single breccia unit. These deposits are consistent with in situ jarosite formation, possibly linked to diagenetic fluids. In a second example, observed changes in the relative proportions of the two minerals appear to follow stratigraphic boundaries, and in all cases the doublet-bearing units lie unconformably over Mg/Fe clay-bearing strata. A detrital origin for both phases cannot be ruled out in this case, but it is also plausible that the observed changes in mineralogy reflect changes in the relative contribution of precipitates (e.g., jarosite) versus detritus (e.g., Al-phyllosilicates) through time. Both detrital and authigenic origins are consistent for different doublet-bearing deposits in lus Chasma, and the complexity of these deposits demonstrates the need for detailed mapping of each occurrence to decipher their likely geologic history. The results of such detailed mapping studies will ultimately provide the most insight into what these deposits record about aqueous activity, preservation potential, and water–rock–atmosphere interaction on Mars.

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Supplementary materials

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References
