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

4   implications for Mars

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15   Short title: Acidic alteration in Riotinto: implication for Mars

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18 **ABSTRACT**

19 Earth analogs are indispensable to investigate mineral assemblages on Mars because they enable

20 detailed analysis of spectroscopic data from Mars and they aid environmental interpretation.

21 Samples from four sites in the Iberian Pyrite Belt (El Villar, Calañas, Quebrantahuesos, and Tharsis)

22 were investigated using mineralogical, chemical and spectroscopic techniques, with a focus on clay

23 minerals and alteration environments. They represent Earth analogs of areas on Mars that

24 underwent acidic alteration. X-ray diffraction and transmittance mid-infrared data indicate that

25 the rocks were subjected to several degrees of acid alteration corresponding to assemblages

26 characterized by the following mixtures: (1) illite, chlorite, interstratified chlorite-vermiculite,

27 kaolinite-smectite, and kaolinite; (2) illite, kaolinite and alunite; (3) jarosite and goethite.

28 According to mineral stability data, these three assemblages correspond to pH values 7-5, 5-3, and

29 < 3, respectively. The lack of goethite in the illite-kaolinite-alunite assemblage suggests alteration

30 in reducing conditions. Illite was progressively dissolved by acidic alteration but is sufficiently

31 resilient not to be diagnostic of the intensity of the alteration. Illite and kaolinite were the two

32 most abundant phyllosilicate minerals observed and the main reaction involving phyllosilicates

33 was the alteration of illite to kaolinite. Mixed-layer phases appeared mainly in the mildest degree

34 of acid alteration, with few exceptions. This suggests a transition from a mechanism dominated by

35 transformation to a mechanism dominated by dissolution-precipitation as the intensity of the acid

36 alteration increases. Our results highlight the sparse kaolinite-alunite occurrences on Mars as

37 worthy of specific investigation. Acid-alteration on Mars is expected to be patchy and/or

38 consisting of fine alteration rims. Alunite occurrences on Mars in the absence of goethite may

39 indicate acid alteration in reducing conditions. Kaolinite produced through acid alteration on Mars

40 is expected to exist mainly as an end-member phase of low crystallinity, which would enhance IR

41 absorption and increase its visibility.

42 **Keywords:** Acid alteration, Alunite, Jarosite, Kaolinite, Mars

INTRODUCTION

43

44 Aluminum-rich phyllosilicate deposits are relatively abundant on Mars, and some of them include

45 kaolinite (Carter et al., 2013). They typically have the spectral character of kaolinite mixed with

46 aluminous smectites (McKeown et al., 2011), also typically associated with deposits of amorphous

47 silica and oxides/hydroxides. For example, in Mawrth Vallis, a widespread deposit contains

48 spectral evidence for kaolinite, hydrated silica, and, occasionally, montmorillonite (Bishop et al.,

49 2008; McKeown et al., 2009; Noe Dobrea et al., 2010). Other phyllosilicate deposits on Mars

50 including kaolinite are found in Nili Fossae (Ehlmann et al., 2009), the Eridania Basin (Noe Dobrea

51 and Swayze, 2010), Sinus Meridiani (Wiseman et al., 2008) and in numerous small outcrops

52 throughout the ancient crust (Wray et al., 2009). Kaolinite-bearing units are typically observed

53 overlying deposits of Fe/Mg-phyllosilicates, which are both thicker and more abundant globally on

54 Mars than the kaolinite deposits (Carter et al., 2013). Observations suggest that the contact

55 relationship between the two is either unconformable sedimentary contacts or an alteration front

56 of pedogenic or acidic character (Ehlmann et al., 2009; Michalski et al., 2013).

57

58 Age estimates of the aluminous clays, where they occur in large areas that allow for statistically

59 significant crater counts, suggest that they date to the Late Noachian-Early Hesperian period (~3.5-

60 3.7 Ga; Bibring et al., 2006; Loizeau et al., 2011). The later dates in this age range are the same of

61 sulfate deposits and correspond to a time of high volcanic activity on Mars (Ehlmann et al., 2011).

62 Sulfate deposits, among which jarosite and alunite have been identified, are considered to indicate

63 a period of acidic alteration. To date, kaolinite has not been found in association with jarosite on

64 Mars but there is evidence of one intimate association of kaolinite and alunite (Ehlmann et al.,

65 2016). Therefore, it is plausible that some of the kaolinite and accompanying Al-rich phyllosilicates

66 developed as a result of acidic alteration of basaltic rock, volcanic ash, Fe/Mg-rich phyllosilicates,

67 or even a mixture of phyllosilicates with a range of Al-Mg-Fe composition (Altheide et al., 2010;

68   Gainey et al., 2014). Acidic alteration would be an effective mechanism of generating kaolinite on

69   Mars and would enable faster reaction than neutral conditions, which could be important as liquid

70   water may not have been available on the surface of Mars long-term.

71

72   Studies of analog sites on Earth highlight components of the geological and mineralogical

73   processes that support interpretation of weathering on Mars. The Iberian Pyrite Belt, SW Iberian

74   Peninsula, contains sites that can be used as natural analogs of Martian rocks that have been

75   altered in acidic environments (Amils et al., 2007). Some of such studies have been conducted in

76   this region aimed at testing the ability of mineralogical identification tools (Sobron et al., 2014)

77   and developing a remote-sensing approach that can be used on Mars to identify sites of

78   mineralogical interest (Roach et al., 2006). Sedimentary mineral assemblages along the Rio Tinto

79   river, which has an average pH ~2, have been investigated concluding that the assemblages were

80   mainly mixtures of minerals formed in a variety of geological environments and that little

81   equilibration of the minerals occurred during transport and deposition (Fernandez-Remolar et al.,

82   2011). These results highlight the challenge of differentiating mineral assemblages representing

83   uniform environmental conditions from those resulting from transport or short-lived processes

84   (Fernandez-Remolar et al., 2011). We have investigated samples from rocks that were altered in

85   situ by acidic fluids during geologically significant times in four different sites within or near the

86   Riotinto area. We are documenting alteration of these rocks using multiple techniques and the

87   alteration phases (phyllosilicates, sulfates, iron oxides/hydroxides) are relevant to alteration on

88   Mars, despite the more silicic parent rocks at the Riotinto site. The present chemical and

89   mineralogical investigation is aiming to set constraints on the mineralogy and composition of

90   assemblages on Mars that may have resulted from acidic alteration, as well as on their textural

91   characteristics and on the specific environmental conditions in which they formed. Although the

92   Riotinto site experienced much greater water availability than expected for Mars and alteration on

93   Mars may have involved a large proportion of water ice (Michalski et al., 2013), characterizing

94   sites such as this provides important geochemical constraints for understanding acid alteration on

95   Mars.

96

97   **MATERIALS AND METHODS**

98   **Geology of the investigated area**

99   Four localities in the Iberian Pyrite Belt (Quebrantahuesos in the Riotinto district, El Villar, Calañas

100   and Tharsis, Appendix Figure A.1) were sampled for the laboratory investigation of the rocks and

101   their clay constituents. The parent rocks belong to an Upper Palaeozoic (Late Famennian-Visean)

102   volcano-sedimentary complex including siliciclastic sediments and mafic and felsic volcanics, all of

103   which underwent hydrothermal alteration associated to the emplacement of large amount of

104   massive sulphide orebodies (Toscano et al., 2014). After this, Miocene erosion and subaerial

105   exposition caused the oxidation of pyrite-rich orebodies which provided mild to extreme acidic

106   fluxes that leached the surrounding rocks for over 20 million years (Essalhi et al., 2011). The

107   mineral assemblages are strongly dependent on their acidic alteration intensity. Thus, the rocks

108   that were altered by the acidic fluids were not the pristine volcanic rocks, but the rocks formed

109   after hydrothermal alteration. In the following paragraphs we provide an introduction to each of

110   the sampled sites. The identification of the original rocks, the products of hydrothermal alteration

111   and the products of the subsequent acidic alteration are based on previous studies, published and

112   unpublished (including confidential information generated by mining activity), and on our

113   investigation. The interpretation of the existence and intensity of acidic alteration in the specific

114   samples follows the standard paragenetic concepts.

115

116   The Quebrantahuesos (Q) area is located in the Cerro Colorado open pit, within the Riotinto

117   mining district. The samples originate from a sequence of felsic porphyritic volcanic rocks and tuffs

118   on top of the Quebrantahuesos-Salomon orebody (Adamides, 2013). These rocks were first

119   hydrothermally altered to chloritic porphyry, rich in chlorite and quartz, during polymetallic

120   sulphide emplacement (Adamides, 2013; Martin-Izard et al., 2015). The later acidic alteration is

121   very intense, generating assemblages with abundant quartz, alunite and minor illite.

122

123   The El Villar section (EV), located west of the Riotinto mine, is a sequence of basic volcanics

124   (basalts) with minor felsic rocks (rhyolites and dacites). The samples for this study come from a 20

125   m horizontal sequence and follow a generally increasing alteration path from hydrothermally

126   altered basalts, with little subsequent acid alteration (plagioclase is still abundant), to kaolinite-

127   rich samples.

128

129   The Calañas (C) outcrop is located in a sequence of acidic tuffs. The mineralogy of the materials

130   that were not altered by acid fluids is mainly quartz and illite due to intense hydrothermal

131   alteration associated with the sulphide mineralization event. Acidic alteration of this sequence is

132   moderate and kaolinite appears as an alteration product of illite.

133

134   The Tharsis (TH) outcrop is a highly deformed and altered sequence of shales with minor felsic

135   volcanics and small lenticular masses of sulfides. Hydrothermal alteration associated with the

136   emplacement of the sulfide masses generated quartz, kaolinite and illite in the country rock

137   shales. The acidic alteration of the shales progressed substantially and there is abundant quartz,

138   with kaolinite, illite, sulfates and goethite, while the sulfide lenses were altered mainly to goethite

139   and jarosite/beudantite (Capitán et al., 2003).

140

141   **Samples**

142   The samples were collected between September 29 and October 3 of 2014. The site with the rock

143   composition and acidic alteration pathway most relevant to Mars is likely that of EV. For this

144   reason, this site was sampled with the greatest detail and resolution. The rocks that underwent

145   the acidic alteration consist of sericitic illite, chlorite, quartz and plagioclase/feldspar, the result of

146   the previous hydrothermal alteration of mafic volcanic rocks. A total of 26 samples were collected.

147   Of these, 16 were selected for the full study after a preliminary X-ray diffraction (XRD)

148   investigation (whole rock, random powder), using criteria of representativeness (samples that best

149   represented the mineralogical changes taking place, avoiding selection of several samples with

150   very similar mineralogy), clay content (other variables being equal, samples with more clay were

151   selected) and clay mineralogy (samples that best represented mineralogical changes by their clay

152   mineralogy and variety of clay minerals present) (Table 1). The same sample selection criteria

153   were applied to the other sites. Another suite of samples are from the Quebrantahuesos (Q site)

154   hill, within the active mine in Riotinto. The rocks sampled have disappeared now due to further

155   mining. Fifteen samples were collected, from which 8 were selected for detailed analyses. They

156   are a suite of strongly altered rocks, situated below or near the original pyrite body that generated

157   the acidic fluids. The rock that underwent acidic alteration (sample QX) consists mainly of quartz

158   and chlorite (Table 1). Three samples were collected from near the village of Calañas (C site), from

159   an outcrop of clay-rich rocks indicating a low level of acidic alteration. Illite and quartz appear to

160   be the main components of the rock subjected to the acidic alteration, although chlorite may have

161   also been present (Table 1). Two samples were selected. Finally, 11 specimens were sampled, and

162   6 selected, from two outcrops near the locality of Tharsis (TH site). These rocks were subjected to

163   medium to strong acidic alteration. No sample representative of the rock before acidic alteration

164   was identified (Table 1).

165

166   **Experimental methods**

167   All samples were crushed mechanically in a jaw crusher and then ground, first with a planetary

168   agate mill and then by hand to a fine powder with a mortar and pestle. Samples were analyzed

169   using XRD for their whole-rock mineralogy in a PANalytical X'Pert Pro diffractometer. The samples

170   were side-loaded to avoid preferred orientation. Measurement conditions were 45 kV, 40 mA, Cu

171   Kα radiation, divergence slit of 0.25°, and Soller 1 and 2 slits of 1.146°. This apparatus uses a solid-

172   state detector (X'Celerator) covering an angle of 2.1° and integrates the diffracted intensity over

173   that angle dynamically as it scans. The powders were scanned in the range 2-80 °2θ, with a

174   resolution of 0.0167 °2θ (scan step in a conventional scanner), and the total collection time was 60

175   min (equivalent to 0.77 s/step).

176

177   Further sample preparation procedures involved the heating of samples at 60 and 107 °C (see

178   below). Such treatments do not cause mineralogical changes in phyllosilicates and are

179   recommended and widely used (Moore and Reynolds, 1997). Phyllosilicates with expandable

180   layers rehydrate after treatment at these temperatures (e.g., Graf et al., 1995; Cases et al., 1997)

181   and they can be properly characterized with subsequent XRD analysis (Moore and Reynolds,

182   1997). The < 2 μm fraction of the rocks was obtained by dispersion in deionized water and

183   centrifugation. The < 2 μm fraction was concentrated by further centrifugation, dried at ~60 °C in

184   an oven, and gently ground with a mortar and pestle. The clay mineralogy was investigated in

185   these samples with the diffractometer indicated above. Samples were prepared as oriented

186   mounts by dispersing 10 mg of each in 2 ml of deionized water, pipetting the dispersion on glass

187   slides (area of ~4 cm^2), and letting them dry. They were studied as air-dry and as treated with

188   ethylene-glycol (EG) by overnight solvation in an EG-saturated atmosphere at 60 °C. The XRD scan

189   range was 2-40 °2θ, with a scan duration of 63 min (equivalent to 1.66 s/step). All other conditions

190   were the same as described above.

191

192   For a full description and the quantitative analysis of the clay mineralogy, the X-ray patterns of the

193   oriented mounts, both air-dry and treated with EG, were modelled using ClaySIM from MDI, which

194   uses the Newmod code (Moore and Reynolds, 1997). This program allows calculation of the

195   relative proportion of phyllosilicate minerals present, whether end-member or interstratified

196   phases. This software models the 00l peaks of interstratified minerals with two layer components,

197   and mixtures of up to ten such phases. The modeling uses the full XRD profile (peak positions,

198   peak relative intensities, and peak shapes). The results correspond to relative proportions of each

199   phyllosilicate component (excluding all other phases) and the relative proportion of layer type in

200   each mixed-layer phase (e.g., 35% of a chlorite-vermiculite phase that contains 60% of chlorite

201   layers). Every mineral phase used in our modeling process was necessary to reproduce a peak or

202   inflection in the XRD patterns. The experimental conditions of the scans were used in the program

203   calculations. Modeling of the patterns from the EG-treated samples is usually most accurate

204   because expanding layers (smectite, vermiculite) adsorb EG and have a more uniform d-spacing

205   than in air-dried systems. For this reason, our analysis is based on the data from EG-treated

206   samples. However, consistency between the EG and air-dried models was checked to test the

207   accuracy of the results. The difference between the two for each individual phases ranged 0-13 %

208   layers, with an average of 3 % layer difference. The main crystal-chemical parameters used in the

209   models are: a) type of layers, their relative proportion and their stacking order in the crystals (R

210   parameter; Moore and Reynolds, 1997); b) octahedral Fe content (on the $O_{10}[OH]_2$ basis for 2:1

211   phyllosilicates, $O_5[OH]_4$ for kaolinite, and $O_{10}[OH]_8$ basis for chlorite) of the layers and of the

212   interlayer brucite-like sheet in the case of chlorite; c) distribution of coherently diffracting crystal

213   thicknesses as defined by the maximum and average number of layers in the coherent X-ray

214   scattering domains; and d) amount of K in illite interlayers. One more calculation parameter is the

215   orientation factor (σ*) that represents the standard deviation (in a Gaussian distribution) of the

216   orientation of the platy clay particles from the horizontal (layers perfectly parallel to the surface of

217   the glass slide).

218

219   The < 2 μm fraction of the samples was also investigated using mid-infrared (MIR) transmittance

220   spectroscopy. Spectra were collected using a Perkin Elmer Spectrum One FTIR spectrometer. One

221   mg of each sample was mixed with ~200 mg of KBr and gently ground to generate a fully

222   homogeneous mixture that was then pressed at 10 t for 1 min to produce a pellet. Pure KBr was

223   used as a background, subtracted from the collected spectra. Infrared transmission spectra were

224   recorded over the range 400–4000 cm^{-1} at a spectral resolution of 4 cm^{-1}. Eight spectra were

225   accumulated for each analysis. The spectra were then converted to absorbance units.

226

227   The chemical composition of the samples was investigated in the whole and < 2 μm fractions

228   following Thompson and Walsh (2003). Samples were kept in a desiccator at room temperature

229   prior to analysis after drying at 107 °C for a minimum of 12 h. For the determination of major

230   elements and a few selected trace elements, powdered samples (0.1 g) were fused in Pt/Au

231   crucibles with 0.3 g of lithium metaborate, subsequently dissolved in 100 ml of ~1.6 M HNO$_3$ and

232   diluted to a final volume of 250 ml for analysis. The resulting solutions were analyzed by

233   inductively coupled plasma-atomic emission spectrometry (ICP-AES) using an iCap 6500 Duo

234   instrument (Thermo Scientific, UK). Reference materials (Stream sediment JSd-2, Geological

235   Survey of Japan; Granite MA-N, International Working Group "Analytical Standards of Minerals,

236   Ores and Rocks"; and Syenite NIM-S, South African Bureau of Standards) prepared by the same

237   method were analyzed with the samples. Analytical error (accuracy) was 3.7-3.8 % of the oxide

238   concentration for Mg, Mn and Na, and < 3 % for all the other major cations.

239

240   Sulfur and H were analyzed using a Vario EL cube analyzer (Elementar, GmbH, Germany). Dried

241   and powdered samples of ~10 mg each were weighed in triplicate with the precision of ± 0.001

242   mg, wrapped in Sn foil capsules, introduced into the furnace and combusted in an oxygen-rich

243   atmosphere at 1150 °C. Reference material JSl-1 (Slate; Geological Survey of Japan) was analyzed

244   with the samples. Analytical error (accuracy) was 12-14 % of the determined SO_2 and H_2O values.

245   Water values were obtained only as a reference (to assess mineral alteration and check

246   coherence with mineralogy) because they represented both hydroxyl water in phyllosilicates and

247   adsorbed water on mineral surfaces.

248

249   **RESULTS**

250   **Whole-rock mineralogy**

251   The mineral content of the samples (Table 1) indicates two groups, one composed by EV and C

252   sites, and the other by TH and Q. Samples from EV and C were subjected to a moderate acidic

253   alteration that produced kaolinite as the most advanced alteration product. The 001 kaolinite peak

254   was wide, indicating high stacking disorder. In samples where other kaolinite peaks were

255   sufficiently intense to be observed, such as the 002 peak and the 020 peak system, they were also

256   wide and lacked modulation, which confirms a low degree of crystal order in the kaolinite resulting

257   from acid alteration. In EV samples, the original rock contained quartz, illite, chlorite and

258   plagioclase/feldspar minerals, as represented by sample EV2 (Table 1). Chlorite disappeared soon

259   as the intensity of the acid alteration increased, in some cases remained with signs of weathering

260   (samples EV5 and EV6; Table 1). Plagioclase was mainly represented by albite, and feldspar by

261   microcline and minor sanidine. Illite and plagioclase/feldspar were present in most samples,

262   indicating that the acidic conditions were not sufficient to destroy them totally. Quartz was not

263   affected. The visual inspection of these rocks indicated that the alteration took place

264   heterogeneously, developing more in fissures and causing patches of different mineralogy to

265 coexist at cm scale, i.e., within the volume of the individual samples collected. The initial

266 mineralogy of the rocks from C cannot be ascertained from the collected samples, where the

267 existence of chlorite is dubious.

268

269 Rocks from TH and Q were subjected to intense acid alteration that produced alunite, jarosite and

270 goethite (Table 1). Chlorite was found only in the rock representing the starting point before acid

271 alteration in Q (sample QX, Table 1). The kaolinite in TH is different from that in EV and C. Kaolinite

272 in TH has narrow peaks and is very abundant in sample TH12, where the lack of alunite and

273 jarosite indicates that the acid alteration here was the least intense. Kaolinite decreased and then

274 disappeared as alunite and jarosite were present (Table 1). Kaolinite and illite coexisted with

275 alunite in one sample, but both phyllosilicates disappeared when jarosite was present. All the

276 above suggests that kaolinite in TH had a hydrothermal origin and was generated together with

277 illite. The subsequent acid alteration was sufficiently intense to destroy kaolinite and illite. Rutile

278 traces were observed in many of the TH and Q samples, indicating concentration due to

279 dissolution of other minerals.

280

281 **Clay mineralogy**

282 The investigation of the < 2 μm fraction provided detailed information about the evolution of the

283 clay minerals in the studied rocks (Appendix Table A.1). For the EV samples, the initial effect was

284 the transformation of chlorite into mixed-layer chlorite-vermiculite (C-V), first coexisting with

285 chlorite (sample EV3; Figure 2) and then without it (samples EV5 and EV6; Figure 2). This C-V,

286 however, only appeared in a few samples (EV3 to EV6). A further effect of acid alteration was the

287 expansion of a few illite layers generating illite-rich illite-smectite (I-S) and illite-vermiculite (I-V)

288 (Appendix Table A.1). However, these changes only generated 2-4% expandable layers that are not

289 easy to observe in Figure 2. There was a clear widening of illite peaks in some cases, indicating

290   illite alteration (EV11, EV13; Figure 2). The main change affecting illite across the EV sample suite

291   was its progressive disappearance (decrease of the intensity of illite peaks; not shown in Figure 2).

292   Coordinated with illite decrease was kaolinite occurrence and increase (samples EV6 to EV19;

293   Figure 2). In some samples, there was little illite and no kaolinite, with only quartz and traces of

294   plagioclase/feldspar (EV21, 26, 27; Figure 2). The above changes suggest the quick loss of chlorite

295   and the slower loss of illite by acid attack, together with the formation of kaolinite. Then, probably

296   more intense attack eliminated kaolinite leaving only quartz and traces of illite and

297   plagioclase/feldspar. However, the sequence from EV2 to EV27 does not exactly represent the

298   increase of acid alteration intensity due to the heterogeneous character of the alteration.

299

300   The two samples from site C contain illite, smectite-rich K-S and kaolinite (Figure 3). Both had little

301   smectite-rich K-S (10 wt% or less) but the amount of interstratified smectite in K-S is larger and

302   more noticeable in C2 (Figure 3; Appendix Table A.1). The amount of kaolinite in C2 was larger

303   than in C1 but still low (~5 wt%, Appendix Table A.1). This is interpreted to indicate that the

304   intensity of acidic alteration increased from C1 to C2.

305

306   In the samples from the Q site the abundant chlorite present in the unaltered rock (sample QX,

307   Figure 4) was not present in any of the altered rocks. Minor illite was observed in the < 2 μm size

308   fraction of sample QX, that was not observed in the whole rock (Table 1). Illite concentration in the

309   altered samples ranged from none to medium. In the Q site the intensity of acidic alteration

310   increased from the group of samples containing alunite (Q2 to Q7, Figure 4) to that with

311   jarosite/beudantite (beudantite was the main component in the < 2 μm size fraction as indicated

312   by the XRD data; Q8, Figure 4) and to that with goethite only (Q13, Figure 4). It is possible that the

313   proportion of illite in the unaltered rock was variable and this is reflected in the variable illite

314 presence in samples Q2 to Q7. No gradual transformation of clays or interstratified minerals were

315 observed in the Q samples.

316

317 In the rocks from the TH site, the original illite and kaolinite of hydrothermal origin were much

318 reduced or disappeared in samples containing alunite, jarosite or goethite. Mixed-layering was

319 found in sample TH7, where two K-S phases, one with 80% smectite and the other with 5%

320 smectite layers, were present. The former made up 5% of the total phyllosilicate content and the

321 latter 18% (Appendix Table A.1). Thus, most of the layers in the two interstratified phases were

322 kaolinite.

323

324 The modeling of the XRD patterns of the oriented mounts consistently indicated that kaolinite

325 layers contained Fe (Appendix Table A.1). This was shown in the reduced intensity of the kaolinite

326 002 peak with respect to the 001 peak. Such a result suggests that Fe was inherited from chlorite

327 and illite layers via the observed interstratified phases or via other mode of transformation

328 involving a close connection between the disappearing layers and the neoformed kaolinite layers.

329 The modeling also indicated the presence of Fe in chlorite, with higher concentration in sample QX

330 than in the EV samples (Appendix Table A.1).

331

332 **Mid-infrared analysis**

333 The results from MIR of the < 2 μm size fraction largely confirmed the results from the XRD

334 analysis, although they provide a different perspective due to the different sensitivity of MIR to

335 the several minerals present. The assignment of the IR peaks is summarized in Table 2, where the

336 diagnostic peaks indicating the presence of the specific mineral phases are listed in bold type. In

337 the EV samples, the O-H stretching region of the spectra (3900-2900 cm^{-1}) was dominated by the

338 kaolinite signature (Table 2) that overwhelmed those of illite, the other major phyllosilicate

339   component. The illite band, however, can be seen at ~3620 cm^{-1} as a wide component in the same

340   position as the sharper kaolinite band (Figure 6). The signatures from chlorite (1-21 % layers within

341   the phyllosilicates), vermiculite (2-12 % layers) and smectite (1-4 % layers; Appendix Table A.1) are

342   obscured by those of illite and kaolinite in this part of the spectra. In sample EV26, kaolinite was

343   detected by MIR, whereas it was not detected by XRD (Figure 6, Appendix Table A.1). Hydration

344   water is detected in most samples. The region 1300-900 cm^{-1} is dominated by the Si-O stretching

345   vibrations, where all silicate minerals have strong bands that combine in a complex system. The

346   band at 916-911 cm^{-1} corresponds to O-H bending in Al$_2$OH groups in illite and kaolinite, and is

347   free from interference from other minerals. This band is more intense and sharper when produced

348   by kaolinite (Figure 6) as described by Russell and Fraser (1994). Quartz is identified by the doublet

349   at ~799 and ~780 cm^{-1}, and plagioclase feldspars by multiple bands in the region 518-475 cm^{-1}

350   (Table 2).

351

352   The MIR spectra of the two samples from the C site (Figure 7) show a mixture of illite and

353   kaolinite, where kaolinite increases from C1 to C2 (1% to 6% kaolinite layers according to XRD,

354   Appendix Table A.1). The small variation of kaolinite content is strongly reflected in the O-H

355   stretch region (3900-2900 cm^{-1}), whereas the modifications are less noticeable in other parts of

356   the spectrum. The existence of 5-8% smectite layers interstratified with kaolinite (Figure 3,

357   Appendix Table A.1) was masked as most smectite bands are coincident with those of kaolinite

358   and illite. The double band at 532 and 475 cm^{-1} is indicative of Al-rich, dioctahedral phyllosilicates.

359   This feature can also be observed in the EV samples, although with greater interference from non-

360   phyllosilicate phases (Figure 6).

361

362   Samples from Q introduce the intense signatures of alunite and jarosite/beudantite (Figure 8).

363   Sample Q2 has a spectrum consisting of alunite only (except for a trace of quartz). The intense

364   bands at 3509-3457, 1220-1027 and 670-600 cm^{-1} overlap only partially with the bands of illite and

365   kaolinite, allowing identification of alunite and the assessment of its relative proportion with

366   respect to the phyllosilicates. Samples Q6 and Q7 are illite and alunite mixtures where the

367   signatures of both minerals can be observed. Interestingly, kaolinite is observable in the spectra of

368   both these samples (band at 3703 cm^{-1} and sharp component at 3623 cm^{-1}), whereas it was not

369   detected in the XRD patterns of Q6 (Figure 4). The spectrum of sample Q8 is dominated by

370   jarosite/beudantite. The other major mineral phase in the < 2 μm size fraction of Q8 is goethite,

371   represented by the broad band at 3137 cm^{-1} and that at 903 cm^{-1}. In the spectrum of sample QX,

372   chlorite is of the trioctahedral type, as indicated by the single intense band at 463 cm^{-1} (in Al-rich,

373   dioctahedral phyllosilicates this band is modulated into two intense bands at 532 and 475 cm^{-1}).

374

375   The samples from the TH site also provide an opportunity to observe the spectral signatures of

376   mineral mixtures (Figure 9). The spectra of TH10 and TH11 correspond entirely to jarosite, which

377   facilitates the identification of the corresponding features in other spectra. Sample TH9 is a

378   mixture of quartz with minor illite, jarosite and goethite (Figure 9). Quartz was obvious in the MIR

379   spectrum (bands at 789, 779 and 696 cm^{-1}). Illite was recognized by the band at 3619 cm^{-1} and the

380   shoulder at 913 cm^{-1}. Jarosite was detected by the wide band at 3380 cm^{-1} and the weak band at

381   630 cm^{-1}. The presence of goethite was indicated by the weak and broad band at 3163 cm^{-1}. The

382   presence of jarosite was suggested in sample TH5 by the shoulders at 3380 cm^{-1} and just below

383   the peak at 1100 cm^{-1}, although no jarosite was detected with XRD (Figure 5). Goethite, kaolinite

384   and quartz were the other phases detected in sample TH5 through intense MIR features (Table 2).

385   Alunite featured prominently with kaolinite in the spectrum of sample TH7. In this sample, illite

386   could be recognized by the shape of the 3621 cm^{-1} peak and by the band at 832 cm^{-1}. These two

387   features also enabled recognizition of illite in the spectrum of sample TH12, where kaolinite

388   features were the most prominent. One interesting feature of kaolinite in the samples from TH is

389　that the low-intensity peak at 3652 cm^{-1} was more prominent than in most other samples in our

390　study. This peak is one of the two low-intensity peaks of kaolinite in this region (3670 and 3650

391　cm^{-1}; Russell and Fraser, 1994). The prominence of this peak (and the hint of the one at 3670 cm^{-1},

392　Figure 9) is consistent with the good kaolinite stacking order indicated by XRD (sharp 00l peaks,

393　Figure 5).

394

395　**Major elements in the bulk rock**

396　The trends defining major chemical changes taking place during the acid alteration are shown in

397　Figure 10. The complete chemical dataset is available in Appendix Table A.2. The best developed

398　trend is the negative correlation between SiO_2 and Al_2O_3 concentration in the rocks (Figure 10a).

399　For most data points, the extent of acid alteration increases from left to right. The acid alteration

400　caused the decrease of Al, due to dissolution of aluminosilicates, and the increase of Si, due to

401　concentration and, possibly, precipitation of quartz. Quartz is typically resistant to acid attack and

402　was originally abundant in the rock (Table 1). It is also possible that the dissolution of

403　aluminosilicate minerals produced local precipitation of silica that then evolved to quartz. The

404　exception to the rule of increasing extent of acid attack from left to right in Figure 10a is in rocks

405　from the Q site. Sample QX, a rock that was not subjected to acid alteration, had 8 wt% Al_2O_3 and

406　74 wt% SiO_2, due to high content of chlorite and quartz. Samples Q6 and Q7 had 18 wt% and 21

407　wt% Al_2O_3 due to high alunite content (Table 1). The two data points with $Al_2O_3 < 5$ wt% (Figure

408　10a) are two heavily altered samples consisting mainly of quartz and goethite (Q13 and TH5, Table

409　1).

410

411　There was a broad positive correlation between Fe and Mg contents in the samples (Figure 10b)

412　indicating that the acid alteration typically caused a decrease in both Mg and Fe, due to

413   dissolution of the silicate phases. The two data points with high Fe and no Mg are Q13 and TH5,

414   mentioned above, both of which had much goethite (Table 1).

415

416   It would be expected that Al, Ti and Zr were correlated in the alteration products because these

417   three elements are rather insoluble, although Al is more soluble in acid conditions than at near-

418   neutral weathering conditions. There is such a positive correlation between Al and Ti, although

419   with two apparent slopes. The two slopes may be caused by the specific alteration conditions

420   and/or the minerals holding Ti (Figure 10c). Rutile was observed in some of the samples with high

421   Ti content (Table 1, Appendix Table A.2). This rutile was probably present originally in the rock and

422   concentrated by dissolution of the silicates. Alteration conditions alone are unable to explain the

423   apparent existence of two groups of data points, corresponding to high and low Ti content, as

424   both groups have samples with little and extensive acid alteration (Table 1, Appendix Table A.2).

425   Zircon also correlated positively with Al (Figure 10d). In this case, all samples from all locations plot

426   in the same broad trend, indicating that the response of Zr and Al to acid dissolution was similar

427   across the several rocks and the range of acid alteration intensity they were subjected to.

428

429   One important observation is that the data points from all locations align within the same broad

430   patterns described above. This provides support to (1) a broadly common rock chemical

431   composition generated by the hydrothermal alteration of the previous rocks, and/or to (2) acidic

432   alteration as the most important control of the final mineral assemblage and sample chemistry. In

433   other words, the relative position of the several samples in the chemical plots (Figrue 10) is

434   controlled mainly by the extent of alteration, rather than by the locality where they were

435   collected.

436

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

438   The chemical composition of the < 2 μm size fraction allows us to trace the reactions taking place

439   among the phyllosilicates (complete dataset in Appendix Table A.3). Comparison of chemical and

440   mineralogical data of this clay-sized fraction highlights points of interest in these reactions (Figure

441   11). The negative correlation between Si and Al observed in the bulk rock was reproduced in the <

442   2 μm size fraction for most samples, indicating that much of this correlation was generated in the

443   < 2 μm size fraction (Figure 11a). The three obvious outliers in the plot are TH10, TH11 and Q8, the

444   three samples with the largest content of jarosite/beudantite. These samples had very little quartz

445   and minor or no goethite.

446

447   The positive Mg vs. Fe correlation seen in the bulk rock (Figure 10b) also held for the clay fraction

448   of many samples (Figure 11b; this plot contains more data points than that of the bulk rock).

449   Samples from EV and C as well as sample QX exhibit the same broad positive correlation. All these

450   samples experienced limited or no acidic alteration. The samples distributed vertically at Fe_2O_3 > 5

451   wt% and with low Mg content are five samples from the TH site (all TH samples except the

452   unaltered TH12), plus samples Q8 and EV26. All these samples contain goethite and/or

453   jarosite/beudantite.

454

455   The only correlation found between phyllosilicates is a negative one between illite and kaolinite

456   contents (Figure 11c). They are the two most abundant phyllosilicate phases. Except in the TH site,

457   kaolinite was not present in the unaltered rock. Thus the main reaction taking place between

458   phyllosilicates is a substitution of kaolinite for illite, which occurred where the acid alteration was

459   mild. The other clay phases were short-lived or produced in minor amounts. Strong alteration

460   dissolved all phyllosilicates. In the case of the TH site, kaolinite of hydrothermal origin was present

461   and was partially or totally dissolved by the acid alteration (Table 1). However, K-S was also

462   detected (Figure 5, Appendix Table A.1), most likely the result of alteration of illite (as the only one

463   of the original minerals in TH12 that can react to K-S in acidic conditions), indicating that illite

464   substitution by kaolinite also took place in TH.

465

466   The plot of Fe_2O_3 wt% vs. kaolinite layer % shows that there is no negative correlation between Fe

467   and kaolinite in the < 2 μm size fraction (Figure 11d). This is partly due to the existence of goethite

468   and kaolinite in some samples. The most clear example is sample TH5, which had only some little

469   kaolinite as the only phyllosilicate (100% kaolinite, as phyllosilicate proportions were calculated

470   relative to phyllosilicate minerals only) and abundant goethite (Figure 5; Appendix Table A.2).

471   However, there is also a lack of negative correlation between kaolinite and Fe contents in the < 2

472   μm size fraction of other samples with no goethite, which supports the existence of Fe in kaolinite,

473   as was found in the XRD simulations (Appendix Table A.1). Indeed, XRD analysis did not detect

474   goethite in many of the samples with kaolinite and low Fe_2O_3 content shown in Figure 11d. This

475   result was supported by the MIR investigation, as most samples with Fe_2O_3 < 10 wt% in Figure 11d

476   did not show traces of goethite in their MIR spectra (Figure 9).

477

478   The plot of illite vs K_2O content showed a broad positive correlation between the two variables,

479   indicating that the XRD modeling is accurate (Figure 11e). Mineral phases containing K other than

480   illite, such as K-feldspar and alunite broadened the correlation. In addition, there are samples that

481   do not contain illite but have other K-bearing phases (jarosite, alunite) and samples containing low

482   levels of illite as the only phyllosilicate (i.e., they correspond to 100 % illite in the plot, as this

483   figure represents the relative proportion of phyllosilicates only). This minor illite component in the

484   < 2 μm fraction of these samples does not control the K abundance in them (EV27 and TH9

485   samples with 100 % illite and K_2O < 4 wt%, Figure 11e).

486

487   The plot of chlorite abundance vs. MgO, Fe_2O_3 and Al_2O_3 contents allows us to investigate the type

488   of chlorite in the unaltered rock. Iron was calculated as Fe^{3+}, although Fe^{2+} was undoubtedly

489   present in chlorite. Mid-IR data indicated a trioctahedral chlorite (i.e., mainly Mg and/or Fe^{2+}, as

490   opposed to Al and Fe^{3+}) (sample QX in Figure 8). Our modeling of the XRD patterns also indicated a

491   moderate Fe content in chlorite (Appendix Table A.1). Both results were confirmed by the

492   chemical data, as the proportion of MgO and Fe_2O_3 both increased with increasing chlorite,

493   whereas Al_2O_3 content decreased with increasing chlorite (Figure 11f). The specific metal oxide

494   values in the plot do not represent the composition of the chlorite(s) because there are other

495   minerals in the < 2 μm size fraction of the samples (non-phyllosilicates) which are included in the

496   chemical analysis, but not in the mineralogical data. Only the trends of MgO and Fe_2O_3 data are

497   indicative of chlorite composition.

498

499   **DISCUSSION**

500   **Mineral assemblages**

501   Overall, the rocks investigated show expected chemical and mineralogical transformations for

502   alteration in an acidic environment. In none of the sampled sites was there a uniform spatial

503   gradation of the intensity of the alteration moving across the entire group of samples (except, of

504   course, for the C site with only two samples). This can be appreciated inspecting Table 1 and

505   Figure 12. Figure 12 shows that the increase of the intensity of the acid alteration from left to right

506   in the plots (generally, but not necessarily for each sample within the sites) is broadly marked by

507   (1) the disappearance of chlorite, which is very sensitive to acid attack, (2) increase of kaolinite

508   content, (3) alunite formation, and (4) jarosite formation. However, the changes are not smooth.

509   This confirms the visual impression from the rocks, especially obvious in EV and TH, that the

510   alteration was patchy and partially controlled by local fissures and local changes in mineralogy of

511   the original rock (Figure 1).

512

513 Figure 12 indicates that alunite is compatible with phyllosilicates, as abundant illite and kaolinite

514 were present with abundant alunite in samples from the TH and Q sites. This is in agreement with

515 frequent mineral assemblages containing these three minerals (Hemley et al., 1969). On the

516 contrary, the presence of jarosite appeared to be largely incompatible with that of phyllosilicates

517 (Figure 12). Jarosite formation typically requires pH < 3 (Brown, 1971; Keith et al., 1979; Das et al.,

518 1996; Arslan and Arslan, 2003), whereas alunite precipitates at pH 2.5-5 (Keith et al., 1979). The

519 stability of kaolinite at pH < 5 requires elevated activities of Al and SiO_2 (Garrels and Christ, 1965;

520 Huang and Keller, 1973). For the same Al and SiO_2 activities, illite is stable at a pH ~1.5 units higher

521 than the corresponding pH stability threshold for kaolinite (Huang and Keller, 1973). Thus, despite

522 the heterogeneous distribution of the alteration, the individual areas sampled (at cm scale in EV,

523 TH and C; at m scale in Q) indicate an approximation to equilibrium conditions at the several

524 ranges of pH at which the alteration took place. The proximity to equilibrium conditions should

525 increase with decreasing pH, as the fluids become more aggressive and the dissolution reactions

526 faster.

527

528 Investigation of an Arctic gossan (High Lake, Nunavut, Canada) has shown coexistence of

529 muscovite and jarosite, both in major amounts (West et al., 2009). Such data do not contradict the

530 above description of mineral stability fields. Rather, they are explained by a large influence of

531 kinetic effects. The acidic attack in the Arctic gossan has been taking place only during the last

532 several thousand years and is slowed down by low temperature and low water activity due to

533 freezing conditions (West et al., 2009). The acidic alteration in Riotinto, however, took place for 40

534 Ma and is expected to be thermodynamically controlled.

535

536 **Mineralogical processes**

537 Three degrees of intensity of acidic alteration can be distinguished in the studied rocks. The first

538 degree corresponds to alteration with fluids at pH reaching down to ~5, with kaolinite as the main

539 product. This level of alteration is represented by the EV and C sites. At the C site, the simplest of

540 the two systems, there is an increase of kaolinite (Table 1), partially via interstratified K-S

541 (Appendix Table A.1). Because there is the hint of chlorite traces in the XRD patterns of the bulk

542 rock of both C1 and C2 (Table 1), and because there is K-S also in both samples (Figure 3; Appendix

543 Table A.1), it can be concluded that the acidic alteration did not take place with the same intensity

544 in the entire volume of these samples. Chlorite may have been present in the original rock and lost

545 shortly after the alteration onset. In EV samples, there was abundant quartz and some

546 plagioclase/feldspar (albite, sanidine and microcline; Table 1). Quartz was not affected by the

547 alteration fluids and plagioclase/feldspar appeared to be little affected, as they remained

548 abundant across these samples (Table 1, Figure 2). It is expected that K-feldspar has greater

549 resistance to acid attack than albite (Garrels and Christ, 1965) and the permanence of the latter

550 may be related to heterogeneity in the rock composition as well as in the spatial distribution of the

551 acid alteration intensity. Dissolution of chlorite was observed, as well as alteration of chlorite to C-

552 V, and alteration of illite to kaolinite (dissolution-precipitation and/or transformation) (Figure 2),

553 that resulted in loss of Fe and Mg (Figures 10b and 11b). There was also loss of Al (Figures 10b and

554 11b) that must be due to dissolution of silicates that did not contribute to precipitation of new

555 phases. This is deduced because although the neoformed kaolinite has a higher Al/Si ratio than

556 chlorite and illite, the Al/Si ratio decreased during the alteration process (Figure 10b). Aluminum

557 solubility increases with decreasing pH (steep increase below pH 5; Garrels and Christ, 1965),

558 while that of silica decreases, which two facts may have fostered Al loss over Si during dissolution

559 of silicate phases. Some of the quartz in the EV samples may have originally precipitated as silica

560 that later recrystallized as quartz. Finally, loss of Fe and Mg in EV and TH samples (Figures 10b and

561 11b; Appendix Tables A.2 and A.4), required reducing conditions to avoid in situ Fe precipitation.

562

563 The second level of intensity of the acid alteration is that caused by fluids at pH 3-5, producing

564 kaolinite and alunite (Figure 12, Table 1). This alteration environment occurred in the TH and Q

565 sites. This alteration increases the Al/Si ratio, contrary to the milder acid attack, as far as indicated

566 by available chemical data (compare sample TH12 with TH7, and QX with Q3 to Q7, Appendix

567 Table A.2). This result is expected because both kaolinite and alunite are Al-rich, and alunite has

568 no Si. In order to produce the observed increase in the Al/Si ratio it is necessary that some Si was

569 lost from the system and that less Al was lost than Si. This trend would occur most easily if the

570 rocks were subjected to fluids at pH 3-5 from the beginning of the acidic alteration. If the rocks

571 had experienced first alteration at pH ~5, their Al/Si would have decreased first, making it more

572 difficult to reverse the trend and produce Al/Si ratios higher than in the unaltered rock.

573 Accordingly, the chemical data suggest that the alteration front was always of similar acidic

574 intensity at pH 3-5.

575

576 The third level of intensity of the acid alteration also took place in TH and Q sites, and

577 corresponded to a pH < 3 that produced jarosite (Figure 12, Table 1). In this strong acid alteration

578 environment Fe does not need to be preserved to explain jarosite formation because the altering

579 fluids would have provided a large supply of Fe from the pyrite generating them. In any case, the

580 altering fluids must have acted in oxidizing conditions at some stage to produce jarosite and

581 goethite (Table 1). Goethite appeared in two samples with jarosite and in some others without it,

582 but in all cases there is an indication of intense acid alteration (Table 1; samples TH5, TH9 in Figure

583 5; samples Q8 and Q13 in Figure 4). All other conditions remaining the same, goethite forms above

584 pH 3 instead of jarosite (Brown, 1971; Bigham et al., 1996; Arslan and Arslan, 2003). Textural

585 observation of thin section in a previous investigation of rocks from the TH site by Capitán et al.

586 (2003; different samples from those in this study) provided evidence for mineralogical changes

587   between goethite and jarosite due to changes in the environmental conditions. Some goethite

588   formed at a first stage of decreasing pH that was later replaced by jarosite; some goethite and

589   jarosite appear as texturally cogenetic phases (pH ~3 and possibly fluctuating); the most abundant

590   case was the replacement of jarosite by goethite due to late weathering at circum-neutral pH

591   (Capitán et al., 2003). These or similar process sequences can explain goethite-jarosite relations in

592   our samples, particularly in the case of samples from the TH site, close to the rocks investigated

593   texturally by Capitán et al. (2003). At pH < 3 there is great loss of Al and Mg (Figure 10a,b).

594

595   **Interstratified phyllosilicates**

596   One of the mechanisms of phyllosilicate substitution was transformation via interstratified phases.

597   These phases were found mainly in the mildest level of alteration (7 > pH ≥ 5) in the EV and C sites.

598   However, there are also samples such as EV16 and EV9, where the low clay mineral content

599   suggests intermediate acidic alteration (Table 1, Figure 2), which also contain a substantial

600   proportion of interstratified minerals (58-68 wt% of I-S with 95% illite layers in EV16; 38 wt% of I-S

601   with 90% illite layers in EV9; Appendix Table A.1). Also, sample TH7, where the intensity of the

602   acidic alteration is confirmed by the presence of alunite (pH 3-5), contains two K-S phases, one

603   with 80% smectite layers, amounting to 5 wt% of phyllosilicate phases, and the other with 95%

604   kaolinite, amounting to 18 wt% of the phyllosilicate minerals (Appendix Table A.1). Thus, kaolinite

605   is more abundant than smectite in the interstratified phases, which is consistent with the pH range

606   of 3-5 assigned to this sample based on the presence of alunite. The other interstratified phases

607   found in our samples were C-V (with chlorite ranging 75-45% layers), I-S or I-V (95-25% illite

608   layers), and K-S (95-80% smectite layers) (Appendix Table A.1). In the case of C-V, the V layers

609   were true vermiculite, as the C-V interstratified phase is very common (de la Calle and Suquet,

610   1988). In the case of I-V, it is not necessarily implied that the V layers were real vermiculite. They

611   may have been vermiculite or high-charge smectite that did not expand with the EG treatment

612   (Mosser-Ruck et al., 2005). There were two sequences of transformation or phyllosilicate

613   replacement taking place. In the first, chlorite transformed to C-V, and there is no evidence of how

614   the C-V evolved subsequently. It may have dissolved to form kaolinite or K-S of variable

615   composition. A similar transformation pattern has been described in the hydrothermal weathering

616   of chlorite into kaolinite within basalt, consisting of the replacement of chlorite by corrensite, of

617   corrensite by vermiculite, and of vermiculite by kaolinite-rich kaolinite-vermiculite (Aspandiar and

618   Eggleton, 2002a). Within fissures in the same basalt, however, chlorite was replaced directly by

619   kaolinite (Aspandiar and Eggleton, 2002b). Our samples behaved similarly, and there is a parallel

620   effect of the intensity of the hydrothermal alteration investigated by Aspandiar and Eggleton

621   (2002a,b) and the acidic alteration investigated here.

622

623   In the second sequence of phyllosilicate replacement, illite was altered to I-S or I-V. These two

624   mixed-layer phases may have been further altered into K-S and finally into kaolinite. Also, illite

625   may have altered directly into K-S. In this alteration sequence, all phyllosilicates are Al-rich and of

626   dioctahedral type. It appears that dissolution of illite and precipitation of kaolinite was the most

627   important process, as the amounts of interstratified phases are typically less than those of illite

628   and kaolinite end-members (Appendix Table A.1). In addition, the crystal order of the neoformed

629   kaolinite was low, whereas that of the original illite was high (well-orderd $2M_1$ polytype), which

630   does not suggest structural continuity between the two. These two arguments are

631   counterbalanced by the existence of Fe in kaolinite, most easily explained as a relic of the original

632   chlorite and illite and that passed to kaolinite by means of subsisting structural elements. The

633   need for a structural preservation becomes more acute considering our suggestion that mildly

634   acidic alteration in these samples ($7 > pH \geq 5$) took place in reducing conditions in order to explain

635   the observed Fe loss. Perhaps the explanation may rest in a hybrid mineral replacement

636   mechanism intermediate between solid-state transformation and dissolution-precipitation

637 (Cuadros, 2012). Such a mechanism is supported by Aspandiar and Eggleton (2002a) in the

638 replacement of vermiculite by kaolinite. These authors support retention of polymeric entities or

639 modular fragments of vermiculite passing to the kaolinite structure.

640

641 Beyond the mildest type of alteration at pH ~5 there is no evidence of mixed-layering except for

642 the sample TH7 mentioned above. At pH < 5 the phyllosilicates were replaced by kaolinite via

643 dissolution-precipitation or no kaolinite formed. Partial dissolution of plagioclase/feldspar

644 probably also contributed to kaolinite formation.

645

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

647 Environments where acidic alteration took place on Mars have been inferred from the

648 identification of both alunite (Ehlmann et al., 2016; Sessa et al., 2018) and jarosite (Farrand et al.,

649 2009; Weitz et al., 2011; Thollot et al., 2012; Ehlmann and Mustard, 2012; Bishop et al., 2018). The

650 mineral assemblages consistent with acid alteration range from kaolinite + aluminous smectite (pH

651 5 or slightly above) to jarosite (pH < 3). In this range, the one of kaolinite + alunite (pH 3-5)

652 appears to be underrepresented, with only one finding so far (Ehlmann et al., 2016). The reason

653 for the apparent scarcity of kaolinite + alunite is unclear. Element depletion of martian rocks

654 previous to acid alteration is unlikely to be the cause because both alunite (K-bearing) and

655 natroalunite (Na-bearing) can precipitate at pH 3-5 and it would be required that both K and Na

656 were depleted in order to preclude precipitation of any form of alunite. Dissolution of alunite at a

657 later stage is a possibility. If this is the reason why kaolinite + alunite assemblages are so

658 underrepresented on Mars, the survival of jarosite and alunite in other sites suggests that acidic

659 episodes on Mars took place in different hydrological contexts, perhaps different stages of Mars

660 geology between the Noachian and Hesperian, some precluding and some allowing preservation

661 of sulfates.

662

663 Three of the sites in our study (EV, C, TH) displayed mineralogical heterogeneity at cm scale due to

664 variations of the intensity of the acid attack. The acidic fluids percolated the rock differentially,

665 depending on fabric and fractures. If such is the case on Earth, where water is abundant, more

666 heterogeneity is expected on Mars, where water abundance is considered to have been always

667 significantly lower than on Earth. On Mars, alteration by percolating acidic fluids would have

668 probably generated steep alteration gradients at and below the m scale that would be reflected in

669 the mineralogy. The very presence of jarosite on Mars has been considered to argue for

670 constrained alteration due to limited acidic fluids (Elwood Madden et al., 2004). However, fluid

671 percolation through rock is not the only possible mechanism of acid alteration on Mars. Acid

672 alteration of volcanic ash and dust mixed with acidic snow and ice during volcanic eruptions

673 (Michalski et al., 2013) would generate altered material with the appearance of a homogeneous

674 deposit.

675

676 Our investigation indicated the existence of two incompatible mineral assemblages:

677 kaolinite/alunite and jarosite/goethite (Table 1). The incompatibility of kaolinite/alunite and

678 jarosite arises from their range of pH stability. However, goethite coexistence with kaolinite and

679 alunite is possible. The lack of goethite in the kaolinite/alunite assemblage is interpreted as due to

680 the redox conditions in which kaolinite and alunite formed, which precluded Fe^{2+} oxidation. On

681 Mars, it is necessary to account for the abundant Fe in the original rocks putatively altered to

682 kaolinite-bearing assemblages by acid attack. Surface acidic alteration would have likely produced

683 goethite together with kaolinite, as the conditions would be oxidizing. Lack of any signs of goethite

684 coexisting with kaolinite will indicate reducing conditions and thus the likelihood of subsurface

685 alteration by percolating fluids.

686

687   It is important to consider interstratified clay minerals on Mars. First, because the possible

688   existence of interstratified minerals may modify spectral signatures in an unforeseen way. Second,

689   because they provide important environmental information. Our study indicates that acid

690   alteration produces interstratified phyllosilicates only or mainly where the intensity of the

691   alteration is low. According to our data, at the point where substantial kaolinite was forming the

692   acidic alteration had entered a phase in which phyllosilicate substitution did not involve

693   interstratified phases.

694

695   The kaolinite in our study produced by the acid alteration had wide 00l XRD peaks indicating high

696   stacking disorder within the crystals and/or small crystal size. This is relevant to the observation of

697   kaolinite with remote sensing. Fine particles (mineral or otherwise) are more efficient absorbing IR

698   radiation than coarse particles (Farmer, 1998). Examples of this effect in kaolinite and dickite show

699   the intensity of absorption bands in the MIR region changing by a factor > 2 where there are large

700   differences in the particle size (Brindley et al., 1986; Cuadros et al., 2015). It is likely that the

701   kaolinite in our study is at the high end of IR absorption efficiency, due to small particle size. This is

702   congruent with the intense kaolinite features in our MIR spectra, especially recognizable in the O-

703   H stretching system (3700-3500 cm^{-1}; Figures 6-9). Kaolinite generated by acid alteration on Mars

704   most likely will also consist of fine particles and absorb IR radiation efficiently. It has been shown

705   that kaolinite is more visible than montmorillonite in physical mixtures investigated with near-

706   infrared (McKeown et al., 2011). Mixtures of kaolinite and montmorillonite end-members produce

707   spectra where kaolinite is more prominent (2.2 μm band) than in the linear mixture of the spectra

708   of the two mineral end-members (McKeown et al., 2011). All the above argue for the possibility

709   that kaolinite may be significantly less abundant in specific sites on Mars than suggested by near-

710   infrared spectra, especially if kaolinite formed by acid alteration. This effect will be incremented if

711   other IR-visible minerals in the mineral assemblage are coarse-grained (i.e., are less efficient

712   absorbers of IR radiation). Further, kaolinite or dickite of hydrothermal origin may be at the

713   opposite extreme of the particle size range. Hydrothermal kaolinite on Mars may be less visible

714   than kaolinite generated by pedogenic and acid processes.

715

716   **ACKNOWLEDGMENTS**

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722

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947

948   Figure 1. Partial view of the four investigated outcrops. From top to bottom and left to right: El

949   Villar, Quebrantahuesos, Tharsis, and Calañas. Quebratahuesos showed acid alteration

950   heterogeneity at m scale, whereas the other three were heterogeneously altered at the cm scale.

951   Quebrantahuesos contains rocks that were in direct proximity to the pyrite orebody that produced

952   the alteration.

953

954   Figure 2. XRD patterns of oriented mounts of the < 2 μm size fraction of the samples from El Villar.

955   Figures are d-spacing values in Å. Sample labels are at the right hand side of the patterns. Peaks at

956   9.96 and 3.34-3.32 Å are truncated. a) All samples, treated with ethylene-glycol. EV2 corresponds

957   to the rock without acidic alteration and the intensity of the weathering increases broadly towards

958   the top. The calculated patterns of phyllosilicates are included in a few cases (grey lines)

959   representative of several phyllosilicate compositions. b) Detail of a few representative cases

960   including the air-dried and ethylene-glycol treated samples. Ab: albite; C: chlorite; C-V:

961   interstratified chlorite-vermiculite; F: K-feldspar; I: illite; K: kaolinite; Q: quartz; V: vermiculite.

962

963   Figure 3. XRD patterns of oriented mounts of the < 2 μm size fraction of the samples from Calañas.

964   Figures are d-spacing values in Å. Sample labels are at the right hand side of the patterns. All

965   samples, air-dried and treated with ethylene-glycol. The calculated patterns of phyllosilicates are

966   included for the ethylene-glycol solvated samples. The most intense peaks are truncated. I: illite;

967   K: kaolinite; K-S: interstratified kaolinite-smectite.

968

969   Figure 4. XRD patterns of oriented mounts of the < 2 μm size fraction of the samples from

970   Quebrantahuesos. Figures are d-spacing values in Å. Sample labels are at the right hand side of the

971   patterns. Sample QX corresponds to the rock previous to acidic alteration. Peaks at 3.34 and 3.079

972   Å of the top patterns are truncated. Al: alunite; B: beudantite; C: chlorite; G: goethite; I: illite; Na-

973   Al: natroalunite; Q: quartz.

974

975   Figure 5. XRD patterns of oriented mounts of the < 2 μm size fraction of the samples from Tharsis.

976   Figures are d-spacing values in Å. Sample labels are at the right hand side of the patterns. All

977   samples treated with ethylene-glycol (where there are phyllosilicates). TH12 corresponds to the

978   rock without acidic alteration. The calculated patterns of phyllosilicates are included for sample

979   TH7. Peaks at 10.01 and 3.34 Å are truncated. Al: alunite; G: goethite; I: illite; J: jarosite; K:

980   kaolinite; K-S: interstratified kaolinite-smectite; Q: quartz.

981

982   Figure 6. Mid-IR spectra of the < 2 μm size fraction of the samples from El Villar. The spectra

983   correspond to complex mineral mixtures. The most prominent features are those of kaolinite, illite

984   and quartz. Some weak bands correspond to the plagioclase-feldspar mineral group. For full

985   assignment of the bands see Table 2. The intensity of some spectra was multiplied by the following

986   factors: EV12 (400-1300 cm^{-1} only) x 2; EV13 x 4; EV19 x 2.

987

988   Figure 7. Mid-IR spectra of the < 2 μm size fraction of the samples from Calañas. The spectra

989   correspond to mineral mixtures of kaolinite, illite and smectite. For full assignment of the bands

990   see Table 2.

991

992   Figure 8. Mid-IR spectra of the < 2 μm size fraction of the samples from Quebrantahuesos. The

993   spectra correspond to mineral mixtures including alunite, beudantite, quartz, chlorite, illite

994   kaolinite and goethite. For full assignment of the bands see Table 2. The intensity of some spectra

995   was multiplied by the following factors: Q2 (2900-3900 cm^{-1} only) x 0.7; Q13 (2900-3900 cm^{-1} only)

996   x 2.

997

998   Figure 9. Mid-IR spectra of the < 2 μm size fraction of the samples from Tharsis. The spectra

999   correspond to mineral mixtures dominated by the IR features of kaolinite, jarosite, alunite, quartz,

1000   illite and goethite. For full assignment see Table 2. The intensity of some spectra was multiplied by

1001   the following factors: TH12 (400-1300 cm^{-1} only) x 0.7; TH5 (2900-3900 cm^{-1}) x 3; TH5 (400-1300

1002   cm^{-1}) x 2; TH7 x 0.7.

1003

1004   Figure 10. Chemical plots of bulk rock samples from the four locations investigated.

1005

1006   Figure 11. Chemical and mineralogical plots of the < 2 μm size fraction of the studied samples. The

1007   mineralogical data are from the simulations of the XRD patterns of the oriented mount

1008   preparations. The proportions of clay minerals are relative to the total amount of phyllosilicates

1009   only. Panel a) provides the key to symbols for panels a) to e). Panel f) provides data for three

1010   metal oxides from sites EV and Q.

1011

1012   Figure 12. Qualitative information about the abundance (y axis) of phyllosilicates, alunite and

1013   jarosite from Table 1 (bulk rock), modified with the results from the XRD modeling of the fraction <

1014   2 μm. The plots are based on a 0-3 score abundance (Table 1).

1015

Table 1. Location of samples and their whole-rock mineralogy from XRD of their randomly oriented powders.

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

Q7	xxx	xx		xx (*)		trace
Q8	x	x			xxx (+)	x
Q13	xxx					x

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.

Region 3900-2900 cm⁻¹		Region 1300-900 cm⁻¹		Region 900-600 cm⁻¹		Region 600-400 cm⁻¹	
Wavenumber (cm⁻¹)	Assignment	Wavenumber (cm⁻¹)	Assignment	Wavenumber (cm⁻¹)	Assignment	Wavenumber (cm⁻¹)	Assignment
3703-3695	**Kaolinite**	1223-1221	Alunite	865	Beudantite (probable)	591-587	Plagioclase-feldspar
3670	Kaolinite	1180-1179	Jarosite, beudantite	832-827	Illite	587-580	Jarosite, beudantite
3652-3648	Kaolinite	1165-1162	Quartz	813	Beudantite (probable)	539-532	Kaolinite
3624-3619	**Kaolinite (sharp), illite, smectite**	1159	Alunite	800	Kaolinite	532	Plagioclase-feldspar
3608	Illite	1130	Plagioclase-feldspar	**799-798**	**Quartz**	532-520	Illite
3570-3547	Chlorite	1109-1100	Kaolinite	**780-779**	**Quartz**	525	Alunite
3512-3509	Alunite	**1094**	**Alunite**	763-762	Plagioclase-feldspar	518-517	Jarosite, beudantite
3486	**Alunite**	1093-1091	Plagioclase-feldspar	757-754	Kaolinite, illite	517-508	Quartz
3457	Alunite (Na)	1091-1078	Quartz	752	Kaolinite	509	Chlorite
3464-3380	Adsorbed water (very broad)	1089-1085	Jarosite, beudantite	745	Plagioclase-feldspar	488	Alunite (Na)
3427	Chlorite	1072	Smectite	725	Plagioclase-feldspar	476-475	Jarosite, beudantite
3380-3378	**Jarosite, beudantite**	1042	Plagioclase-feldspar	697-694	Quartz, kaolinite	475-469	Kaolinite, illite
3163-3137	**Goethite**	1033-1029	Kaolinite	689	Vermiculite	468-463	Quartz
3005	Adsorbed water (very broad)	1029-1025	Illite	685	Alunite	463	Chlorite
		1027	**Alunite**	674-670	Alunite	437-421	Illite, plagioclase-feldspar
		1020	Beudantite	673	Chlorite	430	Kaolinite
		1010	Kaolinite, illite	647-650	Plagioclase-feldspar	429-426	Alunite
		1006-1004	Jarosite, beudantite	630-627	Alunite, jarosite, beudantite, goethite	424	Illite
		990	**Chlorite**	609-607	Plagioclase-feldspar		
		936-933	Kaolinite, illite	603-599	Alunite		
		916-911	Kaolinite, illite	601	Alunite		
		903	Goethite?				

Diagnostic, intense bands are in bold type, for a reference in Figures 6-9.

Assignment based on Russel and Fraser (1994), Farmer (1974), Sejkora et al. (2001), Bishop and Murad (2005) and Murphy et al. (2009).
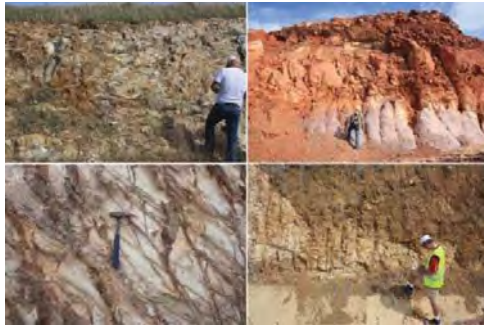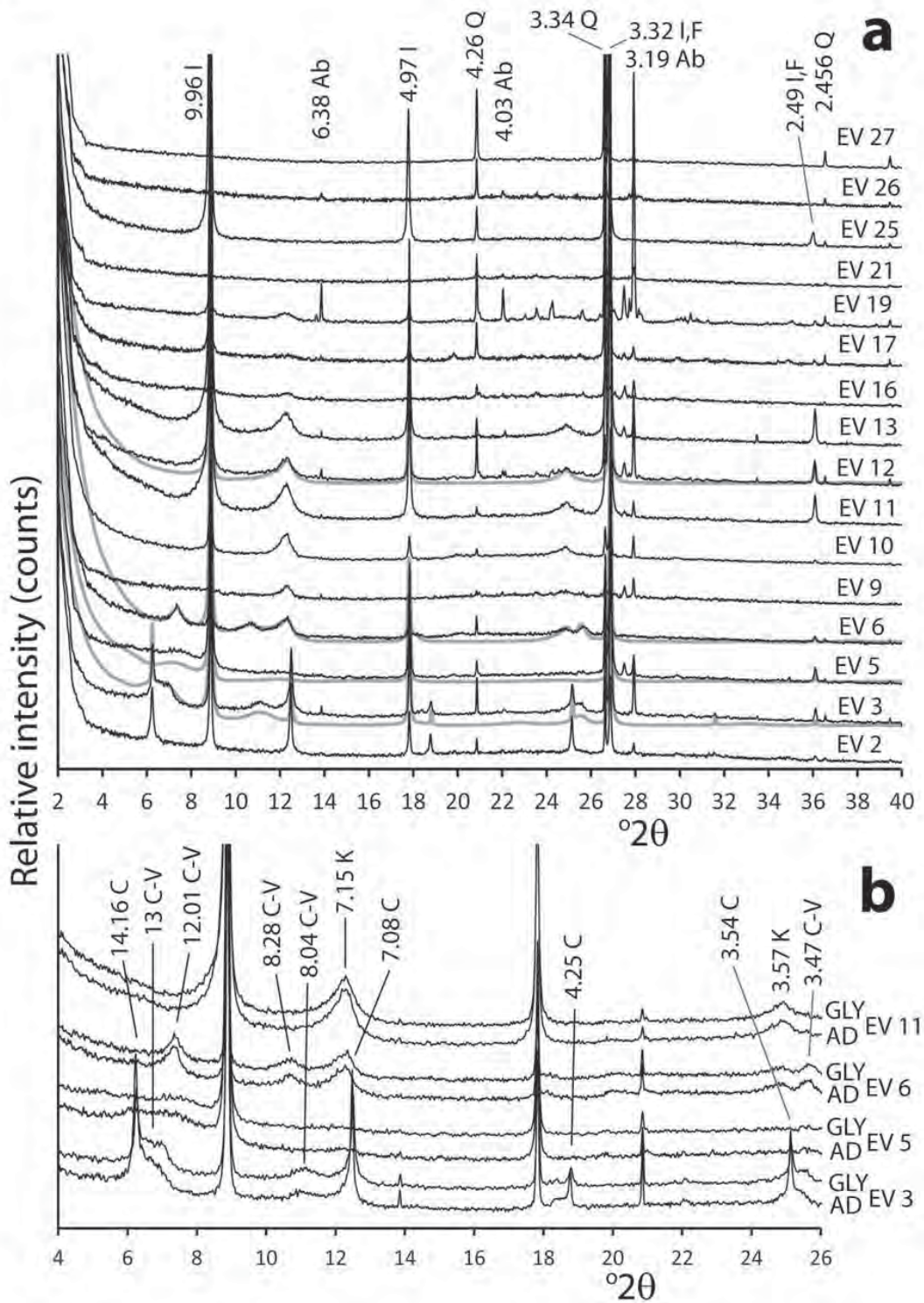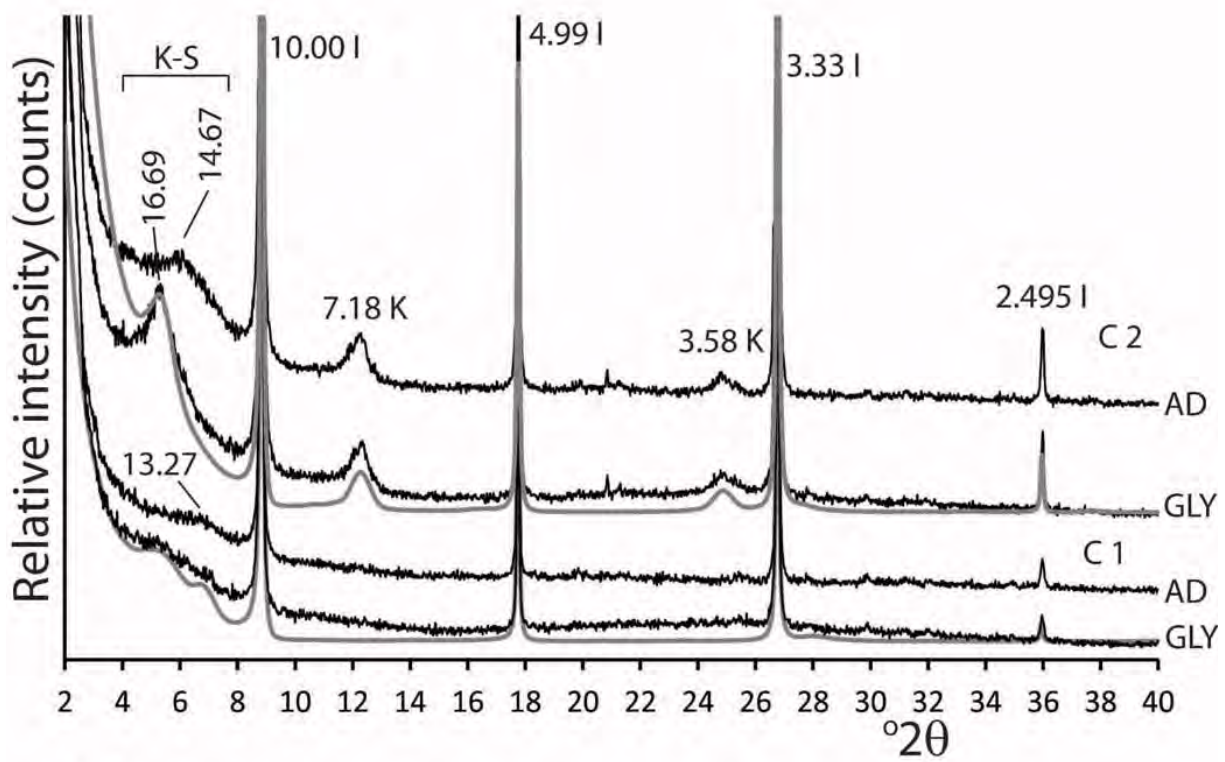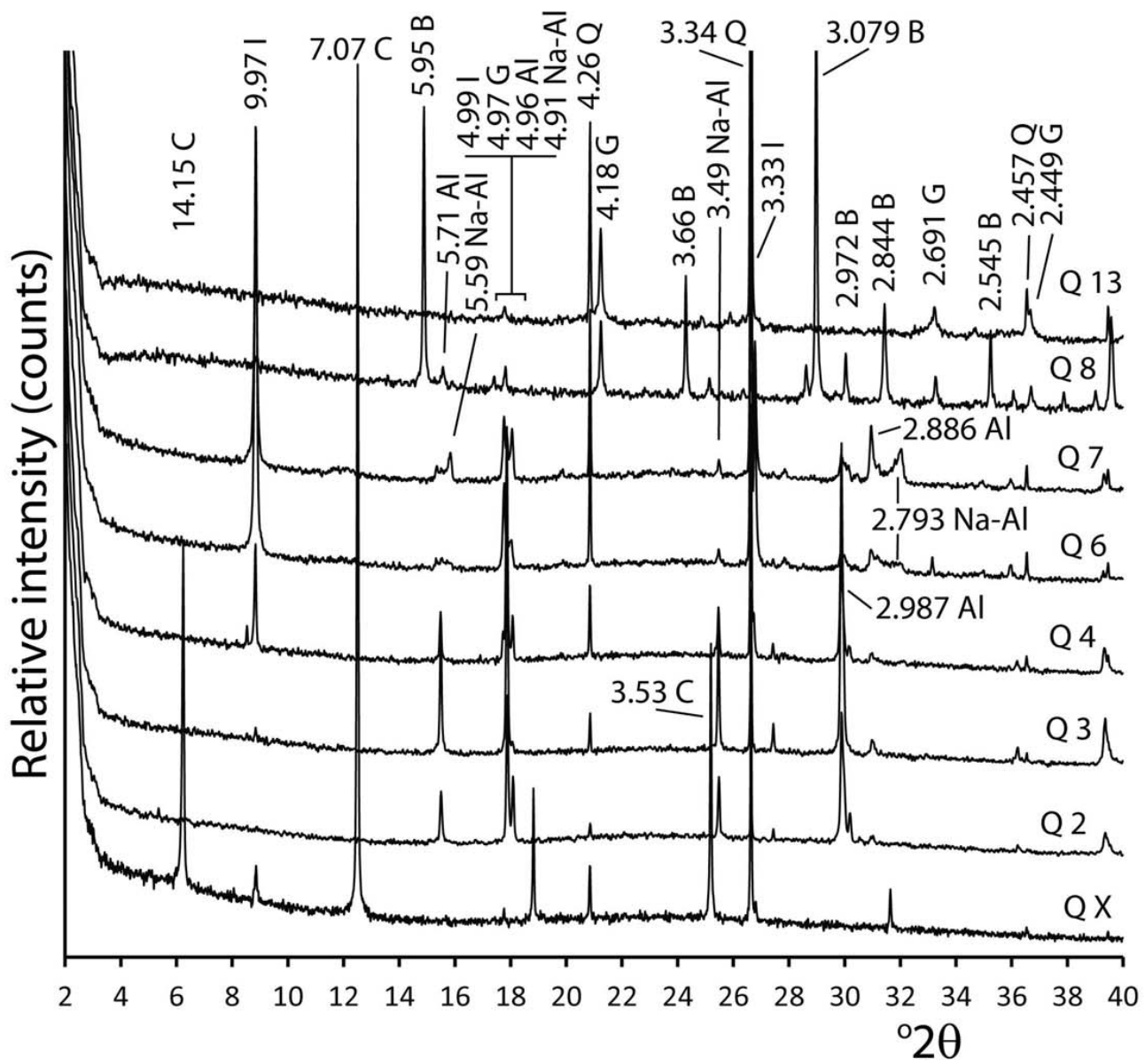
Fig. 1

Fig. 2

Relative intensity (counts)

a

9.96 I
6.38 Ab
4.97 I
4.26 Q
4.03 Ab
3.34 Q
3.32 I,F
3.19 Ab
2.49 I,F
2.456 Q

EV 27
EV 26
EV 25
EV 21
EV 19
EV 17
EV 16
EV 13
EV 12
EV 11
EV 10
EV 9
EV 6
EV 5
EV 3
EV 2

2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40
°2θ

b

14.16 C
13 C-V
12.01 C-V
8.28 C-V
8.04 C-V
7.15 K
7.08 C
4.25 C
3.54 C
3.57 K
3.47 C-V

GLY EV 11
AD
GLY EV 6
AD
GLY EV 5
AD
GLY EV 3
AD

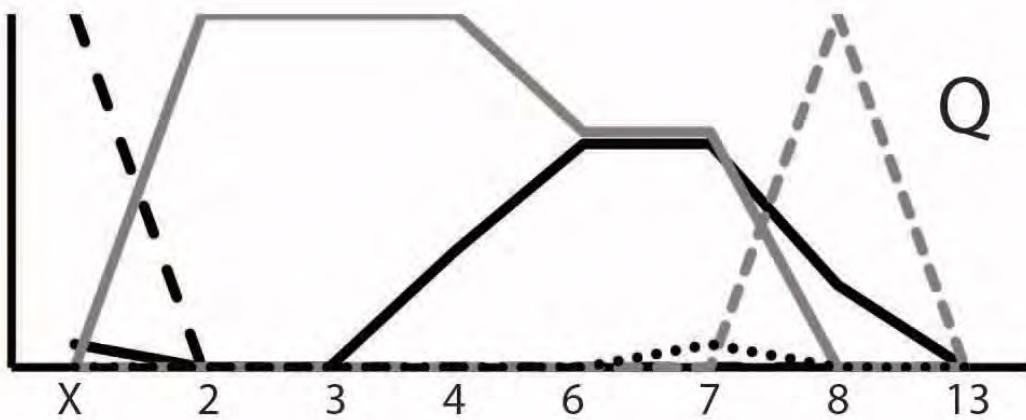4 6 8 10 12 14 16 18 20 22 24 26
°2θ

Fig. 3

Fig. 4
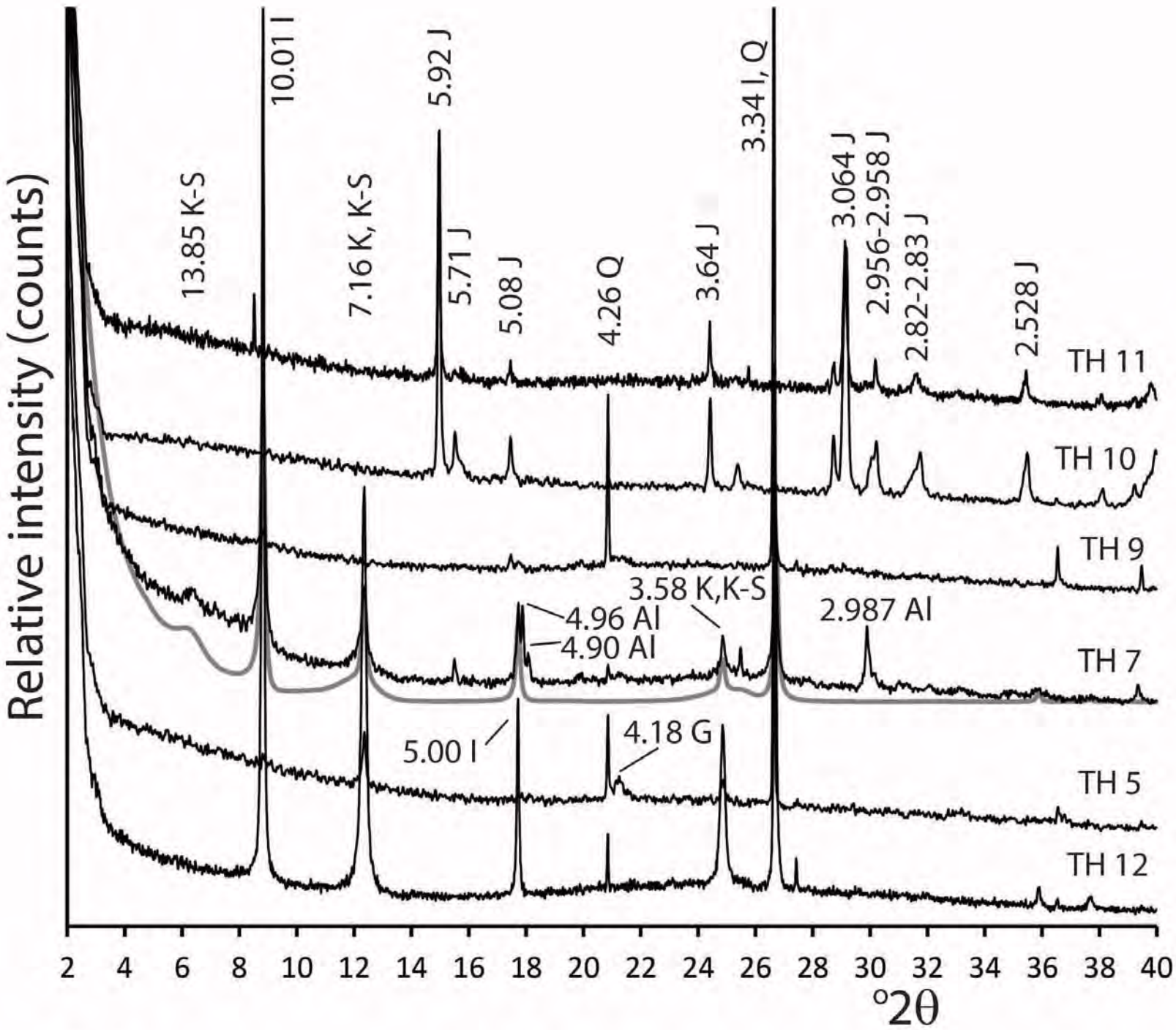
Fig. 5
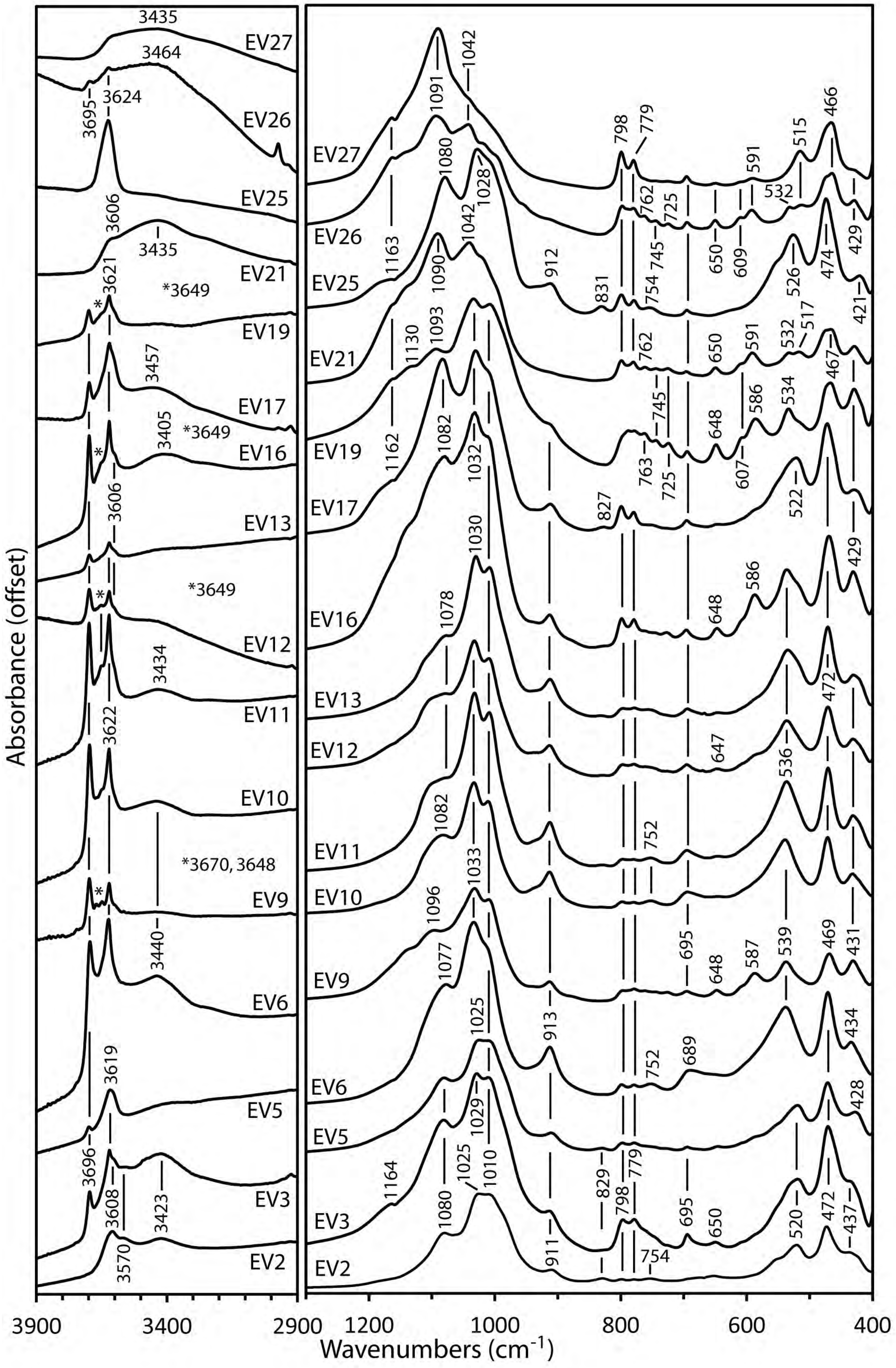
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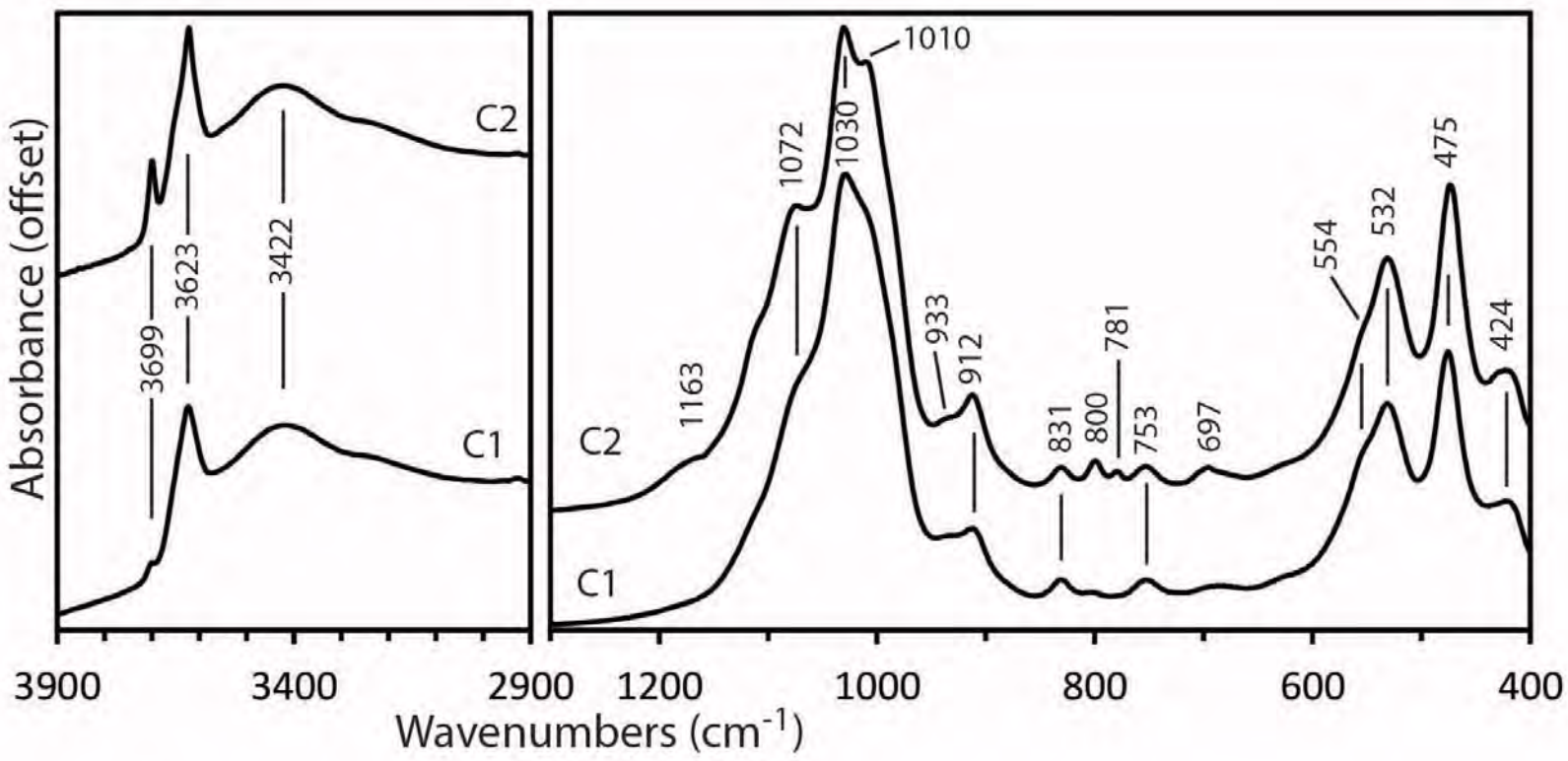
Fig. 7
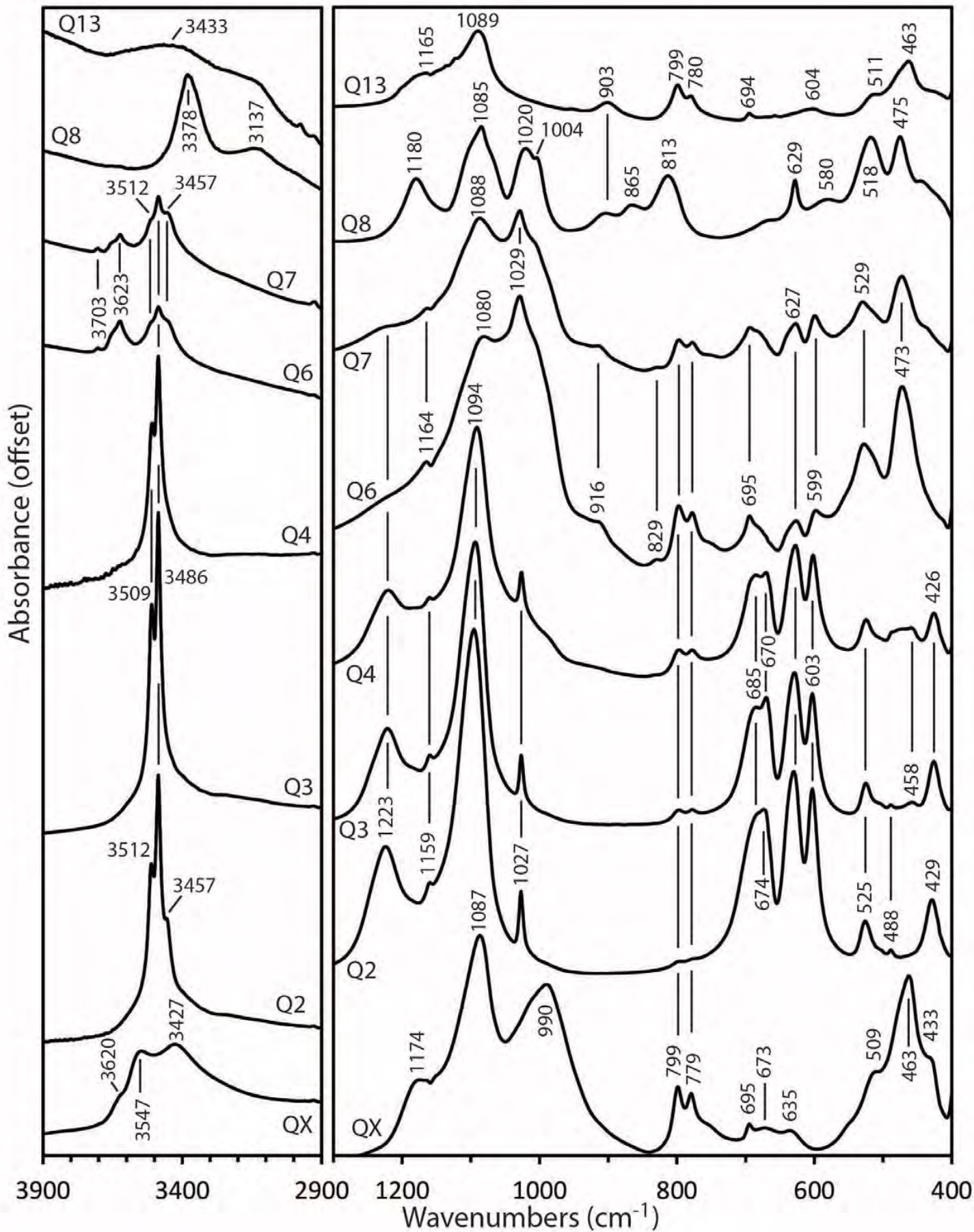
Fig. 8
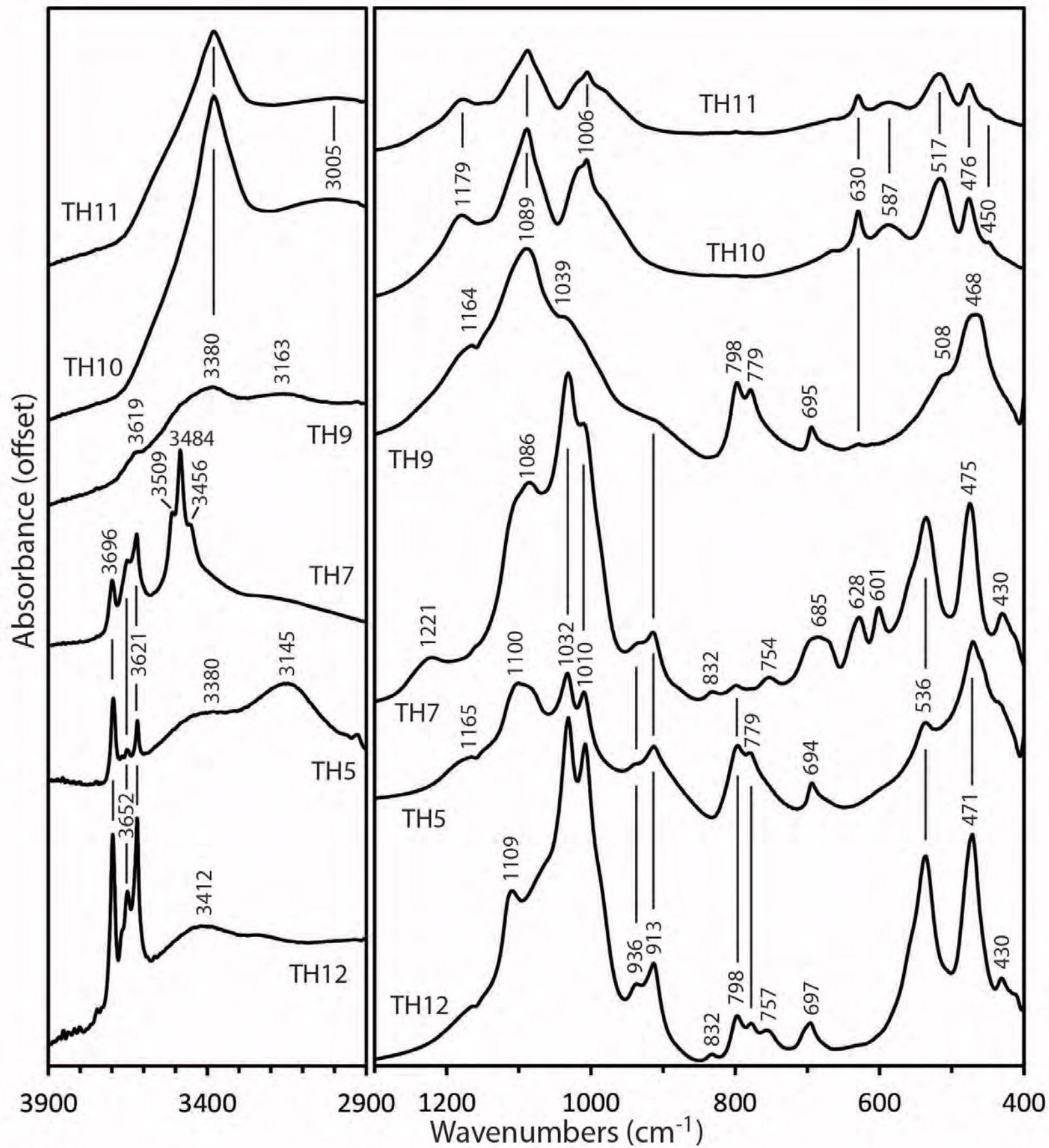
Fig. 9
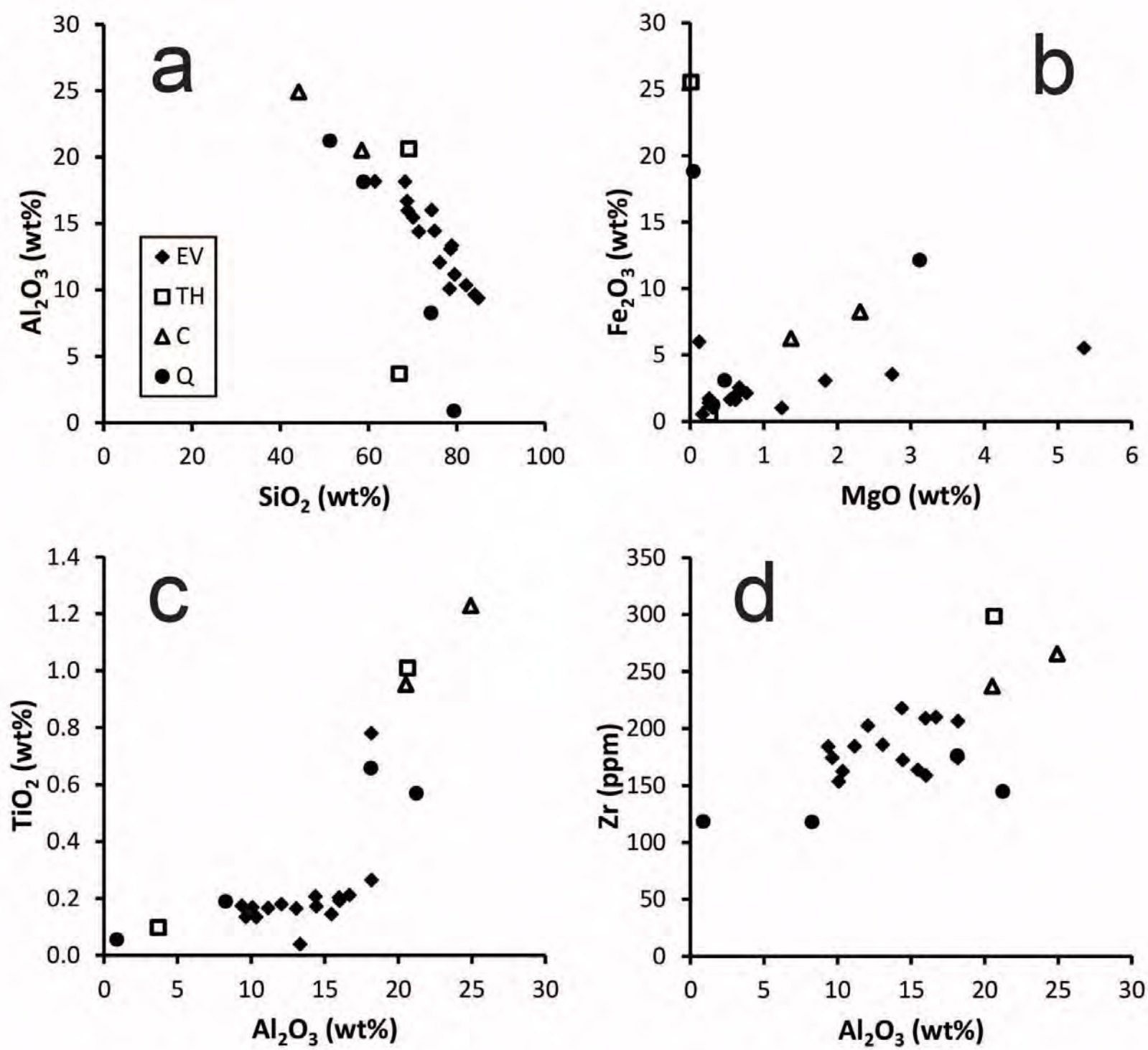
Fig. 10

Figure 11

Figure 12