**CLAY-BEARING PARAGENETIC ASSOCIATIONS IN RIOTINTO (SW SPAIN): DISENTANGLING MULTIPLE PATHWAYS OF ACIDIC BEDROCK ALTERATIONS ON MARS.** C. Mavris[1,2], J. L. Bishop[2], J. Cuadros[1], J.M. Nieto[3] and J. R. Michalski[4]. [1]Dept. Earth Sciences, The Natural History Museum of London (London, SW7 5BD, UK, C.Mavris@nhm.ac.uk), [2]The SETI Institute, Carl Sagan Center, (Mountain View, CA, USA) [3]Department of Earth Sciences, University of Huelva (Huelva, Spain), [4]University of Hong Kong (Hong Kong).

**Introduction:** Numerous studies at the Riotinto mining district have focused on astrobiology, sulfates and extremophilic microbial communities in the highly acidic aqueous environments [1-3]. In contrast, this project investigates past acidic alteration of nearby volcanic rocks. The present study covers a variety of alteration pathways that may influence volcanic protoliths, with the specific types of clay minerals present acting as the key to decode the degree of acidity. Different acidity-dependent alteration pathways are explored that lead to the formation of a variety of secondary clay minerals and sulfates. Examining the alteration pathways at this site is expected to further our understanding of potential alteration on Mars. Characterization of the spectral properties and XRD patterns of these materials will contribute toward interpreting similar data of Mars.

**Materials and Methods:** Three alteration sequences were sampled at the Riotinto mining district (Fig. 1). Geologically, an Upper Palaeozoic (Late Famennian-Tournaisian) complex including siliciclastic sediments and mafic and felsic volcanics underwent hydrothermal alteration. The latter enriched the bedrock with quartz, chlorite and illite ($2M_1$ muscovite). Oxidation of an extensive pyrite-rich orebody occurred due to fluctuation of the water table (Miocene). As a consequence, moderate to extreme acidic fluxes leached the surrounding rocks for over 20 million years [4].

Rock samples were collected at three selected sites for lab analyses. Powder preparations were analysed using a PanAlytical X'PERT-PRO X-ray diffractometer (45 kV and 40 mA, 2-80 °2Θ range) for full mineralogy (not shown). An aliquot was used to extract the clay fraction (<2 µm) by sonication and centrifugation. Oriented aggregates were prepared on glass slides and measured in both air-dried and ethylene-glycol-solvated conditions [5] over the range 2-40 °2Θ. The XRD patterns were then modeled using ClaySim (from MDI) for the quantitative investigation of clay mineralogy as described in [6]. The spectral properties of these samples were measured for comparison with the lab XRD data and spectra of Martian outcrops. Mid-IR transmittance measurements were carried out at the Natural History Museum of London. VNIR and mid-IR reflectance spectra were acquired at ReLAB (Brown University).

**Results and Discussion:** The three alteration se-

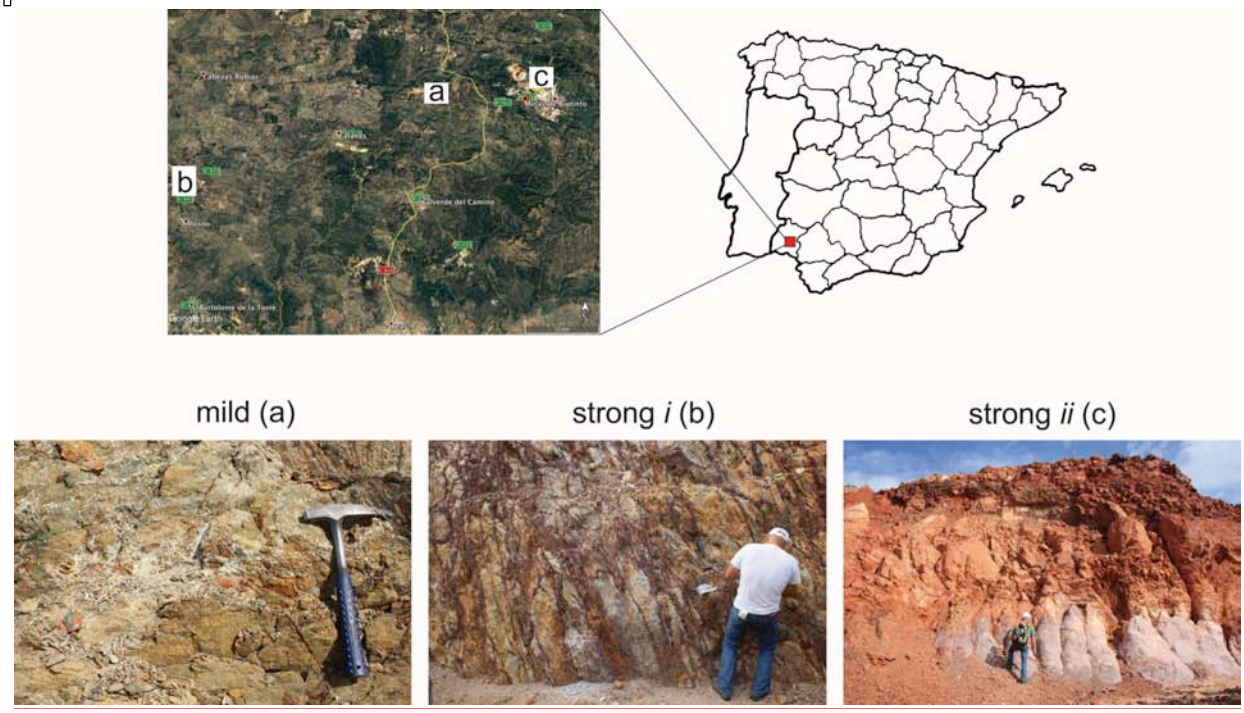


Figure 1. Location of the Riotinto mining district (Huelva, SW Spain) and the field sites for the current study. Images and locations of the three field sites are provided: a) El Villar, b) Tharsis, c) Quebrantahuesos.

quences exemplify alteration in the Riotinto mining district. The mineralogy of each site was determined through coordinated analyses of the XRD and spectral data. Alteration profiles were prepared that document changes in mineralogy as the weathering progressed (Fig. 2).

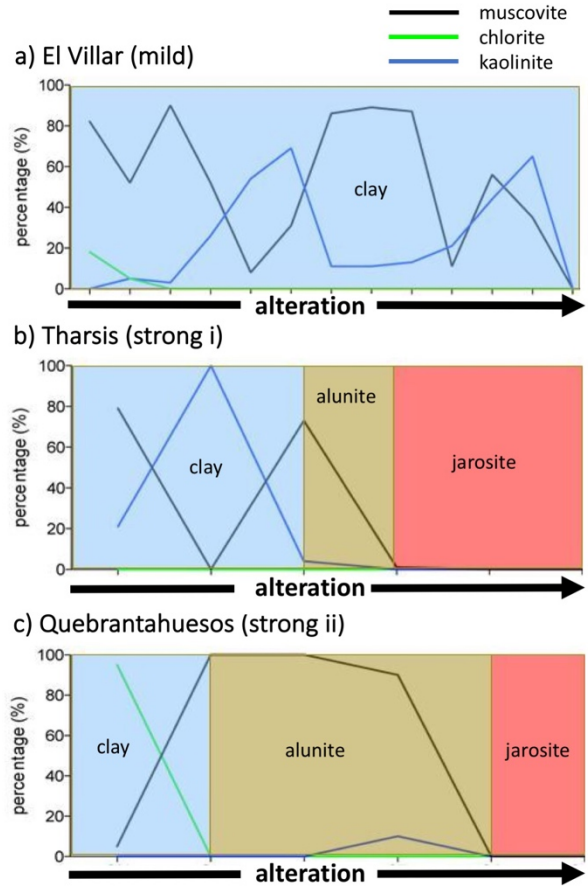


Figure 2. Alteration profiles for the 3 sites studied.

*El Villar (mild)*. A few km from the altering sulfide ore, the site sequence was dominated by a rather unusual clay mineral evolution. The initial chlorite and illite-rich mafic protolith was steadily altered into chlorite-vermiculite mixed-layers, vermiculite, kaolinite-smectite, and finally kaolinite. Such a sequence, and especially the presence of chlorite-vermiculite and vermiculite, favor the hypothesis of an alteration scenario taking place through leaching under mildly acidic conditions [8]. The acid weathering produced in El Villar was controlled by the local intensity of the leaching and the heterogeneous mineralogy of the rock.

*Tharsis (strong i)*. Alteration across this site is quite intense, ranging from kaolinite and $2M_1$ illite at the initial portion of the sequence followed by kaolinite-smectite and alunite. After that, alunite quickly disappears to be replaced by jarosite, which defines a strongly acidic environment where no clay minerals remain.

*Quebrantahuesos (strong ii)*. This site featured the greatest alteration of the three sites presented here. The alteration sequence started with illite and chlorite (protolith), then quickly transitioned to alunite (and traces of kaolinite), indicating a low pH environment. Finally, jarosite and beudantite formed under more acidic conditions. The most altered sample of this sequence contained pure hydrothermal quartz, a witness to the extreme intensity and duration of acidic leaching at this site.

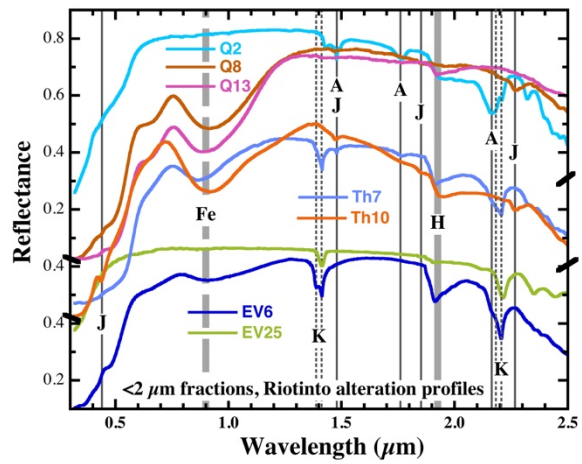


Figure 3. Example VNIR reflectance spectra. EV6, 25 show features due to vermiculite and kaolinite; Th7, 10 indicate alunite and jarosite, Q2 8, 13 indicate alunite, jarosite, and hematite plus quartz. Solid lines represent alunite (A), jarosite (J) and $H_2O$ (H) bands; dotted lines indicate kaolinite (K) bands.

**Conclusions and implications for Mars:** Clay mineralogy served as a valuable tool to disentangle alteration processes at the Riotinto study sites. Utilizing the observed parageneses allowed us to distinguish at least three acidic alteration pathways that could be identified on Mars through determination of phyllosilicate and sulfate components. Future work on this project will involve investigating the whole rock compositions of these outcrops at Riotinto. Another component of this study includes identifying martian outcrops exhibiting similar trends in phyllosilicate and sulfate mineralogy.

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**References:** [1] Sobron P. et al. (2014) *American Mineralogist*, 99, 1199-1205. [2] Amils R. et al. (2002) *Rev. Environ. Science Biotech.,* 1, 299-309. [3] Amils R. et al. (2007) *PSS*, 55, 370-381. [4] Essalhi M. et al. (2011) *Mineralium Deposita, 46,* 981–999. [5] Moore D.M. et al. D.C. (1997). [6] Mavris C. et al. (2017) *EPSL, submitted*.