Diverse mineral assemblages of acidic alteration in the Riotinto area (south-west Spain):
implications for Mars

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Short title: Acidic alteration in Riotinto: implication for Mars

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ABSTRACT

Earth analogs are indispensable to investigate mineral assemblages on Mars because they enable detailed analysis of spectroscopic data from Mars and they aid environmental interpretation. Samples from four sites in the Iberian Pyrite Belt (El Villar, Calañas, Quebrantahuesos, and Tharsis) were investigated using mineralogical, chemical and spectroscopic techniques, with a focus on clay minerals and alteration environments. They represent Earth analogs of areas on Mars that underwent acidic alteration. X-ray diffraction and transmittance mid-infrared data indicate that the rocks were subjected to several degrees of acid alteration corresponding to assemblages characterized by the following mixtures: (1) illite, chlorite, interstratified chlorite-vermiculite, kaolinite-smectite, and kaolinite; (2) illite, kaolinite and alunite; (3) jarosite and goethite. According to mineral stability data, these three assemblages correspond to pH values 7-5, 5-3, and < 3, respectively. The lack of goethite in the illite-kaolinite-alunite assemblage suggests alteration in reducing conditions. Illite was progressively dissolved by acidic alteration but is sufficiently resilient not to be diagnostic of the intensity of the alteration. Illite and kaolinite were the two most abundant phyllosilicate minerals observed and the main reaction involving phyllosilicates was the alteration of illite to kaolinite. Mixed-layer phases appeared mainly in the mildest degree of acid alteration, with few exceptions. This suggests a transition from a mechanism dominated by transformation to a mechanism dominated by dissolution-precipitation as the intensity of the acid alteration increases. Our results highlight the sparse kaolinite-alunite occurrences on Mars as worthy of specific investigation. Acid-alteration on Mars is expected to be patchy and/or consisting of fine alteration rims. Alunite occurrences on Mars in the absence of goethite may indicate acid alteration in reducing conditions. Kaolinite produced through acid alteration on Mars is expected to exist mainly as an end-member phase of low crystallinity, which would enhance IR absorption and increase its visibility.

Keywords: Acid alteration, Alunite, Jarosite, Kaolinite, Mars
Aluminum-rich phyllosilicate deposits are relatively abundant on Mars, and some of them include kaolinite (Carter et al., 2013). They typically have the spectral character of kaolinite mixed with aluminous smectites (McKeown et al., 2011), also typically associated with deposits of amorphous silica and oxides/hydroxides. For example, in Mawrth Vallis, a widespread deposit contains spectral evidence for kaolinite, hydrated silica, and, occasionally, montmorillonite (Bishop et al., 2008; McKeown et al., 2009; Noe Dobrea et al., 2010). Other phyllosilicate deposits on Mars including kaolinite are found in Nili Fossae (Ehlmann et al., 2009), the Eridania Basin (Noe Dobrea and Swayze, 2010), Sinus Meridiani (Wiseman et al., 2008) and in numerous small outcrops throughout the ancient crust (Wray et al., 2009). Kaolinite-bearing units are typically observed overlying deposits of Fe/Mg-phyllosilicates, which are both thicker and more abundant globally on Mars than the kaolinite deposits (Carter et al., 2013). Observations suggest that the contact relationship between the two is either unconformable sedimentary contacts or an alteration front of pedogenic or acidic character (Ehlmann et al., 2009; Michalski et al., 2013).

Age estimates of the aluminous clays, where they occur in large areas that allow for statistically significant crater counts, suggest that they date to the Late Noachian-Early Hesperian period (~3.5-3.7 Ga; Bibring et al., 2006; Loizeau et al., 2011). The later dates in this age range are the same of sulfate deposits and correspond to a time of high volcanic activity on Mars (Ehlmann et al., 2011). Sulfate deposits, among which jarosite and alunite have been identified, are considered to indicate a period of acidic alteration. To date, kaolinite has not been found in association with jarosite on Mars but there is evidence of one intimate association of kaolinite and alunite (Ehlmann et al., 2016). Therefore, it is plausible that some of the kaolinite and accompanying Al-rich phyllosilicates developed as a result of acidic alteration of basaltic rock, volcanic ash, Fe/Mg-rich phyllosilicates, or even a mixture of phyllosilicates with a range of Al-Mg-Fe composition (Altheide et al., 2010;
Acidic alteration would be an effective mechanism of generating kaolinite on Mars and would enable faster reaction than neutral conditions, which could be important as liquid water may not have been available on the surface of Mars long-term.

Studies of analog sites on Earth highlight components of the geological and mineralogical processes that support interpretation of weathering on Mars. The Iberian Pyrite Belt, SW Iberian Peninsula, contains sites that can be used as natural analogs of Martian rocks that have been altered in acidic environments (Amils et al., 2007). Some of such studies have been conducted in this region aimed at testing the ability of mineralogical identification tools (Sobron et al., 2014) and developing a remote-sensing approach that can be used on Mars to identify sites of mineralogical interest (Roach et al., 2006). Sedimentary mineral assemblages along the Rio Tinto river, which has an average pH ~2, have been investigated concluding that the assemblages were mainly mixtures of minerals formed in a variety of geological environments and that little equilibration of the minerals occurred during transport and deposition (Fernandez-Remolar et al., 2011). These results highlight the challenge of differentiating mineral assemblages representing uniform environmental conditions from those resulting from transport or short-lived processes (Fernandez-Remolar et al., 2011). We have investigated samples from rocks that were altered in situ by acidic fluids during geologically significant times in four different sites within or near the Riotinto area. We are documenting alteration of these rocks using multiple techniques and the alteration phases (phyllosilicates, sulfates, iron oxides/hydroxides) are relevant to alteration on Mars, despite the more silicic parent rocks at the Riotinto site. The present chemical and mineralogical investigation is aiming to set constraints on the mineralogy and composition of assemblages on Mars that may have resulted from acidic alteration, as well as on their textural characteristics and on the specific environmental conditions in which they formed. Although the Riotinto site experienced much greater water availability than expected for Mars and alteration on
Mars may have involved a large proportion of water ice (Michalski et al., 2013), characterizing sites such as this provides important geochemical constraints for understanding acid alteration on Mars.

MATERIALS AND METHODS

Geology of the investigated area

Four localities in the Iberian Pyrite Belt (Quebrantahuesos in the Riotinto district, El Villar, Calañas and Tharsis, Appendix Figure A.1) were sampled for the laboratory investigation of the rocks and their clay constituents. The parent rocks belong to an Upper Palaeozoic (Late Famennian-Visean) volcano-sedimentary complex including siliciclastic sediments and mafic and felsic volcanics, all of which underwent hydrothermal alteration associated to the emplacement of large amount of massive sulphide orebodies (Toscano et al., 2014). After this, Miocene erosion and subaerial exposition caused the oxidation of pyrite-rich orebodies which provided mild to extreme acidic fluxes that leached the surrounding rocks for over 20 million years (Essalhi et al., 2011). The mineral assemblages are strongly dependent on their acidic alteration intensity. Thus, the rocks that were altered by the acidic fluids were not the pristine volcanic rocks, but the rocks formed after hydrothermal alteration. In the following paragraphs we provide an introduction to each of the sampled sites. The identification of the original rocks, the products of hydrothermal alteration and the products of the subsequent acidic alteration are based on previous studies, published and unpublished (including confidential information generated by mining activity), and on our investigation. The interpretation of the existence and intensity of acidic alteration in the specific samples follows the standard paragenetic concepts.

The Quebrantahuesos (Q) area is located in the Cerro Colorado open pit, within the Riotinto mining district. The samples originate from a sequence of felsic porphyritic volcanic rocks and tuffs
on top of the Quebrantahuesos-Salomon orebody (Adamides, 2013). These rocks were first
hydrothermally altered to chloritic porphyry, rich in chlorite and quartz, during polymetallic
sulphide emplacement (Adamides, 2013; Martin-Izard et al., 2015). The later acidic alteration is
very intense, generating assemblages with abundant quartz, alunite and minor illite.

The El Villar section (EV), located west of the Riotinto mine, is a sequence of basic volcanics
(basalts) with minor felsic rocks (rhyolites and dacites). The samples for this study come from a 20
m horizontal sequence and follow a generally increasing alteration path from hydrothermally
altered basalts, with little subsequent acid alteration (plagioclase is still abundant), to kaolinite-rich samples.

The Calañas (C) outcrop is located in a sequence of acidic tuffs. The mineralogy of the materials
that were not altered by acid fluids is mainly quartz and illite due to intense hydrothermal
alteration associated with the sulphide mineralization event. Acidic alteration of this sequence is
moderate and kaolinite appears as an alteration product of illite.

The Tharsis (TH) outcrop is a highly deformed and altered sequence of shales with minor felsic
volcanics and small lenticular masses of sulfides. Hydrothermal alteration associated with the
emplacement of the sulfide masses generated quartz, kaolinite and illite in the country rock
shales. The acidic alteration of the shales progressed substantially and there is abundant quartz,
with kaolinite, illite, sulfates and goethite, while the sulfide lenses were altered mainly to goethite
and jarosite/beudantite (Capitán et al., 2003).

**Samples**
The samples were collected between September 29 and October 3 of 2014. The site with the rock composition and acidic alteration pathway most relevant to Mars is likely that of EV. For this reason, this site was sampled with the greatest detail and resolution. The rocks that underwent the acidic alteration consist of sericitic illite, chlorite, quartz and plagioclase/feldspar, the result of the previous hydrothermal alteration of mafic volcanic rocks. A total of 26 samples were collected. Of these, 16 were selected for the full study after a preliminary X-ray diffraction (XRD) investigation (whole rock, random powder), using criteria of representativeness (samples that best represented the mineralogical changes taking place, avoiding selection of several samples with very similar mineralogy), clay content (other variables being equal, samples with more clay were selected) and clay mineralogy (samples that best represented mineralogical changes by their clay mineralogy and variety of clay minerals present) (Table 1). The same sample selection criteria were applied to the other sites. Another suite of samples are from the Quebrantahuesos (Q site) hill, within the active mine in Riotinto. The rocks sampled have disappeared now due to further mining. Fifteen samples were collected, from which 8 were selected for detailed analyses. They are a suite of strongly altered rocks, situated below or near the original pyrite body that generated the acidic fluids. The rock that underwent acidic alteration (sample QX) consists mainly of quartz and chlorite (Table 1). Three samples were collected from near the village of Calañas (C site), from an outcrop of clay-rich rocks indicating a low level of acidic alteration. Illite and quartz appear to be the main components of the rock subjected to the acidic alteration, although chlorite may have also been present (Table 1). Two samples were selected. Finally, 11 specimens were sampled, and 6 selected, from two outcrops near the locality of Tharsis (TH site). These rocks were subjected to medium to strong acidic alteration. No sample representative of the rock before acidic alteration was identified (Table 1).

**Experimental methods**
All samples were crushed mechanically in a jaw crusher and then ground, first with a planetary agate mill and then by hand to a fine powder with a mortar and pestle. Samples were analyzed using XRD for their whole-rock mineralogy in a PANalytical X'Pert Pro diffractometer. The samples were side-loaded to avoid preferred orientation. Measurement conditions were 45 kV, 40 mA, Cu Kα radiation, divergence slit of 0.25°, and Soller 1 and 2 slits of 1.146°. This apparatus uses a solid-state detector (X'Celerator) covering an angle of 2.1° and integrates the diffracted intensity over that angle dynamically as it scans. The powders were scanned in the range 2-80 °2θ, with a resolution of 0.0167 °2θ (scan step in a conventional scanner), and the total collection time was 60 min (equivalent to 0.77 s/step).

Further sample preparation procedures involved the heating of samples at 60 and 107 °C (see below). Such treatments do not cause mineralogical changes in phyllosilicates and are recommended and widely used (Moore and Reynolds, 1997). Phyllosilicates with expandable layers rehydrate after treatment at these temperatures (e.g., Graf et al., 1995; Cases et al., 1997) and they can be properly characterized with subsequent XRD analysis (Moore and Reynolds, 1997). The < 2 μm fraction of the rocks was obtained by dispersion in deionized water and centrifugation. The < 2 μm fraction was concentrated by further centrifugation, dried at ~60 °C in an oven, and gently ground with a mortar and pestle. The clay mineralogy was investigated in these samples with the diffractometer indicated above. Samples were prepared as oriented mounts by dispersing 10 mg of each in 2 ml of deionized water, pipetting the dispersion on glass slides (area of ~4 cm²), and letting them dry. They were studied as air-dry and as treated with ethylene-glycol (EG) by overnight solvation in an EG-saturated atmosphere at 60 °C. The XRD scan range was 2-40 °2θ, with a scan duration of 63 min (equivalent to 1.66 s/step). All other conditions were the same as described above.
For a full description and the quantitative analysis of the clay mineralogy, the X-ray patterns of the oriented mounts, both air-dry and treated with EG, were modelled using ClaySIM from MDI, which uses the Newmod code (Moore and Reynolds, 1997). This program allows calculation of the relative proportion of phyllosilicate minerals present, whether end-member or interstratified phases. This software models the 00l peaks of interstratified minerals with two layer components, and mixtures of up to ten such phases. The modeling uses the full XRD profile (peak positions, peak relative intensities, and peak shapes). The results correspond to relative proportions of each phyllosilicate component (excluding all other phases) and the relative proportion of layer type in each mixed-layer phase (e.g., 35% of a chlorite-vermiculite phase that contains 60% of chlorite layers). Every mineral phase used in our modeling process was necessary to reproduce a peak or inflection in the XRD patterns. The experimental conditions of the scans were used in the program calculations. Modeling of the patterns from the EG-treated samples is usually most accurate because expanding layers (smectite, vermiculite) adsorb EG and have a more uniform d-spacing than in air-dried systems. For this reason, our analysis is based on the data from EG-treated samples. However, consistency between the EG and air-dried models was checked to test the accuracy of the results. The difference between the two for each individual phases ranged 0-13 % layers, with an average of 3 % layer difference. The main crystal-chemical parameters used in the models are: a) type of layers, their relative proportion and their stacking order in the crystals (R parameter; Moore and Reynolds, 1997); b) octahedral Fe content (on the O$_{10}$[OH]$_2$ basis for 2:1 phyllosilicates, O$_5$[OH]$_4$ for kaolinite, and O$_{10}$[OH]$_8$ basis for chlorite) of the layers and of the interlayer brucite-like sheet in the case of chlorite; c) distribution of coherently diffracting crystal thicknesses as defined by the maximum and average number of layers in the coherent X-ray scattering domains; and d) amount of K in illite interlayers. One more calculation parameter is the orientation factor ($\sigma^*$) that represents the standard deviation (in a Gaussian distribution) of the
orientation of the platy clay particles from the horizontal (layers perfectly parallel to the surface of the glass slide).

The < 2 μm fraction of the samples was also investigated using mid-infrared (MIR) transmittance spectroscopy. Spectra were collected using a Perkin Elmer Spectrum One FTIR spectrometer. One mg of each sample was mixed with ~200 mg of KBr and gently ground to generate a fully homogeneous mixture that was then pressed at 10 t for 1 min to produce a pellet. Pure KBr was used as a background, subtracted from the collected spectra. Infrared transmission spectra were recorded over the range 400–4000 cm\(^{-1}\) at a spectral resolution of 4 cm\(^{-1}\). Eight spectra were accumulated for each analysis. The spectra were then converted to absorbance units.

The chemical composition of the samples was investigated in the whole and < 2 μm fractions following Thompson and Walsh (2003). Samples were kept in a desiccator at room temperature prior to analysis after drying at 107 °C for a minimum of 12 h. For the determination of major elements and a few selected trace elements, powdered samples (0.1 g) were fused in Pt/Au crucibles with 0.3 g of lithium metaborate, subsequently dissolved in 100 ml of ~1.6 M HNO\(_3\) and diluted to a final volume of 250 ml for analysis. The resulting solutions were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using an iCap 6500 Duo instrument (Thermo Scientific, UK). Reference materials (Stream sediment JSD-2, Geological Survey of Japan; Granite MA-N, International Working Group “Analytical Standards of Minerals, Ores and Rocks”; and Syenite NIM-S, South African Bureau of Standards) prepared by the same method were analyzed with the samples. Analytical error (accuracy) was 3.7-3.8 % of the oxide concentration for Mg, Mn and Na, and < 3 % for all the other major cations.
Sulfur and H were analyzed using a Vario EL cube analyzer (Elementar, GmbH, Germany). Dried and powdered samples of ~10 mg each were weighed in triplicate with the precision of ± 0.001 mg, wrapped in Sn foil capsules, introduced into the furnace and combusted in an oxygen-rich atmosphere at 1150 °C. Reference material JSl-1 (Slate; Geological Survey of Japan) was analyzed with the samples. Analytical error (accuracy) was 12-14 % of the determined SO\(_2\) and H\(_2\)O values.

Water values were obtained only as a reference (to assess mineral alteration and check coherence with mineralogy) because they represented both hydroxyl water in phyllosilicates and adsorbed water on mineral surfaces.

**RESULTS**

**Whole-rock mineralogy**

The mineral content of the samples (Table 1) indicates two groups, one composed by EV and C sites, and the other by TH and Q. Samples from EV and C were subjected to a moderate acidic alteration that produced kaolinite as the most advanced alteration product. The 001 kaolinite peak was wide, indicating high stacking disorder. In samples where other kaolinite peaks were sufficiently intense to be observed, such as the 002 peak and the 020 peak system, they were also wide and lacked modulation, which confirms a low degree of crystal order in the kaolinite resulting from acid alteration. In EV samples, the original rock contained quartz, illite, chlorite and plagioclase/feldspar minerals, as represented by sample EV2 (Table 1). Chlorite disappeared soon as the intensity of the acid alteration increased, in some cases remained with signs of weathering (samples EV5 and EV6; Table 1). Plagioclase was mainly represented by albite, and feldspar by microcline and minor sanidine. Illite and plagioclase/feldspar were present in most samples, indicating that the acidic conditions were not sufficient to destroy them totally. Quartz was not affected. The visual inspection of these rocks indicated that the alteration took place heterogeneously, developing more in fissures and causing patches of different mineralogy to
coexist at cm scale, i.e., within the volume of the individual samples collected. The initial mineralogy of the rocks from C cannot be ascertained from the collected samples, where the existence of chlorite is dubious.

Rocks from TH and Q were subjected to intense acid alteration that produced alunite, jarosite and goethite (Table 1). Chlorite was found only in the rock representing the starting point before acid alteration in Q (sample QX, Table 1). The kaolinite in TH is different from that in EV and C. Kaolinite in TH has narrow peaks and is very abundant in sample TH12, where the lack of alunite and jarosite indicates that the acid alteration here was the least intense. Kaolinite decreased and then disappeared as alunite and jarosite were present (Table 1). Kaolinite and illite coexisted with alunite in one sample, but both phyllosilicates disappeared when jarosite was present. All the above suggests that kaolinite in TH had a hydrothermal origin and was generated together with illite. The subsequent acid alteration was sufficiently intense to destroy kaolinite and illite. Rutile traces were observed in many of the TH and Q samples, indicating concentration due to dissolution of other minerals.

**Clay mineralogy**

The investigation of the < 2 µm fraction provided detailed information about the evolution of the clay minerals in the studied rocks (Appendix Table A.1). For the EV samples, the initial effect was the transformation of chlorite into mixed-layer chlorite-vermiculite (C-V), first coexisting with chlorite (sample EV3; Figure 2) and then without it (samples EV5 and EV6; Figure 2). This C-V, however, only appeared in a few samples (EV3 to EV6). A further effect of acid alteration was the expansion of a few illite layers generating illite-rich illite-smectite (I-S) and illite-vermiculite (I-V) (Appendix Table A.1). However, these changes only generated 2-4% expandable layers that are not easy to observe in Figure 2. There was a clear widening of illite peaks in some cases, indicating
illite alteration (EV11, EV13; Figure 2). The main change affecting illite across the EV sample suite was its progressive disappearance (decrease of the intensity of illite peaks; not shown in Figure 2). Coordinated with illite decrease was kaolinite occurrence and increase (samples EV6 to EV19; Figure 2). In some samples, there was little illite and no kaolinite, with only quartz and traces of plagioclase/feldspar (EV21, 26, 27; Figure 2). The above changes suggest the quick loss of chlorite and the slower loss of illite by acid attack, together with the formation of kaolinite. Then, probably more intense attack eliminated kaolinite leaving only quartz and traces of illite and plagioclase/feldspar. However, the sequence from EV2 to EV27 does not exactly represent the increase of acid alteration intensity due to the heterogeneous character of the alteration.

The two samples from site C contain illite, smectite-rich K-S and kaolinite (Figure 3). Both had little smectite-rich K-S (10 wt% or less) but the amount of interstratified smectite in K-S is larger and more noticeable in C2 (Figure 3; Appendix Table A.1). The amount of kaolinite in C2 was larger than in C1 but still low (~5 wt%, Appendix Table A.1). This is interpreted to indicate that the intensity of acidic alteration increased from C1 to C2.

In the samples from the Q site the abundant chlorite present in the unaltered rock (sample QX, Figure 4) was not present in any of the altered rocks. Minor illite was observed in the < 2 µm size fraction of sample QX, that was not observed in the whole rock (Table 1). Illite concentration in the altered samples ranged from none to medium. In the Q site the intensity of acidic alteration increased from the group of samples containing alunite (Q2 to Q7, Figure 4) to that with jarosite/beudantite (beudantite was the main component in the < 2 µm size fraction as indicated by the XRD data; Q8, Figure 4) and to that with goethite only (Q13, Figure 4). It is possible that the proportion of illite in the unaltered rock was variable and this is reflected in the variable illite
presence in samples Q2 to Q7. No gradual transformation of clays or interstratified minerals were observed in the Q samples.

In the rocks from the TH site, the original illite and kaolinite of hydrothermal origin were much reduced or disappeared in samples containing alunite, jarosite or goethite. Mixed-layering was found in sample TH7, where two K-S phases, one with 80% smectite and the other with 5% smectite layers, were present. The former made up 5% of the total phyllosilicate content and the latter 18% (Appendix Table A.1). Thus, most of the layers in the two interstratified phases were kaolinite.

The modeling of the XRD patterns of the oriented mounts consistently indicated that kaolinite layers contained Fe (Appendix Table A.1). This was shown in the reduced intensity of the kaolinite 002 peak with respect to the 001 peak. Such a result suggests that Fe was inherited from chlorite and illite layers via the observed interstratified phases or via other mode of transformation involving a close connection between the disappearing layers and the neoformed kaolinite layers. The modeling also indicated the presence of Fe in chlorite, with higher concentration in sample QX than in the EV samples (Appendix Table A.1).

Mid-infrared analysis

The results from MIR of the < 2 μm size fraction largely confirmed the results from the XRD analysis, although they provide a different perspective due to the different sensitivity of MIR to the several minerals present. The assignment of the IR peaks is summarized in Table 2, where the diagnostic peaks indicating the presence of the specific mineral phases are listed in bold type. In the EV samples, the O-H stretching region of the spectra (3900-2900 cm⁻¹) was dominated by the kaolinite signature (Table 2) that overwhelmed those of illite, the other major phyllosilicate
component. The illite band, however, can be seen at ~3620 cm\(^{-1}\) as a wide component in the same position as the sharper kaolinite band (Figure 6). The signatures from chlorite (1-21 % layers within the phyllosilicates), vermiculite (2-12 % layers) and smectite (1-4 % layers; Appendix Table A.1) are obscured by those of illite and kaolinite in this part of the spectra. In sample EV26, kaolinite was detected by MIR, whereas it was not detected by XRD (Figure 6, Appendix Table A.1). Hydration water is detected in most samples. The region 1300-900 cm\(^{-1}\) is dominated by the Si-O stretching vibrations, where all silicate minerals have strong bands that combine in a complex system. The band at 916-911 cm\(^{-1}\) corresponds to O-H bending in Al\(_2\)OH groups in illite and kaolinite, and is free from interference from other minerals. This band is more intense and sharper when produced by kaolinite (Figure 6) as described by Russell and Fraser (1994). Quartz is identified by the doublet at ~799 and ~780 cm\(^{-1}\), and plagioclase feldspars by multiple bands in the region 518-475 cm\(^{-1}\) (Table 2).

The MIR spectra of the two samples from the C site (Figure 7) show a mixture of illite and kaolinite, where kaolinite increases from C1 to C2 (1% to 6% kaolinite layers according to XRD, Appendix Table A.1). The small variation of kaolinite content is strongly reflected in the O-H stretch region (3900-2900 cm\(^{-1}\)), whereas the modifications are less noticeable in other parts of the spectrum. The existence of 5-8% smectite layers interstratified with kaolinite (Figure 3, Appendix Table A.1) was masked as most smectite bands are coincident with those of kaolinite and illite. The double band at 532 and 475 cm\(^{-1}\) is indicative of Al-rich, dioctahedral phyllosilicates. This feature can also be observed in the EV samples, although with greater interference from non-phyllosilicate phases (Figure 6).

Samples from Q introduce the intense signatures of alunite and jarosite/beudantite (Figure 8). Sample Q2 has a spectrum consisting of alunite only (except for a trace of quartz). The intense
bands at 3509-3457, 1220-1027 and 670-600 cm$^{-1}$ overlap only partially with the bands of illite and kaolinite, allowing identification of alunite and the assessment of its relative proportion with respect to the phyllosilicates. Samples Q6 and Q7 are illite and alunite mixtures where the signatures of both minerals can be observed. Interestingly, kaolinite is observable in the spectra of both these samples (band at 3703 cm$^{-1}$ and sharp component at 3623 cm$^{-1}$), whereas it was not detected in the XRD patterns of Q6 (Figure 4). The spectrum of sample Q8 is dominated by jarosite/beudantite. The other major mineral phase in the < 2 µm size fraction of Q8 is goethite, represented by the broad band at 3137 cm$^{-1}$ and that at 903 cm$^{-1}$. In the spectrum of sample QX, chlorite is of the trioctahedral type, as indicated by the single intense band at 463 cm$^{-1}$ (in Al-rich, dioctahedral phyllosilicates this band is modulated into two intense bands at 532 and 475 cm$^{-1}$).

The samples from the TH site also provide an opportunity to observe the spectral signatures of mineral mixtures (Figure 9). The spectra of TH10 and TH11 correspond entirely to jarosite, which facilitates the identification of the corresponding features in other spectra. Sample TH9 is a mixture of quartz with minor illite, jarosite and goethite (Figure 9). Quartz was obvious in the MIR spectrum (bands at 789, 779 and 696 cm$^{-1}$). Illite was recognized by the band at 3619 cm$^{-1}$ and the shoulder at 913 cm$^{-1}$. Jarosite was detected by the wide band at 3380 cm$^{-1}$ and the weak band at 630 cm$^{-1}$. The presence of goethite was indicated by the weak and broad band at 3163 cm$^{-1}$. The presence of jarosite was suggested in sample TH5 by the shoulders at 3380 cm$^{-1}$ and just below the peak at 1100 cm$^{-1}$, although no jarosite was detected with XRD (Figure 5). Goethite, kaolinite and quartz were the other phases detected in sample TH5 through intense MIR features (Table 2). Alunite featured prominently with kaolinite in the spectrum of sample TH7. In this sample, illite could be recognized by the shape of the 3621 cm$^{-1}$ peak and by the band at 832 cm$^{-1}$. These two features also enabled recognition of illite in the spectrum of sample TH12, where kaolinite features were the most prominent. One interesting feature of kaolinite in the samples from TH is...
that the low-intensity peak at 3652 cm⁻¹ was more prominent than in most other samples in our study. This peak is one of the two low-intensity peaks of kaolinite in this region (3670 and 3650 cm⁻¹; Russell and Fraser, 1994). The prominence of this peak (and the hint of the one at 3670 cm⁻¹, Figure 9) is consistent with the good kaolinite stacking order indicated by XRD (sharp 00l peaks, Figure 5).

Major elements in the bulk rock

The trends defining major chemical changes taking place during the acid alteration are shown in Figure 10. The complete chemical dataset is available in Appendix Table A.2. The best developed trend is the negative correlation between SiO₂ and Al₂O₃ concentration in the rocks (Figure 10a). For most data points, the extent of acid alteration increases from left to right. The acid alteration caused the decrease of Al, due to dissolution of aluminosilicates, and the increase of Si, due to concentration and, possibly, precipitation of quartz. Quartz is typically resistant to acid attack and was originally abundant in the rock (Table 1). It is also possible that the dissolution of aluminosilicate minerals produced local precipitation of silica that then evolved to quartz. The exception to the rule of increasing extent of acid attack from left to right in Figure 10a is in rocks from the Q site. Sample QX, a rock that was not subjected to acid alteration, had 8 wt% Al₂O₃ and 74 wt% SiO₂, due to high content of chlorite and quartz. Samples Q6 and Q7 had 18 wt% and 21 wt% Al₂O₃ due to high alunite content (Table 1). The two data points with Al₂O₃ < 5 wt% (Figure 10a) are two heavily altered samples consisting mainly of quartz and goethite (Q13 and TH5, Table 1).

There was a broad positive correlation between Fe and Mg contents in the samples (Figure 10b) indicating that the acid alteration typically caused a decrease in both Mg and Fe, due to
dissolution of the silicate phases. The two data points with high Fe and no Mg are Q13 and TH5, mentioned above, both of which had much goethite (Table 1).

It would be expected that Al, Ti, and Zr were correlated in the alteration products because these three elements are rather insoluble, although Al is more soluble in acid conditions than at near-neutral weathering conditions. There is such a positive correlation between Al and Ti, although with two apparent slopes. The two slopes may be caused by the specific alteration conditions and/or the minerals holding Ti (Figure 10c). Rutile was observed in some of the samples with high Ti content (Table 1, Appendix Table A.2). This rutile was probably present originally in the rock and concentrated by dissolution of the silicates. Alteration conditions alone are unable to explain the apparent existence of two groups of data points, corresponding to high and low Ti content, as both groups have samples with little and extensive acid alteration (Table 1, Appendix Table A.2). Zircon also correlated positively with Al (Figure 10d). In this case, all samples from all locations plot in the same broad trend, indicating that the response of Zr and Al to acid dissolution was similar across the several rocks and the range of acid alteration intensity they were subjected to.

One important observation is that the data points from all locations align within the same broad patterns described above. This provides support to (1) a broadly common rock chemical composition generated by the hydrothermal alteration of the previous rocks, and/or to (2) acidic alteration as the most important control of the final mineral assemblage and sample chemistry. In other words, the relative position of the several samples in the chemical plots (Figure 10) is controlled mainly by the extent of alteration, rather than by the locality where they were collected.

**Major elements in the < 2 μm size fraction**

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The chemical composition of the < 2 µm size fraction allows us to trace the reactions taking place among the phyllosilicates (complete dataset in Appendix Table A.3). Comparison of chemical and mineralogical data of this clay-sized fraction highlights points of interest in these reactions (Figure 11). The negative correlation between Si and Al observed in the bulk rock was reproduced in the < 2 µm size fraction for most samples, indicating that much of this correlation was generated in the < 2 µm size fraction (Figure 11a). The three obvious outliers in the plot are TH10, TH11 and Q8, the three samples with the largest content of jarosite/beudantite. These samples had very little quartz and minor or no goethite.

The positive Mg vs. Fe correlation seen in the bulk rock (Figure 10b) also held for the clay fraction of many samples (Figure 11b; this plot contains more data points than that of the bulk rock). Samples from EV and C as well as sample QX exhibit the same broad positive correlation. All these samples experienced limited or no acidic alteration. The samples distributed vertically at Fe₂O₃ > 5 wt% and with low Mg content are five samples from the TH site (all TH samples except the unaltered TH12), plus samples Q8 and EV26. All these samples contain goethite and/or jarosite/beudantite.

The only correlation found between phyllosilicates is a negative one between illite and kaolinite contents (Figure 11c). They are the two most abundant phyllosilicate phases. Except in the TH site, kaolinite was not present in the unaltered rock. Thus the main reaction taking place between phyllosilicates is a substitution of kaolinite for illite, which occurred where the acid alteration was mild. The other clay phases were short-lived or produced in minor amounts. Strong alteration dissolved all phyllosilicates. In the case of the TH site, kaolinite of hydrothermal origin was present and was partially or totally dissolved by the acid alteration (Table 1). However, K-S was also detected (Figure 5, Appendix Table A.1), most likely the result of alteration of illite (as the only one
of the original minerals in TH12 that can react to K-S in acidic conditions), indicating that illite
substitution by kaolinite also took place in TH.

The plot of Fe₂O₃ wt% vs. kaolinite layer % shows that there is no negative correlation between Fe
and kaolinite in the < 2 µm size fraction (Figure 11d). This is partly due to the existence of goethite
and kaolinite in some samples. The most clear example is sample TH5, which had only some little
kaolinite as the only phyllosilicate (100% kaolinite, as phyllosilicate proportions were calculated
relative to phyllosilicate minerals only) and abundant goethite (Figure 5; Appendix Table A.2).
However, there is also a lack of negative correlation between kaolinite and Fe contents in the < 2
µm size fraction of other samples with no goethite, which supports the existence of Fe in kaolinite,
as was found in the XRD simulations (Appendix Table A.1). Indeed, XRD analysis did not detect
goethite in many of the samples with kaolinite and low Fe₂O₃ content shown in Figure 11d. This
result was supported by the MIR investigation, as most samples with Fe₂O₃ < 10 wt% in Figure 11d
did not show traces of goethite in their MIR spectra (Figure 9).

The plot of illite vs K₂O content showed a broad positive correlation between the two variables,
indicating that the XRD modeling is accurate (Figure 11e). Mineral phases containing K other than
illite, such as K-feldspar and alunite broadened the correlation. In addition, there are samples that
do not contain illite but have other K-bearing phases (jarosite, alunite) and samples containing low
levels of illite as the only phyllosilicate (i.e., they correspond to 100 % illite in the plot, as this
figure represents the relative proportion of phyllosilicates only). This minor illite component in the
< 2 µm fraction of these samples does not control the K abundance in them (EV27 and TH9
samples with 100 % illite and K₂O < 4 wt%, Figure 11e).
The plot of chlorite abundance vs. MgO, Fe$_2$O$_3$ and Al$_2$O$_3$ contents allows us to investigate the type of chlorite in the unaltered rock. Iron was calculated as Fe$^{3+}$, although Fe$^{2+}$ was undoubtedly present in chlorite. Mid-IR data indicated a trioctahedral chlorite (i.e., mainly Mg and/or Fe$^{3+}$, as opposed to Al and Fe$^{3+}$) (sample QX in Figure 8). Our modeling of the XRD patterns also indicated a moderate Fe content in chlorite (Appendix Table A.1). Both results were confirmed by the chemical data, as the proportion of MgO and Fe$_2$O$_3$ both increased with increasing chlorite, whereas Al$_2$O$_3$ content decreased with increasing chlorite (Figure 11f). The specific metal oxide values in the plot do not represent the composition of the chlorite(s) because there are other minerals in the < 2 µm size fraction of the samples (non-phyllosilicates) which are included in the chemical analysis, but not in the mineralogical data. Only the trends of MgO and Fe$_2$O$_3$ data are indicative of chlorite composition.

DISCUSSION

Mineral assemblages

Overall, the rocks investigated show expected chemical and mineralogical transformations for alteration in an acidic environment. In none of the sampled sites was there a uniform spatial gradation of the intensity of the alteration moving across the entire group of samples (except, of course, for the C site with only two samples). This can be appreciated inspecting Table 1 and Figure 12. Figure 12 shows that the increase of the intensity of the acid alteration from left to right in the plots (generally, but not necessarily for each sample within the sites) is broadly marked by (1) the disappearance of chlorite, which is very sensitive to acid attack, (2) increase of kaolinite content, (3) alunite formation, and (4) jarosite formation. However, the changes are not smooth. This confirms the visual impression from the rocks, especially obvious in EV and TH, that the alteration was patchy and partially controlled by local fissures and local changes in mineralogy of the original rock (Figure 1).
Figure 12 indicates that alunite is compatible with phyllosilicates, as abundant illite and kaolinite were present with abundant alunite in samples from the TH and Q sites. This is in agreement with frequent mineral assemblages containing these three minerals (Hemley et al., 1969). On the contrary, the presence of jarosite appeared to be largely incompatible with that of phyllosilicates (Figure 12). Jarosite formation typically requires pH < 3 (Brown, 1971; Keith et al., 1979; Das et al., 1996; Arslan and Arslan, 2003), whereas alunite precipitates at pH 2.5-5 (Keith et al., 1979). The stability of kaolinite at pH < 5 requires elevated activities of Al and SiO$_2$ (Garrels and Christ, 1965; Huang and Keller, 1973). For the same Al and SiO$_2$ activities, illite is stable at a pH ~1.5 units higher than the corresponding pH stability threshold for kaolinite (Huang and Keller, 1973). Thus, despite the heterogeneous distribution of the alteration, the individual areas sampled (at cm scale in EV, TH and C; at m scale in Q) indicate an approximation to equilibrium conditions at the several ranges of pH at which the alteration took place. The proximity to equilibrium conditions should increase with decreasing pH, as the fluids become more aggressive and the dissolution reactions faster.

Investigation of an Arctic gossan (High Lake, Nunavut, Canada) has shown coexistence of muscovite and jarosite, both in major amounts (West et al., 2009). Such data do not contradict the above description of mineral stability fields. Rather, they are explained by a large influence of kinetic effects. The acidic attack in the Arctic gossan has been taking place only during the last several thousand years and is slowed down by low temperature and low water activity due to freezing conditions (West et al., 2009). The acidic alteration in Riotinto, however, took place for 40 Ma and is expected to be thermodynamically controlled.

**Mineralogical processes**
Three degrees of intensity of acidic alteration can be distinguished in the studied rocks. The first degree corresponds to alteration with fluids at pH reaching down to ~5, with kaolinite as the main product. This level of alteration is represented by the EV and C sites. At the C site, the simplest of the two systems, there is an increase of kaolinite (Table 1), partially via interstratified K-S (Appendix Table A.1). Because there is the hint of chlorite traces in the XRD patterns of the bulk rock of both C1 and C2 (Table 1), and because there is K-S also in both samples (Figure 3; Appendix Table A.1), it can be concluded that the acidic alteration did not take place with the same intensity in the entire volume of these samples. Chlorite may have been present in the original rock and lost shortly after the alteration onset. In EV samples, there was abundant quartz and some plagioclase/feldspar (albite, sanidine and microcline; Table 1). Quartz was not affected by the alteration fluids and plagioclase/feldspar appeared to be little affected, as they remained abundant across these samples (Table 1, Figure 2). It is expected that K-feldspar has greater resistance to acid attack than albite (Garrels and Christ, 1965) and the permanence of the latter may be related to heterogeneity in the rock composition as well as in the spatial distribution of the acid alteration intensity. Dissolution of chlorite was observed, as well as alteration of chlorite to C-V, and alteration of illite to kaolinite (dissolution-precipitation and/or transformation) (Figure 2), that resulted in loss of Fe and Mg (Figures 10b and 11b). There was also loss of Al (Figures 10b and 11b) that must be due to dissolution of silicates that did not contribute to precipitation of new phases. This is deduced because although the neoformed kaolinite has a higher Al/Si ratio than chlorite and illite, the Al/Si ratio decreased during the alteration process (Figure 10b). Aluminum solubility increases with decreasing pH (steep increase below pH 5; Garrels and Christ, 1965), while that of silica decreases, which two facts may have fostered Al loss over Si during dissolution of silicate phases. Some of the quartz in the EV samples may have originally precipitated as silica that later recrystallized as quartz. Finally, loss of Fe and Mg in EV and TH samples (Figures 10b and 11b; Appendix Tables A.2 and A.4), required reducing conditions to avoid in situ Fe precipitation.
The second level of intensity of the acid alteration is that caused by fluids at pH 3-5, producing kaolinite and alunite (Figure 12, Table 1). This alteration environment occurred in the TH and Q sites. This alteration increases the Al/Si ratio, contrary to the milder acid attack, as far as indicated by available chemical data (compare sample TH12 with TH7, and QX with Q3 to Q7, Appendix Table A.2). This result is expected because both kaolinite and alunite are Al-rich, and alunite has no Si. In order to produce the observed increase in the Al/Si ratio it is necessary that some Si was lost from the system and that less Al was lost than Si. This trend would occur most easily if the rocks were subjected to fluids at pH 3-5 from the beginning of the acidic alteration. If the rocks had experienced first alteration at pH ~5, their Al/Si would have decreased first, making it more difficult to reverse the trend and produce Al/Si ratios higher than in the unaltered rock. Accordingly, the chemical data suggest that the alteration front was always of similar acidic intensity at pH 3-5.

The third level of intensity of the acid alteration also took place in TH and Q sites, and corresponded to a pH < 3 that produced jarosite (Figure 12, Table 1). In this strong acid alteration environment Fe does not need to be preserved to explain jarosite formation because the altering fluids would have provided a large supply of Fe from the pyrite generating them. In any case, the altering fluids must have acted in oxidizing conditions at some stage to produce jarosite and goethite (Table 1). Goethite appeared in two samples with jarosite and in some others without it, but in all cases there is an indication of intense acid alteration (Table 1; samples TH5, TH9 in Figure 5; samples Q8 and Q13 in Figure 4). All other conditions remaining the same, goethite forms above pH 3 instead of jarosite (Brown, 1971; Bigham et al., 1996; Arslan and Arslan, 2003). Textural observation of thin section in a previous investigation of rocks from the TH site by Capitán et al. (2003; different samples from those in this study) provided evidence for mineralogical changes.
between goethite and jarosite due to changes in the environmental conditions. Some goethite formed at a first stage of decreasing pH that was later replaced by jarosite; some goethite and jarosite appear as texturally cogenetic phases (pH ~3 and possibly fluctuating); the most abundant case was the replacement of jarosite by goethite due to late weathering at circum-neutral pH (Capitán et al., 2003). These or similar process sequences can explain goethite-jarosite relations in our samples, particularly in the case of samples from the TH site, close to the rocks investigated texturally by Capitán et al. (2003). At pH < 3 there is great loss of Al and Mg (Figure 10a,b).

**Interstratified phyllosilicates**

One of the mechanisms of phyllosilicate substitution was transformation via interstratified phases. These phases were found mainly in the mildest level of alteration (7 > pH ≥ 5) in the EV and C sites. However, there are also samples such as EV16 and EV9, where the low clay mineral content suggests intermediate acidic alteration (Table 1, Figure 2), which also contain a substantial proportion of interstratified minerals (58-68 wt% of I-S with 95% illite layers in EV16; 38 wt% of I-S with 90% illite layers in EV9; Appendix Table A.1). Also, sample TH7, where the intensity of the acidic alteration is confirmed by the presence of alunite (pH 3-5), contains two K-S phases, one with 80% smectite layers, amounting to 5 wt% of phyllosilicate phases, and the other with 95% kaolinite, amounting to 18 wt% of the phyllosilicate minerals (Appendix Table A.1). Thus, kaolinite is more abundant than smectite in the interstratified phases, which is consistent with the pH range of 3-5 assigned to this sample based on the presence of alunite. The other interstratified phases found in our samples were C-V (with chlorite ranging 75-45% layers), I-S or I-V (95-25% illite layers), and K-S (95-80% smectite layers) (Appendix Table A.1). In the case of C-V, the V layers were true vermiculite, as the C-V interstratified phase is very common (de la Calle and Suquet, 1988). In the case of I-V, it is not necessarily implied that the V layers were real vermiculite. They may have been vermiculite or high-charge smectite that did not expand with the EG treatment
There were two sequences of transformation or phyllosilicate replacement taking place. In the first, chlorite transformed to C-V, and there is no evidence of how the C-V evolved subsequently. It may have dissolved to form kaolinite or K-S of variable composition. A similar transformation pattern has been described in the hydrothermal weathering of chlorite into kaolinite within basalt, consisting of the replacement of chlorite by corrensite, of corrensite by vermiculite, and of vermiculite by kaolinite-rich kaolinite-vermiculite (Aspandiar and Eggleton, 2002a). Within fissures in the same basalt, however, chlorite was replaced directly by kaolinite (Aspandiar and Eggleton, 2002b). Our samples behaved similarly, and there is a parallel effect of the intensity of the hydrothermal alteration investigated by Aspandiar and Eggleton (2002a,b) and the acidic alteration investigated here.

In the second sequence of phyllosilicate replacement, illite was altered to I-S or I-V. These two mixed-layer phases may have been further altered into K-S and finally into kaolinite. Also, illite may have altered directly into K-S. In this alteration sequence, all phyllosilicates are Al-rich and of dioctahedral type. It appears that dissolution of illite and precipitation of kaolinite was the most important process, as the amounts of interstratified phases are typically less than those of illite and kaolinite end-members (Appendix Table A.1). In addition, the crystal order of the neoformed kaolinite was low, whereas that of the original illite was high (well-ordered 2M₁ polytype), which does not suggest structural continuity between the two. These two arguments are counterbalanced by the existence of Fe in kaolinite, most easily explained as a relic of the original chlorite and illite and that passed to kaolinite by means of subsisting structural elements. The need for a structural preservation becomes more acute considering our suggestion that mildly acidic alteration in these samples (7 > pH ≥ 5) took place in reducing conditions in order to explain the observed Fe loss. Perhaps the explanation may rest in a hybrid mineral replacement mechanism intermediate between solid-state transformation and dissolution-precipitation.
(Cuadros, 2012). Such a mechanism is supported by Aspandiar and Eggleton (2002a) in the replacement of vermiculite by kaolinite. These authors support retention of polymeric entities or modular fragments of vermiculite passing to the kaolinite structure.

Beyond the mildest type of alteration at pH ~5 there is no evidence of mixed-layering except for the sample TH7 mentioned above. At pH < 5 the phyllosilicates were replaced by kaolinite via dissolution-precipitation or no kaolinite formed. Partial dissolution of plagioclase/feldspar probably also contributed to kaolinite formation.

**IMPLICATIONS FOR MARS ENVIRONMENTS AND REMOTE SENSING INVESTIGATION**

Environments where acidic alteration took place on Mars have been inferred from the identification of both alunite (Ehlmann et al., 2016; Sessa et al., 2018) and jarosite (Farrand et al., 2009; Weitz et al., 2011; Thollot et al., 2012; Ehlmann and Mustard, 2012; Bishop et al., 2018). The mineral assemblages consistent with acid alteration range from kaolinite + aluminous smectite (pH 5 or slightly above) to jarosite (pH < 3). In this range, the one of kaolinite + alunite (pH 3-5) appears to be underrepresented, with only one finding so far (Ehlmann et al., 2016). The reason for the apparent scarcity of kaolinite + alunite is unclear. Element depletion of martian rocks previous to acid alteration is unlikely to be the cause because both alunite (K-bearing) and natroalunite (Na-bearing) can precipitate at pH 3-5 and it would be required that both K and Na were depleted in order to preclude precipitation of any form of alunite. Dissolution of alunite at a later stage is a possibility. If this is the reason why kaolinite + alunite assemblages are so underrepresented on Mars, the survival of jarosite and alunite in other sites suggests that acidic episodes on Mars took place in different hydrological contexts, perhaps different stages of Mars geology between the Noachian and Hesperian, some precluding and some allowing preservation of sulfates.
Three of the sites in our study (EV, C, TH) displayed mineralogical heterogeneity at cm scale due to variations of the intensity of the acid attack. The acidic fluids percolated the rock differentially, depending on fabric and fractures. If such is the case on Earth, where water is abundant, more heterogeneity is expected on Mars, where water abundance is considered to have been always significantly lower than on Earth. On Mars, alteration by percolating acidic fluids would have probably generated steep alteration gradients at and below the m scale that would be reflected in the mineralogy. The very presence of jarosite on Mars has been considered to argue for constrained alteration due to limited acidic fluids (Elwood Madden et al., 2004). However, fluid percolation through rock is not the only possible mechanism of acid alteration on Mars. Acid alteration of volcanic ash and dust mixed with acidic snow and ice during volcanic eruptions (Michalski et al., 2013) would generate altered material with the appearance of a homogeneous deposit.

Our investigation indicated the existence of two incompatible mineral assemblages: kaolinite/alunite and jarosite/goethite (Table 1). The incompatibility of kaolinite/alunite and jarosite arises from their range of pH stability. However, goethite coexistence with kaolinite and alunite is possible. The lack of goethite in the kaolinite/alunite assemblage is interpreted as due to the redox conditions in which kaolinite and alunite formed, which precluded Fe\(^{2+}\) oxidation. On Mars, it is necessary to account for the abundant Fe in the original rocks putatively altered to kaolinite-bearing assemblages by acid attack. Surface acidic alteration would have likely produced goethite together with kaolinite, as the conditions would be oxidizing. Lack of any signs of goethite coexisting with kaolinite will indicate reducing conditions and thus the likelihood of subsurface alteration by percolating fluids.
It is important to consider interstratified clay minerals on Mars. First, because the possible existence of interstratified minerals may modify spectral signatures in an unforeseen way. Second, because they provide important environmental information. Our study indicates that acid alteration produces interstratified phyllosilicates only or mainly where the intensity of the alteration is low. According to our data, at the point where substantial kaolinite was forming the acidic alteration had entered a phase in which phyllosilicate substitution did not involve interstratified phases.

The kaolinite in our study produced by the acid alteration had wide 00l XRD peaks indicating high stacking disorder within the crystals and/or small crystal size. This is relevant to the observation of kaolinite with remote sensing. Fine particles (mineral or otherwise) are more efficient absorbing IR radiation than coarse particles (Farmer, 1998). Examples of this effect in kaolinite and dickite show the intensity of absorption bands in the MIR region changing by a factor > 2 where there are large differences in the particle size (Brindley et al., 1986; Cuadros et al., 2015). It is likely that the kaolinite in our study is at the high end of IR absorption efficiency, due to small particle size. This is congruent with the intense kaolinite features in our MIR spectra, especially recognizable in the O-H stretching system (3700-3500 cm\(^{-1}\); Figures 6-9). Kaolinite generated by acid alteration on Mars most likely will also consist of fine particles and absorb IR radiation efficiently. It has been shown that kaolinite is more visible than montmorillonite in physical mixtures investigated with near-infrared (McKeown et al., 2011). Mixtures of kaolinite and montmorillonite end-members produce spectra where kaolinite is more prominent (2.2 \(\mu\)m band) than in the linear mixture of the spectra of the two mineral end-members (McKeown et al., 2011). All the above argue for the possibility that kaolinite may be significantly less abundant in specific sites on Mars than suggested by near-infrared spectra, especially if kaolinite formed by acid alteration. This effect will be incremented if other IR-visible minerals in the mineral assemblage are coarse-grained (i.e., are less efficient
absorbers of IR radiation). Further, kaolinite or dickite of hydrothermal origin may be at the
opposite extreme of the particle size range. Hydrothermal kaolinite on Mars may be less visible
than kaolinite generated by pedogenic and acid processes.

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Figure 1. Partial view of the four investigated outcrops. From top to bottom and left to right: El Villar, Quebrantahuesos, Tharsis, and Calañas. Quebrantahuesos showed acid alteration heterogeneity at m scale, whereas the other three were heterogeneously altered at the cm scale. Quebrantahuesos contains rocks that were in direct proximity to the pyrite orebody that produced the alteration.

Figure 2. XRD patterns of oriented mounts of the < 2 µm size fraction of the samples from El Villar. Figures are d-spacing values in Å. Sample labels are at the right hand side of the patterns. Peaks at 9.96 and 3.34-3.32 Å are truncated. a) All samples, treated with ethylene-glycol. EV2 corresponds to the rock without acidic alteration and the intensity of the weathering increases broadly towards the top. The calculated patterns of phyllosilicates are included in a few cases (grey lines) representative of several phyllosilicate compositions. b) Detail of a few representative cases including the air-dried and ethylene-glycol treated samples. Ab: albite; C: chlorite; C-V: interstratified chlorite-vermiculite; F: K-feldspar; I: illite; K: kaolinite; Q: quartz; V: vermiculite.

Figure 3. XRD patterns of oriented mounts of the < 2 µm size fraction of the samples from Calañas. Figures are d-spacing values in Å. Sample labels are at the right hand side of the patterns. All samples, air-dried and treated with ethylene-glycol. The calculated patterns of phyllosilicates are included for the ethylene-glycol solvated samples. The most intense peaks are truncated. I: illite; K: kaolinite; K-S: interstratified kaolinite-smectite.

Figure 4. XRD patterns of oriented mounts of the < 2 µm size fraction of the samples from Quebrantahuesos. Figures are d-spacing values in Å. Sample labels are at the right hand side of the patterns. Sample QX corresponds to the rock previous to acidic alteration. Peaks at 3.34 and 3.079
of the top patterns are truncated. Al: alunite; B: beudantite; C: chlorite; G: goethite; I: illite; Na-
Al: natroalunite; Q: quartz.

Figure 5. XRD patterns of oriented mounts of the < 2 µm size fraction of the samples from Tharsis.
Figures are d-spacing values in Å. Sample labels are at the right hand side of the patterns. All
samples treated with ethylene-glycol (where there are phyllosilicates). TH12 corresponds to the
rock without acidic alteration. The calculated patterns of phyllosilicates are included for sample
TH7. Peaks at 10.01 and 3.34 Å are truncated. Al: alunite; G: goethite; I: illite; J: jarosite; K:
kaolinite; K-S: interstratified kaolinite-smectite; Q: quartz.

Figure 6. Mid-IR spectra of the < 2 µm size fraction of the samples from El Villar. The spectra
correspond to complex mineral mixtures. The most prominent features are those of kaolinite, illite
and quartz. Some weak bands correspond to the plagioclase-feldspar mineral group. For full
assignment of the bands see Table 2. The intensity of some spectra was multiplied by the following
factors: EV12 (400-1300 cm\(^{-1}\) only) x 2; EV13 x 4; EV19 x 2.

Figure 7. Mid-IR spectra of the < 2 µm size fraction of the samples from Calañas. The spectra
correspond to mineral mixtures of kaolinite, illite and smectite. For full assignment of the bands
see Table 2.

Figure 8. Mid-IR spectra of the < 2 µm size fraction of the samples from Quebrantahuesos. The
spectra correspond to mineral mixtures including alunite, beudantite, quartz, chlorite, illite
kaolinite and goethite. For full assignment of the bands see Table 2. The intensity of some spectra
was multiplied by the following factors: Q2 (2900-3900 cm\(^{-1}\) only) x 0.7; Q13 (2900-3900 cm\(^{-1}\) only)
x 2.
Figure 9. Mid-IR spectra of the < 2 μm size fraction of the samples from Tharsis. The spectra correspond to mineral mixtures dominated by the IR features of kaolinite, jarosite, alunite, quartz, illite and goethite. For full assignment see Table 2. The intensity of some spectra was multiplied by the following factors: TH12 (400-1300 cm\(^{-1}\) only) x 0.7; TH5 (2900-3900 cm\(^{-1}\)) x 3; TH5 (400-1300 cm\(^{-1}\)) x 2; TH7 x 0.7.

Figure 10. Chemical plots of bulk rock samples from the four locations investigated.

Figure 11. Chemical and mineralogical plots of the < 2 μm size fraction of the studied samples. The mineralogical data are from the simulations of the XRD patterns of the oriented mount preparations. The proportions of clay minerals are relative to the total amount of phyllosilicates only. Panel a) provides the key to symbols for panels a) to e). Panel f) provides data for three metal oxides from sites EV and Q.

Figure 12. Qualitative information about the abundance (y axis) of phyllosilicates, alunite and jarosite from Table 1 (bulk rock), modified with the results from the XRD modeling of the fraction < 2 μm. The plots are based on a 0-3 score abundance (Table 1).
Table 1. Location of samples and their whole-rock mineralogy from XRD of their randomly oriented powders.

<p>| Sample | Location                  | Quartz | Illite | Chlorite | Plagioclase / feldspar | Kaolinite | Mixed-layer phase | Smectite | Alunite | Jarosite | Goethite | Rutile |
|--------|----------------------------|--------|--------|----------|-------------------------|-----------|-------------------|----------|---------|----------|----------|--------|        |
| EV2    | xxx                        | xx     | xx     | xx       |                         |           |                   |          |         |          |          |        |        |
| EV3    | xxx                        | xx     | xx     | x        |                         |           |                   |          |         |          |          |        |        |
| EV5    | xx                         | xx     | xx (w) | xx       |                         |           |                   |          |         |          |          |        |        |
| EV6    | xxx                        | x      | x (w)  | x        |                         | x         |                   |          |         |          |          |        |        |
| EV9    | xxx                        | xx     | xx     | x        |                         |           |                   |          |         |          |          |        |        |
| EV10   | xxx                        | trace  | xx     | xx       |                         |           |                   |          |         |          |          |        |        |
| EV11   | xxx                        | xx     | xx     | xx       | trace (&amp;)               |           |                   |          |         |          |          |        |        |
| EV12   | El Villar                  | xxx    | xx     | xx       |                         |           |                   |          |         |          |          |        |        |
| EV13   | 0699742 N, 4174375 W       | xxx    | xx     | xx       |                         |           |                   |          |         |          |          |        |        |
| EV16   | xxx                        | trace  | xx     | xx       |                         |           |                   |          |         |          |          |        |        |
| EV17   | xxx                        | x      | x      | xx       |                         |           |                   |          |         |          |          |        |        |
| EV19   | xxx                        | x      | xx     | x        |                         |           |                   |          |         |          |          |        |        |
| EV21   | xxx                        | xx     |       |          |                         |           |                   |          |         |          |          |        |        |
| EV25   | xx                         | xxx    |       |          |                         |           |                   |          |         |          |          |        |        |
| EV26   | xxx                        | xx     |       | x (#)    |                         |           |                   |          |         |          |          |        |        |
| EV27   | xxx                        | xx     |       |          |                         |           |                   |          |         |          |          |        |        |
| TH12   | xxx                        | xxx    |       | xxx      |                         |           |                   |          |         |          |          |        |        |
| TH5    | xxx                        | x      |       | xxx      | trace                  |           |                   |          |         |          |          |        |        |
| TH7    | Tharsis                    | xxx    | xxx    | xx       |                         |           |                   | trace    | xxx (<em>) | x (</em>)    |          |        |        |
| TH9    | 0666156 N, 4161820 W       | xxx    |       | xx       |                         |           |                   |          |         |          |          |        |        |
| TH10   | xx                         |       |       | xx       |                         |           |                   |          |         |          |          |        |        |
| TH11   | xxx                        |       |       | xxx      |                         |           |                   |          |         |          |          |        |        |
| C1     | Calañas                    | xx     | xxx    | x (?)    |                         |           |                   |          |         |          |          |        |        |
| C2     | Road A-496, km 18          | xxx    | xxx    | x (?)    |                         |           |                   |          |         |          |          |        |        |
| QX     | xxx                        | xxx    |       |          |                         |           |                   |          |         |          |          |        |        |
| Q2     | xxx                        |       |       | xxx (<em>)  |                         |           |                   | trace    |         |          |          |        |        |
| Q3     | xxx                        |       |       | xxx (</em>)  |                         |           |                   | trace    |         |          |          |        |        |
| Q4     | Quebrantahuesos            | xxx    | x      | xxx (<em>)  |                         |           |                   | trace    |         |          |          |        |        |
| Q6     | 0713844 N, 4175477 W       | xxx    | xx     | xx (</em>)   |                         |           |                   | trace    |         |          |          |        |        |</p>
<table>
<thead>
<tr>
<th>Q7</th>
<th>xxx</th>
<th>xx</th>
<th>xx (*)</th>
<th>trace</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q8</td>
<td>x</td>
<td>x</td>
<td>xxx (+)</td>
<td>x</td>
</tr>
<tr>
<td>Q13</td>
<td>xxx</td>
<td>xxx</td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

Mineral phase abundance increases with the number of “x”.

(w): Signs of weathering; wide peaks.

(?): Dubious.

(*): Alunite and natroalunite.

(+) : Range of composition beudantite-jarosite.

(&): Low peak at 11.5 Å.

(#) : Broad elevation at ~4.18 Å; high background in entire pattern: Fe fluorescence.

(^) : High background in all diagram: Fe fluorescence.
Table 2. Wavenumber values of the IR bands in the spectra of samples from all four localities and their mineral assignment.

<table>
<thead>
<tr>
<th>Region 3900-2900 cm(^{-1})</th>
<th>Region 1300-900 cm(^{-1})</th>
<th>Region 900-600 cm(^{-1})</th>
<th>Region 600-400 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavenumber (cm(^{-1}))</td>
<td>Assignment</td>
<td>Wavenumber (cm(^{-1}))</td>
<td>Assignment</td>
</tr>
<tr>
<td>3703-3695</td>
<td>Kaolinite</td>
<td>1223-1221</td>
<td>Alunite</td>
</tr>
<tr>
<td>3670</td>
<td>Kaolinite</td>
<td>1180-1179</td>
<td>Jarosite, beudantite</td>
</tr>
<tr>
<td>3652-3648</td>
<td>Kaolinite</td>
<td>1165-1162</td>
<td>Quartz</td>
</tr>
<tr>
<td><strong>3624-3619</strong></td>
<td><strong>Kaolinite (sharp), illite, smectite</strong></td>
<td>1159</td>
<td>Alunite</td>
</tr>
<tr>
<td>3608</td>
<td>Illite</td>
<td>1130</td>
<td>Plagioclase-feldspar</td>
</tr>
<tr>
<td>3570-3547</td>
<td>Chlorite</td>
<td>1109-1100</td>
<td>Kaolinite</td>
</tr>
<tr>
<td>3512-3509</td>
<td>Alunite</td>
<td>1094</td>
<td><strong>Alunite</strong></td>
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<td><strong>3486</strong></td>
<td><strong>Alunite</strong></td>
<td>1093-1091</td>
<td>Plagioclase-feldspar</td>
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<tr>
<td>3457</td>
<td>Alunite (Na)</td>
<td>1091-1078</td>
<td>Quartz</td>
</tr>
<tr>
<td>3464-3380</td>
<td>Adsorbed water (very broad)</td>
<td>1089-1085</td>
<td>Jarosite, beudantite</td>
</tr>
<tr>
<td>3427</td>
<td>Chlorite</td>
<td>1072</td>
<td>Smectite</td>
</tr>
<tr>
<td><strong>3380-3378</strong></td>
<td><strong>Jarosite, beudantite</strong></td>
<td>1042</td>
<td>Plagioclase-feldspar</td>
</tr>
<tr>
<td><strong>3163-3137</strong></td>
<td><strong>Goethite</strong></td>
<td>1033-1029</td>
<td>Kaolinite</td>
</tr>
<tr>
<td>3005</td>
<td>Adsorbed water (very broad)</td>
<td>1029-1025</td>
<td>Illite</td>
</tr>
<tr>
<td><strong>1027</strong></td>
<td><strong>Alunite</strong></td>
<td>674-670</td>
<td>Alunite</td>
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<tr>
<td>1020</td>
<td>Beudantite</td>
<td>673</td>
<td>Chlorite</td>
</tr>
<tr>
<td>1010</td>
<td>Kaolinite, illite</td>
<td>647-650</td>
<td>Plagioclase-feldspar</td>
</tr>
<tr>
<td>1006-1004</td>
<td>Jarosite, beudantite</td>
<td>630-627</td>
<td>Alunite, jarosite, beudantite, goethite</td>
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<tr>
<td><strong>990</strong></td>
<td><strong>Chlorite</strong></td>
<td>609-607</td>
<td>Plagioclase-feldspar</td>
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<td>936-933</td>
<td>Kaolinite, illite</td>
<td>603-599</td>
<td>Alunite</td>
</tr>
<tr>
<td>916-911</td>
<td>Kaolinite, illite</td>
<td>601</td>
<td>Alunite</td>
</tr>
<tr>
<td>903</td>
<td>Goethite?</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Diagnostic, intense bands are in bold type, for a reference in Figures 6-9.
Fig. 1
Fig. 7
Fig. 9
Fig. 10
Figure 11
Figure 12