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**NEW INSIGHTS ON MINERALOGY AND GENESIS OF KAOLIN DEPOSITS:
THE BURELA KAOLIN DEPOSIT (NORTHWESTERN SPAIN)**

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34 16 **ABSTRACT**

35
36 17 **The** Burela deposit is the largest kaolin deposit in Spain, mined for more than 50
37 18 years, the product being mainly used for porcelain. Kaolin is dominantly
38 19 associated **to** **with** Lower Cambrian felsites, interbedded with quartzites,
39 20 micaschists and metapelites (Cándana Series), and **was** strongly folded during
40 21 the Hercycian orogeny. Kaolin layers were ductile and incompetent materials
41 22 among more competent ones, producing many slides with a diastrophic
42 23 appearance. Consequently, kaolin outcrops are morphologically very variable, -
43 24 i.e. pockets -, and interlayered between metapelites and/or quartzites, resulting
44 25 in **difficult** **complication** **for** prospection and mining.
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53 26 **The** kaolin consists mainly of kaolinite, tubular halloysite, and spherical allophane
54 27 along with quartz and minor illite. The content of kaolin minerals reaches up to
55 28 90% in the finer fraction (<2µm and <1µm).
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29 Geochemical analyses of trace and REE show a close relationship between
30 kaolin and associated rocks. Two kaolin types can be differentiated: (i) massive,
31 associated to felsite; and (ii) related to metapelite. A temperature range from 20
32 to 35°C, with an average of approximately 28°C was calculated on the basis of
33 the isotopic signatures ($\delta^{18}\text{O}$, δD) for the kaolin materials. This scatter suggests
34 that if continental weathering was involved in the kaolin formation on the lower
35 side of the temperatures, it was not the only process, especially for kaolin
36 associate **to with** felsites and metapelites. The higher temperatures are indicative
37 of a hydrothermal auto-metamorphic alteration, followed by a folding of the series
38 that induced an apparently chaotic kaolin distribution with a combined continental
39 weathering superimposed on the previous low-temperature hydrothermal felsite
40 transformation.

41 Key words: kaolin genesis, trace elements, isotopes, halloysite, Galicia, Spain

43 INTRODUCTION

44 The origin of primary kaolin deposits is usually a matter of controversy because
45 kaolinite can be formed *in situ* by weathering reactions (supergene kaolins),
46 hydrothermal alteration during the late stages of magma cooling (hydrothermal
47 kaolins), or by a combination of both processes (Murray, 1988). Kaolinite can be
48 formed also within sedimentary continental basins by diagenetic processes
49 (Galán and Ferrell, 2013). Various criteria and indicators have been proposed to
50 distinguish supergene from hypogene kaolins (e.g. Dill et al., 1997, Gilg et al.,
51 1999), although some of them are considered as ambiguous. Unravelling the
52 genesis of kaolinite in deeply weathered magmatic rocks is, **therefore**, one of the
53 most important challenges faced by clay geologists.

54 In the Variscan belt of Galicia (NW Spain) kaolinization of crystalline rocks is
55 widespread. Large high-grade deposits of kaolin (e.g. Vimianzo, Nuevo
56 Montecastelo) and other minor occurrences are found in association with
57 weathered granites. The combined oxygen and hydrogen isotope composition of
58 kaolinite from such deposits is consistent with data of supergene kaolin formation
59 (Clauer et al., 2010, **2015**; Fernández-Caliani et al., 2010; **Clauer et al.**
60 **submitted**). However, some deposits associated with felsite dykes or sills and

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61 quartz vein networks could have been formed *in situ* by complex fluid/rock
62 hydrothermal and supergene interactions.

63 The Burela kaolin deposit (Northern Galicia) is a volcanic-hosted deposit, which
64 is of particular interest in addressing the origin and timing of kaolinization.
65 Volcanic-hosted kaolin occurrences of no current economic interest are also
66 found in other areas of Spain, such as the Canary Islands and within the volcano-
67 sedimentary complex of the Iberian Pyrite Belt, but However it is in the Burela
68 area that the type where kaolinization is best represented. The deposit is
69 geologically located (Fig. 1) in the West Asturian-Leonese Zone (WALZ), one of
70 the major tectono-stratigraphic terranes into which the Iberian Massif is classically
71 subdivided (Julivert et al., 1972). The WALZ exposes Precambrian to Devonian
72 metasediments that experienced the effects of the Variscan orogeny between
73 Late Devonian and Late Carboniferous times (Martínez-Catalán et al., 1997;
74 Pérez-Estaún and Bea, 2004).

75 The main Burela quarries are of San Andrés and Ramón Fazouro that are located
76 near the western edge of Fazouro village (Fig. 1). The kaolin is spatially and
77 genetically related to felsites and a swarm of quartz-porphyry dykes that intruded
78 Lower Cambrian metasediments. Kaolin is dominantly associated with Lower
79 Cambrian felsites, interbedded with quartzites and sandstones, and metapelites
80 (Cándana Series), and it was which were strongly folded during the Hercynian
81 orogeny. Kaolin-rich layers were became a ductile and incompetent materials
82 interleaved among the more competent ones, producing many slides with a
83 diastrophic appearance. Consequently, the kaolin outcrops are morphologically
84 very variable (i.e. pockets) interlayered between other rocks, resulting in difficult
85 prospection and mining.

86 This world-class kaolin deposit has been mined by ECESA for more than half a
87 century (1957-2014), with the kaolin being mainly used as raw material in the
88 manufacture of high quality ceramics, especially porcelain-ware. The kaolin
89 material consists of a mixture of kaolinite and halloysite with minor allophane
90 (Galán et al., 2013). The origin of this important economic deposit is still an
91 ongoing matter of debate. It is unclear if extensive kaolinization resulted from
92 hydrothermal (by meteoric fluids) alteration of felsitic rocks, or if weathering
93 affected material that was already subjected to a first stage of auto-low grade

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94 ~~metamorphic alteration~~ **metamorphism**, or a combination of the two processes
95 induced the deposit (Galán and Martín Vivaldi, 1972). The aim of this paper is to
96 revisit the arguments first presented, (i.e. hydrothermal alteration by meteoric
97 fluids) **on** the basis ~~of~~ **on** new insights from mineralogy, trace-element
98 geochemistry and stable isotope data, ~~and to contribute to~~ **Such understanding**
99 **will be helpful for future** ~~the~~ exploration for new deposits in the region and to the
100 rationalization of ~~their~~ mining operations.

101 102 **SAMPLING AND ANALYTICAL METHODS**

103 A representative sampling of the Burela kaolin deposit was undertaken in the
104 Ramón Fazouro quarry (Fig. 2). **A total of fourteen samples of** ~~The~~ different kaolin
105 occurrences and their associated rocks were sampled. Three size fractions (<45,
106 <2 and <1 μm) were extracted from each whole rock by wet sieving,
107 sedimentation in distilled water and centrifugation. The size fractions were
108 mineralogically analysed by X-ray diffraction (XRD) on a Bruker D8 Advance
109 instrument with a scanning speed of $0.5^\circ(2\theta)/\text{min}$, 0.15 step/size, and Cu- $\text{K}\alpha$
110 radiation (40 kV, 30 mA). The quantitative composition was carried out following
111 the procedures of Schultz (1964), Martín-Pozas et al. (1971) and Galán and
112 Martín Vivaldi (1973) for the whole kaolin and the <45 and <2 μm fractions. In
113 order to resolve the unequivocal identification of kaolinite and halloysite from the
114 XRD patterns, and to provide a method of quantification in these types of
115 samples, a fitting process was applied to the 002 XRD reflections ($\sim 3.5 \text{ \AA}$), using
116 a pseudovoigt function for minimising the effect of the Lorentz-Polarization
117 factor, since this signal appears at relatively high angles ($24\text{-}26^\circ$) (Márquez et al,
118 2009).

119 The Rietveld method was used with the TOPAS program to evaluate the
120 mineralogical composition of the <1 μm separates, to obtain a very precise
121 mineralogical composition for this size fraction, potentially the least modified by
122 contaminant minerals, and to quantify the proportions of the different kaolin
123 minerals (e.g. kaolinite vs. halloysite). This procedure was applied to the <1 μm
124 fraction to relate the isotopic with the mineralogical data.

125 A few samples (5) were selected for high-resolution observation by a scanning
126 electron (HRSEM) HITACHI S5200 instrument, fitted with an EDS detector. The
127 particle morphology was also studied by atomic force microscopy with a Pico Plus
128 instrument. In addition the country rocks were optically examined under polarizing
129 photomicroscope. X-ray analyses and microscopy observations were performed
130 at the CITIUS (Research Facilities Centre at the University of Seville, Spain).

131 For the bulk sample and <45 and <2 μm fractions, chemical analyses were carried
132 out at the Activation Laboratories Ltd. (Ontario, Canada) following a lithium
133 metaborate/tetraborate fusion technique that ensures dissolution of the entire
134 sample. Major-element concentrations were determined by inductively coupled
135 plasma-optical emission spectrometry (ICP-OES) on a Thermo Jarrell Ash
136 ENVIRO II, and trace elements were analyzed by inductively coupled plasma-
137 mass spectrometry (ICP-MS) on a Perkin Elmer Optima 3000. Quality control
138 included the use of several certified reference materials, duplicates and blanks
139 by the laboratory to check accuracy and precision. The chemical results were
140 statistically treated in order to realize cluster analysis.

141 The mineralogical maturity of weathering was estimated using the mineralogical
142 index alteration (MIA; Johnsson, 1993; Nesbitt et al., 1996), which is a
143 dimensionless number between 0 and 100, calculated from mineral weight
144 percentages derived from XRD analysis as follows:

$$145 \quad \text{MIA} = [\text{quartz} / (\text{quartz} + \text{K-feldspar} + \text{plagioclase})] \times 100$$

146 The chemical index of alteration (CIA, Nesbitt and Young, 1982) was calculated
147 to evaluate the degree of chemical weathering. CIA is also a dimensionless
148 number between 0 and 100, and shows the weathering of feldspar minerals. It is
149 calculated using molecular proportions as follows:

$$150 \quad \text{CIA} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})] \times 100$$

151 where CaO^* presents the amount of CaO combined in the silicate fraction of the
152 rock.

153 The stable isotope data were obtained in two different laboratories. In both
154 places, samples were vacuum-degassed at 200°C overnight to remove the
155 interlayer and absorbed surface water prior to hydrogen isotope analysis. Then,

156 they were transferred to an out-gassed Pt crucible and the water released by
157 heating was reacted with hot metal, producing H₂ for determination of δD. For the
158 samples analysed at the Activation Laboratories (Canada), uranium at 900°C was
159 used for D/H; for δ¹⁸O analysis, BrF₅ at 650°C was reacted with the kaolin in a Ni
160 chamber (Clayton and Mayeda, 1963) to generate O₂ that was reduced to CO₂
161 with graphite using Pt as catalyst at 550-600°C. The precision at 1σ was ± 2‰
162 and 0.3‰ respectively for δD and δ¹⁸O. For those results obtained at East
163 Kilbride (UK), dehydroxylation was achieved by heating the Pt crucible at 1200°C
164 by radiofrequency induction. The water released was converted to H₂ by reacting
165 with Cr at 800°C (Bigeleisen et al., 1952; Donnelly et al., 2001) in a multiple-pass
166 system. The H₂ yield was measured manometrically and the δD determined on a
167 gas-source mass spectrometer calibrated via water and mineral standards. Using
168 these techniques, the NBS30 biotite standard gave a δD of -65‰ (V-SMOW) with
169 an analytical reproducibility of ± 2‰ (1σ), ± 3‰ (1σ) being more appropriate for
170 clay material. The oxygen isotope composition was determined by laser
171 fluorination (Macaulay et al., 2000) using the Borthwick and Harmon (1982) ClF₃
172 modification of Clayton and Mayeda (1963). The precision for the clay material is
173 ± 0.3‰ (1σ), the NBS28 quartz standard giving a δ¹⁸O of 9.6‰ (V-SMOW). All
174 clay isotope data are reported in parts per mil (‰) relative to the V-SMOW
175 standard. No significant systematic isotope ratio difference between the two
176 laboratories was observed. Stable isotopes were determined for **four samples**
177 **<45 μm fraction and eight samples <2 and <1μm fractions.**

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179 **RESULTS AND DISCUSSION**

180

181 ***Precursor host rocks***

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183 The Burela kaolin deposit is hosted in felsic porphyritic volcanic rocks interbedded
184 with metasedimentary rocks, notably Lower Cambrian metapelites and quartzites
185 (Cándana Quartzite). Representative mineralogical and chemical analyses of the
186 precursor rocks of the kaolin deposit are given in Tables 1 and 2.

187 In thin section the felsic volcanic rocks display a holocrystalline, porphyritic
188 texture (Fig. 3a), with phenocrysts of feldspar and partially reabsorbed quartz and
189 set in a groundmass composed of fine-grained plagioclase, muscovite, and biotite
190 (often altered to chlorite and associated to iron oxides). Quantitative XRD
191 mineralogical determination showed that quartz accounts for 24-33% of the bulk
192 sample, the feldspars range from 60 to 67%, with mica contents up to 30%. In
193 partially altered samples, the amount of feldspars decreases by up to 35%
194 yielding MIA values of 46. ~~Based on their total alkali-silica content (“TAS~~
195 ~~diagram”, Le Bas et al., 1986),~~ According to the TAS binary diagram (total silica
196 vs alkali content) of Le Bas et al. (1986), the felsic rocks can be classified as
197 lavas of rhyolite-to-trachydacite composition.

198 The pelitic schists have a lepidoblastic texture and exhibit a strong penetrative
199 foliation defined by preferred orientation of muscovite laths and quartz ribbons
200 (Fig. 3b). ~~Heterogenic~~ Chlorite and relict detrital grains of tourmaline, rutile and
201 zircon are present as accessory phases. Intensely altered metapelitic rocks (MIA
202 value as high as 87) are characterized by high content of clay minerals, notably
203 kaolinite, ~~accounting~~ which can account for up to 38% (Table 1).

204 The Cándana quartzite shows a medium-grained granoblastic texture, in which
205 quartz exhibiting undulate extinction typically forms a mosaic of polygonal
206 crystals (Fig. 3c), with muscovite, tourmaline, zircon and rutile as subordinate
207 minerals].

208

209 ***Mineralogical characteristics of kaolin.***

210 The mineralogy of the bulk samples is dominated by highly variable contents of
211 kaolin minerals (17-74%) and quartz (16-69%), accompanied by mica (up to 33%)
212 (Table 3). Other phases that may be present, usually in subordinate or trace
213 amounts, are feldspars and smectites. Additionally, SEM-BSE observations in
214 combination with EDS microanalysis revealed a distinctive suite of heavy
215 minerals including zircon, monazite, rutile, ilmenite and iron oxides.

216 ~~For~~ Within the <45µm fraction, the amounts of kaolin minerals ~~scatter notably in a~~
217 is variable with a wide concentration range (62-90%), with kaolinite being

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218 dominant over halloysite. The contents of quartz and illite were lower than 24%
219 in all the samples, whereas feldspars, smectites and allophane were found as
220 accessory phases. In the fine fractions, the amount of kaolin minerals reached up
221 to 92 % (Table 4-2). Traces of allophane, gibbsite and chlorite were detected in
222 some samples and fractions. The fractions <2µm and <1µm contains mostly
223 kaolinite and halloysite, with minor illite and quartz (Table 4).

224 Tubular halloysite accounts for 11 to 60% of the kaolin, while kaolinite content
225 varies between 23 and 60%, with kaolinite/halloysite ratios ranging from 6 to 0.5.
226 These results substantially agree with the microscopic observations (Figure 4).
227 Tubular crystals of halloysite (0.5-8µm of length) appear to be joined to book-like
228 kaolinite aggregates (Figure 4a, 4e and 4f) and kaolinite crystals are oriented face
229 to face (Fig 4 b and 4d). Halloysite crystals appear also in the form of clusters
230 (Fig 4c). Spherical shaped particles (0.5µm in diameter) were also detected by
231 AFM, which correspond to allophane: it is not common to find at the same time
232 tubular and spherical halloysite (Fig 4f). Tubular halloysite mostly corresponds to
233 a weathering phase while spherical halloysite is instead formed by direct
234 precipitation (neof ormation) and it is usually considered as a precursor of tubular
235 halloysite (Duzgoren-Aydin et al. 2002).

236 237 **Major and trace element geochemistry**

238
239 Chemical analysis analyses of the whole rock samples shows that the
240 geochemistry of major elements (Table 3) is largely dominated by Si and Al,
241 reflecting the high content of kaolin minerals in the altered rocks. Silica displays
242 a broad range of concentrations (58.2-76.3 wt % SiO₂), except for the altered
243 quartzite (RF-12) which is also strongly and negatively correlated with both the
244 alumina content (r= -0.99) and the weight loss on ignition (LOI; r= -0.88). The
245 highest abundances of alumina (23-27 wt % Al₂O₃) and LOI (8-12 wt %) were
246 found in samples from the upper part of the studied section.

247 The remaining major elements, except potassium, are all present at
248 concentrations less than 1wt%. The K₂O content varies from 4.8wt% to 0.8wt%,
249 with a mean value of 2.3wt%. The variations are closely related to the presence

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250 of orthoclase and muscovite in the samples. The low content of calcium and
251 sodium oxides is likely considered due to weathering of the plagioclases. The CIA
252 varies from about 65 in the fresh felsitic rocks to around 96 in the most weathered
253 felsite, suggesting a significant removal of labile basic cations (mainly K, Na, and
254 Mg) relative to stable residual elements (Si, Al, Fe). The loss of alkaline and
255 alkaline-earth elements can be attributed to the alteration (kaolinization) of
256 alkaline alkali feldspar and mica, which are the minerals in the felsitic rocks most
257 prone to weathering. In addition, the CIA of the metapelite is 84%, which indicates
258 that this rock is highly altered, as confirmed by the high kaolin minerals content
259 (31wt%).

260 The fine-grained kaolin rich samples (the <45 and <2µm fractions) contain a
261 higher proportion of alumina (up to 37 wt % Al₂O₃) and concomitantly less silica
262 (44-59 wt %) (Table 5). An enrichment in titanium oxide is detected in metapelite
263 (RF-2) and in the samples RF3-05, RF-12 and RF-14, when the major elements
264 composition is normalized to felsite (RF-8) (Figure 5a). As was noted above, the
265 metapelite presents abundant rutile. The other kaolin samples do not present
266 contains any significant anomaly in comparison with the felsite host rock.

267 When the major element compositions of samples RF3-05, RF-12 and RF-14 are
268 normalized to the metapelite reference (Figure 5b), no striking anomaly is visible
269 and the signatures of the samples are very similar to metapelite. The egregious
270 unexpectedly high anomaly is of 2.5 in the case of iron oxide for <45µm fraction
271 of sample RF-14.

272 An enrichment in the high field strength elements (HFSE) Sc, Zr, Hf and Th has
273 been detected in kaolin when the data are normalized to felsite (RF-8) (Figure
274 6a), probably due to their resistance to weathering (e.g. Middelburg et al., 1988;
275 Panahi et al., 2000). Thus the HFSE remained relatively immobile, linked to
276 resistant heavy minerals (zircon, monazite and titanium oxides) that tend to be
277 residually concentrated in the finer fractions of the kaolin. A very high statistical
278 correlation (r= 0.97) was obtained between Zr and Hf, so that both elements
279 mostly reside in the crystal structure of zircon. Elevated correlation coefficients
280 were also observed between Nb and Ta (r= 0.88) because of the close
281 geochemical affinity of such elements. Thorium shows a positive correlation (r=
282 0.65) with the light rare earth elements (LREE) consistently indicating that it is

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283 hosted by monazite, which is the only LREE-rich accessory phase occurring in
284 the kaolin.

285 High enrichments for large ion lithophile elements (LILE), such as Rb, Sr and Cs,
286 are found in relation to metapelite for the samples RF-12 and RF-14, especially
287 in the <45µm fraction (Figure 6b). But, when the trace-element compositions of
288 samples RF-3-05, RF-12 and RF-14 are normalized to the metapelite
289 composition, no anomaly is apparent with the signature of these samples very
290 similar to that of the metapelite. On the contrary, the major anomalies are for Cs,
291 Tl, Pb, Rb, Sr and Ta of the felsite and the other kaolin samples. The LILE
292 probably were preferentially removed from the felsite rock during kaolinization, as
293 noted by the depletion of Rb, Sr, and particularly Ba, in the kaolin.

294 The kaolin is not especially enriched in trace elements, although the overall
295 abundance varies with the grain-size distribution (Tables 6 and 7). The <45µm
296 fraction of the kaolin tends to have greater concentrations (Σ REE= 237-440 ppm)
297 than the whole sample (Σ REE= 65-209 ppm), indicating a relative accumulation
298 of REE-carrying minerals in the finer fractions. Seemingly, kaolinite could have
299 played a role in scavenging REE, as reported in some weathering systems (Putter
300 et al., 2002; Papoulis et al., 2004). Exceptionally, the sample RF-17 is markedly
301 depleted in total REE (whole sample: 29 ppm; <45µm fraction: 37 ppm; <2µm
302 fraction: 85 ppm) relative to the felsite rock, although the REE concentration level
303 also exhibits the same dependence on the particle size of the kaolin.

304 Similar overall enrichments in REE have been documented in weathering profiles
305 developed on granitoids elsewhere in the Galician region (Galán et al., 2007,
306 Fernández-Caliani et al., 2010). However, at the Burela deposit the total REE
307 content shows no significant correlation with the intensity of the chemical
308 alteration (as shown by the CIA values), suggesting that other processes of
309 remobilization and redistribution of REE occurred in this deposit. In addition, all
310 the samples yield a similar pattern of the REE composition: in fact the shape of
311 the REE patterns is identical for all grain-size fractions, characterized by a slight
312 LREE enrichment ($La_n/Sm_n=3.50-13.56$) and a HREE depletion ($Gd_n/Yb_n= 1.70-$
313 5.24). The positive Ce anomaly is due to the residual character of this element,
314 which undergoes only partial oxidation (Gouveia et al., 1993).

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315 The REE diagrams of the kaolin whole samples normalized against the fresh
316 felsite (Fig. 7a) exhibit a nearly flat pattern with a slight enrichment in heavy REE
317 (HREE), which is more prominent in the fine-grained samples (Fig. 7b). The
318 HREE distribution seems to be controlled, therefore, by HREE-enriched phases
319 like zircon, ilmenite, and rutile (Laveuf and Cornu, 2009). These resistant
320 minerals are not expected to be highly mobilized during alteration, and therefore
321 they tend to be residually accumulated in the kaolin deposit, thus increasing the
322 HREE budget. A cluster analysis identifies two types of geochemical signature
323 (trace elements and REE) and the massive kaolin samples can be grouped into
324 two main groups: associated to felsite and associated to metapelite (Figure 8).

325 In summary, the geochemical study of trace elements and REE showed a close
326 relationship between kaolin and associated rocks, and from the geochemical
327 point of view two kaolin types can be differentiated: massive kaolin associated to
328 felsite and massive kaolin associated to metapelite, as above it has been largely
329 discussed.

330

331 ***Stable isotope geochemistry***

332 Combined stable oxygen and hydrogen (deuterium) isotope studies are
333 commonly used to help discriminate between supergene and hypogene kaolins,
334 and are considered to be the most powerful method to constrain temperatures of
335 kaolinization (Gilg, et al. 1999).

336 The isotopic composition of nearly pure kaolin samples (<1 μ m fraction) from
337 Burela deposit showed a narrow range of $\delta^{18}\text{O}$ values (19.8-21.0‰) and δD ratios
338 ranging from -85 to -63‰, with the mean $\delta^{18}\text{O}$ and δD values being $20.4\pm 0.4\text{‰}$
339 and $-74\pm 3\text{‰}$, respectively (Table 8). The scatter is close to the analytical error,
340 indicating little geological variation. There is no statistically significant correlation
341 between the two isotope ratios ($r = -0.39$, less than 80% significant for $n=7$). The
342 mean water content of $7.4\pm 0.4\text{wt.}\%$ corresponds to $13.3\pm 0.7 \mu\text{moles mg}^{-1}$ of
343 water, compared to the theoretical value of 14 for stoichiometric kaolin.

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344 When plotted on a $\delta^{18}\text{O}$ - δD diagram (Fig.9), all the points plot in the supergene
345 field, *i.e.* on the right of the supergene-hypogene line of Sheppard et al. (1969),
346 and very close to the kaolinite weathering line (KWL), which represents the
347 isotopic compositions of kaolinites in equilibrium with meteoric waters at 20 °C.
348 Similar values are given in the literature for residual kaolin deposits derived from
349 Variscan granites (Bobos and Gomes, 1998; Boulvais et al., 2000; Clauer et al.,
350 2010, 2015; Fernández-Caliani et al., 2010; Galán et al., 2010; Clauer et al.,
351 submitted). Here, the overall range of the calculated temperatures from studied
352 kaolin separates ranges from 20 to 35 °C. These temperatures are compatible
353 with a low-temperature hydrothermal activity, *i.e.*: a hydrothermal auto-
354 metamorphic alteration that could occur on the felsite during submarine volcanic
355 activity.

356 On the basis of a variety of assumptions involving plausible formation in an open
357 system with high water–rock ratio and near-surface temperatures, a comparison
358 with Delgado and Reyes (1996) modelling appears appropriate at this point,
359 remembering that these authors assume an interaction with meteoric waters.
360 Thus, the temperature and isotopic composition of the water from which kaolinite
361 formed in equilibrium can be determined from the following equations:

362 [1] The meteoric-water equation: $\delta\text{D} = 8\delta^{18}\text{O} + 10$ (Craig, 1961)

363 [2] The equilibrium hydrogen isotope fractionation factor (α^{H}) between kaolinite
364 and water (Gilg and Sheppard, 1996): $1000 \ln \alpha^{\text{H}}_{\text{kaol-water}} = -2.2 \times 10^6 T^{-2} - 7.7$

365 [3] The equilibrium oxygen isotope fractionation factor (α^{18}) between kaolinite and
366 water (Sheppard and Gilg, 1996): $1000 \ln \alpha^{18}_{\text{kaol-water}} = 2.76 \times 10^6 T^{-2} - 6.75$.

367 In combining the equations of Sheppard and Gilg (1996) for kaolinite, $\delta^{18}\text{O}_w$, δD_w
368 can be eliminated by using the meteoric water line equation, giving:

369
$$3.04 \cdot 10^6 T^{-2} = \delta^{18}\text{O}_k - 0.125 \delta\text{D}_k + 7.04$$

370 The crystallization temperature of kaolinite obtained by applying this equation to

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371 the average of the measured <1 μm kaolin separates at 14.7 °C is compatible
372 with the supergene environment. This value is slightly higher than the current
373 annual mean temperature of the Galician region (12 °C), but is a reasonable
374 surface temperature expected during the Pliocene (Boulvais et al., 2000), with an
375 accuracy of the equations representing the temperature dependence of the stable
376 isotope fractionation equations (in (2) and (3) above) not at all well quantified.
377 The possible mean isotopic composition of the meteoric water with which kaolinite
378 crystallized at isotopic equilibrium has been calculated at $\delta^{18}\text{O} = -6\text{‰}$ and $\delta\text{D} = -$
379 40‰ (Fig. 9; mean values for the minerals taken from Table 8), using the above
380 average temperature and the isotope fractionation factors of Sheppard and Gilg
381 (1996) and Gilg and Sheppard (1996), respectively.

382

383 CONCLUSIONS

384 The Burela deposit is characterized by a high concentration of kaolin minerals
385 (kaolinite and halloysite). In the coarse fraction the most abundant kaolin mineral
386 is kaolinite of perfect pseudo-hexagonal morphology. Tubular halloysite is
387 concentrated in the finer fractions.

388 The geochemical study of the trace elements and REE showed a close
389 relationship between kaolin and associated rocks, and from the geochemical
390 point of view two kaolin types can be differentiated: associated to felsite and
391 associated to metapelite.

392 A felsite hydrothermal auto-metamorphic alteration is suggested for the origin of
393 the kaolin, as an initial kaolinization step. Later a folding of the series led to an
394 apparently chaotic kaolin distribution and a weathering action on the felsite
395 completed the kaolin formation, superimposed on a low-temperature
396 hydrothermal felsite transformation, ~~as kaolinite is not mixed with common~~
397 ~~minerals typical for hydrothermal kaolins (pyrophyllite, dickite and nacrite, among~~
398 ~~others)~~. On the contrary, the occurrence of ~~gibbsite and~~ allophone in some
399 samples point toward a supergene origin of the kaolin. On the other hand,
400 micaschists were also kaolinized by weathering. The kaolin was a plastic
401 incompetent material during the folding, which accumulated in the weaker zones,

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402 and was a detachment level for the more competent materials (mainly quartzite
403 and sandstone).

404 The isotopic composition of the nearly pure kaolin is consistent with a supergene
405 origin. The mean $\delta^{18}\text{O}$ and δD values of the $<1\ \mu\text{m}$ fraction indicate that the most
406 likely scenario is formation in equilibrium with meteoric waters at near surface
407 temperatures (between 20 and 36°C). The scenario of a continental weathering
408 followed by a low-temperature hydrothermal episode is therefore plausible.

409 These new insights into the genesis of the Burela volcanic-hosted kaolin deposit
410 may provide useful information to guide kaolin regional exploration.

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417 collaboration during the field research (Figure 10).

418

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550 **CAPTIONS OF TABLES AND FIGURES**

551

552 **TABLES**

553 Table 1.- Mineralogical and chemical analysis (major elements in %wt) for the
554 representative rocks of the deposit.

555 Table 2.- Chemical analysis (trace elements in mg/kg) for the representative rocks of the
556 deposit.

557 Table 3.- Mineralogical and chemical composition (%wt) for the bulk kaolins.

558 Table 4.- Mineralogical composition (%wt) of the finer fractions.

559 Table 5. Chemical composition (major elements in wt%) of the finer fractions.

560 Table 6. Chemical composition (trace elements in mg/kg) of the bulk samples.

561 Table 7. Chemical composition (trace elements in mg/kg) of the finer fractions.

562 Table 8.- H₂O yields, $\delta^{18}\text{O}$ and δD values of the analyzed $<1\mu\text{m}$ size fractions, and $\delta^{18}\text{O}$
563 and δD average values of the separates with the same sizes.

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566 **FIGURES**

567 Figure 1.- Regional geological map of Galicia (NW Spain) after Martinez-Catalán et al.
568 (1997) showing the location of the studied kaolin deposit.

569 Figure 2.- Panoramic view of the kaolin quarries at Ramón-Fazouro and sketch of the
570 sample location in the studied outcrops.

571 Figure 3. a) Micro-photographs of felsite (RF-8) **showing feldspars crystals in a**
572 **microcrystalline matrix composed of plagioclase, quartz, muscovite and**
573 **biotite**; b) micaschist (RF-2) **showing oriented micaceous minerals bands**
574 **alternating with quartz plus feldspars bands**; c) quartzite (RF-3) **(polygonal**
575 **quartz grains)**. PXA, 4x.

576 Figure 4.- a) Halloysite joined to book-like kaolinite aggregate; (b and e)Kaolinite crystals
577 oriented face to face; (c) halloysite crystals in clusters; (d) Halloysite in tubular
578 shape with kaolinite crystals oriented face to face; (f) tubular halloysite crystals
579 and spherical particles which could be allophane.

580 Figure 5.- a) Major chemical composition normalized to felsite; b) normalized to
581 metapelite.

582 Figure 6.- a) Trace elements composition normalized to felsite; b) normalized to
583 metapelite.

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584 Figure 7.- a) Felsite normalized REE distribution pattern of the kaolin samples; b) felsite-
585 normalized REE distribution patterns of different grain-size fractions of the
586 same sample.

587 Figure 8. Cluster analysis.

588 Figure 9. $\delta^{18}\text{O}$ versus δD diagram for the $<1 \mu\text{m}$ fraction of the kaolin. The meteoric
589 water, supergene/hypogene and kaolinite weathering lines (KWL) are given
590 for reference. The dashed line indicates the oxygen and deuterium isotopic
591 composition of water in equilibrium with a kaolinite with the mean isotope ratios
592 ($\delta^{18}\text{O} = 20.4\text{‰}$ and $\delta\text{D} = -74\text{‰}$). Abundances are expressed as parts per
593 thousand relative to Vienna Standard Mean Ocean Water (V-SMOW).

594 Figure 10.- Some pictures realized during the visit of Prof. Haydn Murray to Burela kaolin
595 deposit and Sargadelos Ceramic factory (2005) with some of the authors of
596 this paper.

**NEW INSIGHTS ON MINERALOGY AND GENESIS OF KAOLIN DEPOSITS:
THE BURELA KAOLIN DEPOSIT (NORTHWESTERN SPAIN)**

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1 **NEW INSIGHTS ON MINERALOGY AND GENESIS OF KAOLIN DEPOSITS:**
2 **THE BURELA KAOLIN DEPOSIT (NORTHWESTERN SPAIN)**

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33 **ABSTRACT**

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36 17 The Burela deposit is the largest kaolin deposit in Spain, mined for more than 50
37 18 years, the product being mainly used for porcelain. Kaolin is dominantly
38 19 associated with Lower Cambrian felsites, interbedded with quartzites,
39 20 micaschists and metapelites (Cándana Series), and was strongly folded during
40 21 the Hercycian orogeny. Kaolin layers were ductile and incompetent materials
41 22 among more competent ones, producing many slides with a diastrophic
42 23 appearance. Consequently, kaolin outcrops are morphologically very variable, -
43 24 i.e. pockets -, and interlayered between metapelites and/or quartzites, resulting
44 25 in complication for prospection and mining.
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49 26 The kaolin consists mainly of kaolinite, tubular halloysite, and spherical allophane
50 27 along with quartz and minor illite. The content of kaolin minerals reaches up to
51 28 90% in the finer fraction (<2µm and <1µm).
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29 Geochemical analyses of trace and REE show a close relationship between
30 kaolin and associated rocks. Two kaolin types can be differentiated: (i) massive,
31 associated to felsite; and (ii) related to metapelite. A temperature range from 20
32 to 35°C, with an average of approximately 28°C was calculated on the basis of
33 the isotopic signatures ($\delta^{18}\text{O}$, δD) for the kaolin materials. This scatter suggests
34 that if continental weathering was involved in the kaolin formation on the lower
35 side of the temperatures, it was not the only process, especially for kaolin
36 associate with felsites and metapelites. The higher temperatures are indicative of
37 a hydrothermal auto-metamorphic alteration, followed by a folding of the series
38 that induced an apparently chaotic kaolin distribution with a combined continental
39 weathering superimposed on the previous low-temperature hydrothermal felsite
40 transformation.

41 Key words: kaolin genesis, trace elements, isotopes, halloysite, Galicia, Spain

42 43 **INTRODUCTION**

44 The origin of primary kaolin deposits is usually a matter of controversy because
45 kaolinite can be formed *in situ* by weathering reactions (supergene kaolins),
46 hydrothermal alteration during the late stages of magma cooling (hydrothermal
47 kaolins), or by a combination of both processes (Murray, 1988). Kaolinite can be
48 formed also within sedimentary continental basins by diagenetic processes
49 (Galán and Ferrell, 2013). Various criteria and indicators have been proposed to
50 distinguish supergene from hypogene kaolins (e.g. Dill et al., 1997, Gilg et al.,
51 1999), although some of them are considered as ambiguous. Unravelling the
52 genesis of kaolinite in deeply weathered magmatic rocks is one of the most
53 important challenges faced by clay geologists.

54 In the Variscan belt of Galicia (NW Spain) kaolinization of crystalline rocks is
55 widespread. Large high-grade deposits of kaolin (e.g. Vimianzo, Nuevo
56 Montecastelo) and other minor occurrences are found in association with
57 weathered granites. The combined oxygen and hydrogen isotope composition of
58 kaolinite from such deposits is consistent with data of supergene kaolin formation
59 (Clauer et al., 2010, 2015; Fernández-Caliani et al., 2010). However, some
60 deposits associated with felsite dykes or sills and quartz vein networks could have

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61 been formed *in situ* by complex fluid/rock hydrothermal and supergene
62 interactions.

63 The Burela kaolin deposit (Northern Galicia) is a volcanic-hosted deposit, which
64 is of particular interest in addressing the origin and timing of kaolinization.
65 Volcanic-hosted kaolin occurrences of no current economic interest are also
66 found in other areas of Spain, such as the Canary Islands and within the volcano-
67 sedimentary complex of the Iberian Pyrite Belt. However it is in the Burela area
68 where kaolinization is best represented. The deposit is geologically located (Fig.
69 1) in the West Asturian-Leonese Zone (WALZ), one of the major tectono-
70 stratigraphic terranes into which the Iberian Massif is classically subdivided
71 (Julivert et al., 1972). The WALZ exposes Precambrian to Devonian
72 metasediments that experienced the effects of the Variscan orogeny between
73 Late Devonian and Late Carboniferous times (Martínez-Catalán et al., 1997;
74 Pérez-Estaún and Bea, 2004).

75 The main Burela quarries are San Andrés and Ramón Fazouro that are located
76 near the western edge of Fazouro village (Fig. 1). The kaolin is spatially and
77 genetically related to felsites and a swarm of quartz-porphyry dykes that intruded
78 Lower Cambrian metasediments. Kaolin is dominantly associated with Lower
79 Cambrian felsites, interbedded with quartzites and sandstones, and metapelites
80 (Cándana Series), and which were strongly folded during the Hercynian orogeny.
81 Kaolin-rich layers became a ductile and incompetent materials interleaved among
82 the more competent ones, producing many slides with a diastrophic appearance.
83 Consequently, the kaolin outcrops are morphologically very variable (i.e. pockets)
84 interlayered between other rocks, resulting in difficult prospection and mining.

85 This world-class kaolin deposit has been mined by ECESA for more than half a
86 century (1957-2014), with the kaolin being mainly used as raw material in the
87 manufacture of high quality ceramics, especially porcelain-ware. The kaolin
88 material consists of a mixture of kaolinite and halloysite with minor allophane
89 (Galán et al., 2013). The origin of this important economic deposit is still an
90 ongoing matter of debate. It is unclear if extensive kaolinization resulted from
91 hydrothermal (by meteoric fluids) alteration of felsitic rocks, or if weathering
92 affected material that was already subjected to a first stage of low grade
93 metamorphism, or a combination of the two processes induced the deposit

94 (Galán and Martín Vivaldi, 1972). The aim of this paper is to revisit the arguments
95 first presented, (i.e. hydrothermal alteration by meteoric fluids), on the basis of
96 new insights from mineralogy, trace-element geochemistry and stable isotope
97 data. Such understanding will be helpful for future exploration for new deposits in
98 the region and to the rationalization of mining operations.

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100 **SAMPLING AND ANALYTICAL METHODS**

101 A representative sampling of the Burela kaolin deposit was undertaken in the
102 Ramón Fazouro quarry (Fig. 2). A total of fourteen samples of different kaolin
103 occurrences and their associated rocks were sampled. Three size fractions (<45,
104 <2 and <1 μm) were extracted from each whole rock by wet sieving,
105 sedimentation in distilled water and centrifugation. The size fractions were
106 mineralogically analysed by X-ray diffraction (XRD) on a Bruker D8 Advance
107 instrument with a scanning speed of $0.5^\circ(2\theta)/\text{min}$, 0.15 step/size, and Cu- α
108 radiation (40 kV, 30 mA). The quantitative composition was carried out following
109 the procedures of Schultz (1964), Martín-Pozas et al. (1971) and Galán and
110 Martín Vivaldi (1973) for the whole kaolin and the <45 and <2 μm fractions. In
111 order to resolve the unequivocal identification of kaolinite and halloysite from the
112 XRD patterns, and to provide a method of quantification in these types of
113 samples, a fitting process was applied to the 002 XRD reflections ($\sim 3.5 \text{ \AA}$), using
114 a pseudovoigt function for minimising the effect of the Lorentz-Polarization
115 factor, since this signal appears at relatively high angles ($24\text{-}26^\circ$) (Márquez et al,
116 2009).

117 The Rietveld method was used with the TOPAS program to evaluate the
118 mineralogical composition of the <1 μm separates, to obtain a very precise
119 mineralogical composition for this size fraction, potentially the least modified by
120 contaminant minerals, and to quantify the proportions of the different kaolin
121 minerals (e.g. kaolinite vs. halloysite). This procedure was applied to the <1 μm
122 fraction to relate the isotopic with the mineralogical data.

123 A few samples (5) were selected for high-resolution observation by a scanning
124 electron (HRSEM) HITACHI S5200 instrument, fitted with an EDS detector. The
125 particle morphology was also studied by atomic force microscopy with a Pico Plus

126 instrument. In addition the country rocks were optically examined under polarizing
127 photomicroscope. X-ray analyses and microscopy observations were performed
128 at the CITIUS (Research Facilities Centre at the University of Seville, Spain).

129 For the bulk sample and <45 and <2 μm fractions, chemical analyses were carried
130 out at the Activation Laboratories Ltd. (Ontario, Canada) following a lithium
131 metaborate/tetraborate fusion technique that ensures dissolution of the entire
132 sample. Major-element concentrations were determined by inductively coupled
133 plasma-optical emission spectrometry (ICP-OES) on a Thermo Jarrell Ash
134 ENVIRO II, and trace elements were analyzed by inductively coupled plasma-
135 mass spectrometry (ICP-MS) on a Perkin Elmer Optima 3000. Quality control
136 included the use of several certified reference materials, duplicates and blanks
137 by the laboratory to check accuracy and precision. The chemical results were
138 statistically treated in order to realize cluster analysis.

139 The mineralogical maturity of weathering was estimated using the mineralogical
140 index alteration (MIA; Johnsson, 1993; Nesbitt et al., 1996), which is a
141 dimensionless number between 0 and 100, calculated from mineral weight
142 percentages derived from XRD analysis as follows:

$$143 \quad \text{MIA} = [\text{quartz} / (\text{quartz} + \text{K-feldspar} + \text{plagioclase})] \times 100$$

144 The chemical index of alteration (CIA, Nesbitt and Young, 1982) was calculated
145 to evaluate the degree of chemical weathering. CIA is also a dimensionless
146 number between 0 and 100, and shows the weathering of feldspar minerals. It is
147 calculated using molecular proportions as follows:

$$148 \quad \text{CIA} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})] \times 100$$

149 where CaO^* presents the amount of CaO combined in the silicate fraction of the
150 rock.

151 The stable isotope data were obtained in two different laboratories. In both
152 places, samples were vacuum-degassed at 200°C overnight to remove the
153 interlayer and absorbed surface water prior to hydrogen isotope analysis. Then,
154 they were transferred to an out-gassed Pt crucible and the water released by
155 heating was reacted with hot metal, producing H_2 for determination of δD . For the
156 samples analysed at the Activation Laboratories (Canada), uranium at 900°C was

157 used for D/H; for $\delta^{18}\text{O}$ analysis, BrF_5 at 650°C was reacted with the kaolin in a Ni
158 chamber (Clayton and Mayeda, 1963) to generate O_2 that was reduced to CO_2
159 with graphite using Pt as catalyst at $550\text{--}600^\circ\text{C}$. The precision at 1σ was $\pm 2\text{‰}$
160 and 0.3‰ respectively for δD and $\delta^{18}\text{O}$. For those results obtained at East
161 Kilbride (UK), dehydroxylation was achieved by heating the Pt crucible at 1200°C
162 by radiofrequency induction. The water released was converted to H_2 by reacting
163 with Cr at 800°C (Bigeleisen et al., 1952; Donnelly et al., 2001) in a multiple-pass
164 system. The H_2 yield was measured manometrically and the δD determined on a
165 gas-source mass spectrometer calibrated via water and mineral standards. Using
166 these techniques, the NBS30 biotite standard gave a δD of -65‰ (V-SMOW) with
167 an analytical reproducibility of $\pm 2\text{‰}$ (1σ), $\pm 3\text{‰}$ (1σ) being more appropriate for
168 clay material. The oxygen isotope composition was determined by laser
169 fluorination (Macaulay et al., 2000) using the Borthwick and Harmon (1982) ClF_3
170 modification of Clayton and Mayeda (1963). The precision for the clay material is
171 $\pm 0.3\text{‰}$ (1σ), the NBS28 quartz standard giving a $\delta^{18}\text{O}$ of 9.6‰ (V-SMOW). All
172 clay isotope data are reported in parts per mil (‰) relative to the V-SMOW
173 standard. No significant systematic isotope ratio difference between the two
174 laboratories was observed. Stable isotopes were determined for four samples
175 $<45\ \mu\text{m}$ fraction and eight samples <2 and $<1\ \mu\text{m}$ fractions.

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177 **RESULTS AND DISCUSSION**

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179 ***Precursor host rocks***

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181 The Burela kaolin deposit is hosted in felsic porphyritic volcanic rocks interbedded
182 with metasedimentary rocks, notably Lower Cambrian metapelites and quartzites
183 (Cándana Quartzite). Representative mineralogical and chemical analyses of the
184 precursor rocks of the kaolin deposit are given in Tables 1 and 2.

185 In thin section the felsic volcanic rocks display a holocrystalline, porphyritic
186 texture (Fig. 3a), with phenocrysts of feldspar and partially reabsorbed quartz and
187 set in a groundmass composed of fine-grained plagioclase, muscovite, and biotite

188 (often altered to chlorite and associated to iron oxides). Quantitative XRD
189 mineralogical determination showed that quartz accounts for 24-33% of the bulk
190 sample, the feldspars range from 60 to 67%, with mica contents up to 30%. In
191 partially altered samples, the amount of feldspars decreases by up to 35%
192 yielding MIA values of 46. According to the TAS binary diagram (total silica **vs**
193 alkali content) of Le Bas et al. (1986), the felsic rocks can be classified as lavas
194 of rhyolite-to-trachydacite composition.

195 The pelitic schists have a lepidoblastic texture and exhibit a strong penetrative
196 foliation defined by preferred orientation of muscovite laths and quartz ribbons
197 (Fig. 3b). Chlorite and relict detrital grains of tourmaline, rutile and zircon are
198 present as accessory phases. Intensely altered metapelitic rocks (MIA value as
199 high as 87) are characterized by high content of clay minerals, notably kaolinite,
200 which can account for up to 38% (Table 1).

201 The Cándana quartzite shows a medium-grained granoblastic texture, in which
202 quartz exhibiting undulate extinction typically forms a mosaic of polygonal
203 crystals (Fig. 3c), with muscovite, tourmaline, zircon and rutile as subordinate
204 minerals].

205

206 ***Mineralogical characteristics of kaolin.***

207 The mineralogy of the bulk samples is dominated by highly variable contents of
208 kaolin minerals (17-74%) and quartz (16-69%), accompanied by mica (up to 33%)
209 (Table 3). Other phases that may be present, usually in subordinate or trace
210 amounts, are feldspars and smectites. Additionally, SEM-BSE observations in
211 combination with EDS microanalysis revealed a distinctive suite of heavy
212 minerals including zircon, monazite, rutile, ilmenite and iron oxides.

213 Within the <45µm fraction, the amounts of kaolin minerals is variable with a wide
214 concentration range (62-90%), with kaolinite being dominant over halloysite. The
215 contents of quartz and illite were lower than 24% in all the samples, whereas
216 feldspars, smectites and allophane were found as accessory phases. In the fine
217 fractions, the amount of kaolin minerals reached up to 92 % (Table 4). Traces of
218 allophane and chlorite were detected in some samples and fractions. The

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219 fractions <2µm and <1µm contains mostly kaolinite and halloysite, with minor illite
220 and quartz (Table 4).

221 Tubular halloysite accounts for 11 to 60% of the kaolin, while kaolinite content
222 varies between 23 and 60%, with kaolinite/halloysite ratios ranging from 6 to 0.5.
223 These results substantially agree with the microscopic observations (Figure 4).
224 Tubular crystals of halloysite (0.5-8µm of length) appear to be joined to book-like
225 kaolinite aggregates (Figure 4a, 4e and 4f) and kaolinite crystals are oriented face
226 to face (Fig 4 b and 4d). Halloysite crystals appear also in the form of clusters
227 (Fig 4c). Spherical shaped particles (0.5µm in diameter) were also detected by
228 AFM, which correspond to allophane: it is not common to find at the same time
229 tubular and spherical halloysite (Fig 4f). Tubular halloysite mostly corresponds to
230 a weathering phase while spherical halloysite is instead formed by direct
231 precipitation (neof ormation) and it is usually considered as a precursor of tubular
232 halloysite (Duzgoren-Aydin et al. 2002).

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234 ***Major and trace element geochemistry***

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236 Chemical analyses of the whole rock samples shows that the geochemistry of
237 major elements (Table 3) is largely dominated by Si and Al, reflecting the high
238 content of kaolin minerals in the altered rocks. Silica displays a broad range of
239 concentrations (58.2-76.3 wt % SiO₂), except for the altered quartzite (RF-12),
240 which is also strongly and negatively correlated with both the alumina content (r=
241 -0.99) and the weight loss on ignition (LOI; r= -0.88). The highest abundances of
242 alumina (23-27 wt % Al₂O₃) and LOI (8-12 wt %) were found in samples from the
243 upper part of the studied section.

244 The remaining major elements, except potassium, are all present at
245 concentrations less than 1wt%. The K₂O content varies from 4.8wt% to 0.8wt%,
246 with a mean value of 2.3wt%. The variations are closely related to the presence
247 of orthoclase and muscovite in the samples. The low content of calcium and
248 sodium oxides is considered due to weathering of the plagioclases. The CIA
249 varies from about 65 in the fresh felsitic rocks to around 96 in the most weathered
250 felsite, suggesting a significant removal of labile basic cations (mainly K, Na, and

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251 Mg) relative to stable residual elements (Si, Al, Fe). The loss of alkaline and
252 alkaline-earth elements can be attributed to the alteration (kaolinization) of alkali
253 feldspar and mica, which are the minerals in the felsitic rocks most prone to
254 weathering. In addition, the CIA of the metapelite is 84%, which indicates that this
255 rock is highly altered, as confirmed by the high kaolin minerals content (31wt%).

256 The fine-grained kaolin rich samples (the <45 and <2µm fractions) contain a
257 higher proportion of alumina (up to 37 wt % Al₂O₃) and concomitantly less silica
258 (44-59 wt %) (Table 5). An enrichment in titanium oxide is detected in metapelite
259 (RF-2) and in the samples RF3-05, RF-12 and RF-14, when the major elements
260 composition is normalized to felsite (RF-8) (Figure 5a). As was noted above, the
261 metapelite presents abundant rutile. The other kaolin samples do not contains
262 any significant anomaly in comparison with the felsite host rock.

263 When the major element compositions of samples RF3-05, RF-12 and RF-14 are
264 normalized to the metapelite reference (Figure 5b), no striking anomaly is visible
265 and the signatures of the samples are very similar to metapelite. The
266 unexpectedly high anomaly is of 2.5 in the case of iron oxide for <45µm fraction
267 of sample RF-14.

268 An enrichment in the high field strength elements (HFSE) Sc, Zr, Hf and Th has
269 been detected in kaolin when the data are normalized to felsite (RF-8) (Figure
270 6a), probably due to their resistance to weathering (e.g. Middelburg et al., 1988;
271 Panahi et al., 2000). Thus the HFSE remained relatively immobile, linked to
272 resistant heavy minerals (zircon, monazite and titanium oxides) that tend to be
273 residually concentrated in the finer fractions of the kaolin. A very high statistical
274 correlation (r= 0.97) was obtained between Zr and Hf, so that both elements
275 mostly reside in the crystal structure of zircon. Elevated correlation coefficients
276 were also observed between Nb and Ta (r= 0.88) because of the close
277 geochemical affinity of such elements. Thorium shows a positive correlation (r=
278 0.65) with the light rare earth elements (LREE) consistently indicating that it is
279 hosted by monazite, which is the only LREE-rich accessory phase occurring in
280 the kaolin.

281 High enrichments for large ion lithophile elements (LILE), such as Rb, Sr and Cs,
282 are found in relation to metapelite for the samples RF-12 and RF-14, especially

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283 in the <45 μ m fraction (Figure 6b). But, when the trace-element compositions of
284 samples RF-3-05, RF-12 and RF-14 are normalized to the metapelite
285 composition, no anomaly is apparent with the signature of these samples very
286 similar to that of the metapelite. On the contrary, the major anomalies are for Cs,
287 Tl, Pb, Rb, Sr and Ta of the felsite and the other kaolin samples. The LILE
288 probably were preferentially removed from the felsite rock during kaolinization, as
289 noted by the depletion of Rb, Sr, and particularly Ba, in the kaolin.

290 The kaolin is not especially enriched in trace elements, although the overall
291 abundance varies with the grain-size distribution (Tables 6 and 7). The <45 μ m
292 fraction of the kaolin tends to have greater concentrations (Σ REE= 237-440 ppm)
293 than the whole sample (Σ REE= 65-209 ppm), indicating a relative accumulation
294 of REE-carrying minerals in the finer fractions. Seemingly, kaolinite could have
295 played a role in scavenging REE, as reported in some weathering systems (Putter
296 et al., 2002; Papoulis et al., 2004). Exceptionally, the sample RF-17 is markedly
297 depleted in total REE (whole sample: 29 ppm; <45 μ m fraction: 37 ppm; <2 μ m
298 fraction: 85 ppm) relative to the felsite rock, although the REE concentration level
299 also exhibits the same dependence on the particle size of the kaolin.

300 Similar overall enrichments in REE have been documented in weathering profiles
301 developed on granitoids elsewhere in the Galician region (Galán et al., 2007,
302 Fernández-Caliani et al., 2010). However, at the Burela deposit the total REE
303 content shows no significant correlation with the intensity of the chemical
304 alteration (as shown by the CIA values), suggesting that other processes of
305 remobilization and redistribution of REE occurred in this deposit. In addition, all
306 the samples yield a similar pattern of the REE composition: in fact the shape of
307 the REE patterns is identical for all grain-size fractions, characterized by a slight
308 LREE enrichment ($La_n/Sm_n=3.50-13.56$) and a HREE depletion ($Gd_n/Yb_n= 1.70-$
309 5.24). The positive Ce anomaly is due to the residual character of this element,
310 which undergoes only partial oxidation (Gouveia et al., 1993).

311 The REE diagrams of the kaolin whole samples normalized against the fresh
312 felsite (Fig. 7a) exhibit a nearly flat pattern with a slight enrichment in heavy REE
313 (HREE), which is more prominent in the fine-grained samples (Fig. 7b). The
314 HREE distribution seems to be controlled, therefore, by HREE-enriched phases

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315 like zircon, ilmenite, and rutile (Laveuf and Cornu, 2009). These resistant
316 minerals are not expected to be highly mobilized during alteration, and therefore
317 they tend to be residually accumulated in the kaolin deposit, thus increasing the
318 HREE budget. A cluster analysis identifies two types of geochemical signature
319 (trace elements and REE) and the massive kaolin samples can be grouped into
320 two main groups: associated to felsite and associated to metapelite (Figure 8).

321 In summary, the geochemical study of trace elements and REE showed a close
322 relationship between kaolin and associated rocks, and from the geochemical
323 point of view two kaolin types can be differentiated: massive kaolin associated to
324 felsite and massive kaolin associated to metapelite, as above it has been largely
325 discussed.

326

327 ***Stable isotope geochemistry***

328 Combined stable oxygen and hydrogen (deuterium) isotope studies are
329 commonly used to help discriminate between supergene and hypogene kaolins,
330 and are considered to be the most powerful method to constrain temperatures of
331 kaolinization (Gilg, et al. 1999).

332 The isotopic composition of nearly pure kaolin samples (<1 μ m fraction) from
333 Burela deposit showed a narrow range of $\delta^{18}\text{O}$ values (19.8-21.0‰) and δD ratios
334 ranging from -85 to -63‰, with the mean $\delta^{18}\text{O}$ and δD values being $20.4\pm 0.4\text{‰}$
335 and $-74\pm 3\text{‰}$, respectively (Table 8). The scatter is close to the analytical error,
336 indicating little geological variation. There is no statistically significant correlation
337 between the two isotope ratios ($r = -0.39$, less than 80% significant for $n=7$). The
338 mean water content of $7.4\pm 0.4\text{wt.}\%$ corresponds to $13.3\pm 0.7 \mu\text{moles mg}^{-1}$ of
339 water, compared to the theoretical value of 14 for stoichiometric kaolin.

340 When plotted on a $\delta^{18}\text{O}$ - δD diagram (Fig.9), all the points plot in the supergene
341 field, *i.e.* on the right of the supergene-hypogene line of Sheppard et al. (1969),
342 and very close to the kaolinite weathering line (KWL), which represents the
343 isotopic compositions of kaolinites in equilibrium with meteoric waters at 20 °C.
344 Similar values are given in the literature for residual kaolin deposits derived from

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345 Variscan granites (Bobos and Gomes, 1998; Boulvais et al., 2000; Clauer et al.,
346 2010, 2015; Fernández-Caliani et al., 2010; Galán et al., 2010). Here, the overall
347 range of the calculated temperatures from studied kaolin separates ranges from
348 20 to 35 °C. These temperatures are compatible with a low-temperature
349 hydrothermal activity, i.e.: a hydrothermal auto-metamorphic alteration that could
350 occur on the felsite during submarine volcanic activity.

351 On the basis of a variety of assumptions involving plausible formation in an open
352 system with high water–rock ratio and near-surface temperatures, a comparison
353 with Delgado and Reyes (1996) modelling appears appropriate at this point,
354 remembering that these authors assume an interaction with meteoric waters.
355 Thus, the temperature and isotopic composition of the water from which kaolinite
356 formed in equilibrium can be determined from the following equations:

357 [1] The meteoric-water equation: $\delta D = 8\delta^{18}O + 10$ (Craig, 1961)

358 [2] The equilibrium hydrogen isotope fractionation factor (α^H) between kaolinite
359 and water (Gilg and Sheppard, 1996): $1000 \ln \alpha^H_{kaol-water} = -2.2 \times 10^6 T^{-2} - 7.7$

360 [3] The equilibrium oxygen isotope fractionation factor (α^{18}) between kaolinite and
361 water (Sheppard and Gilg, 1996): $1000 \ln \alpha^{18}_{kaol-water} = 2.76 \times 10^6 T^{-2} - 6.75$.

362 In combining the equations of Sheppard and Gilg (1996) for kaolinite, $\delta^{18}O_w$, δD_w
363 can be eliminated by using the meteoric water line equation, giving:

$$3.04 \cdot 10^6 T^{-2} = \delta^{18}O_k - 0.125 \delta D_k + 7.04$$

365 The crystallization temperature of kaolinite obtained by applying this equation to
366 the average of the measured <1 μm kaolin separates at 14.7 °C is compatible
367 with the supergene environment. This value is slightly higher than the current
368 annual mean temperature of the Galician region (12 °C), but is a reasonable
369 surface temperature expected during the Pliocene (Boulvais et al., 2000), with an
370 accuracy of the equations representing the temperature dependence of the stable
371 isotope fractionation equations (in (2) and (3) above) not at all well quantified.

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372 The possible mean isotopic composition of the meteoric water with which kaolinite
373 crystallized at isotopic equilibrium has been calculated at $\delta^{18}\text{O} = -6\text{‰}$ and $\delta\text{D} = -$
374 40‰ (Fig. 9; mean values for the minerals taken from Table 8), using the above
375 average temperature and the isotope fractionation factors of Sheppard and Gilg
376 (1996) and Gilg and Sheppard (1996), respectively.

377

378 **CONCLUSIONS**

379 The Burela deposit is characterized by a high concentration of kaolin minerals
380 (kaolinite and halloysite). In the coarse fraction the most abundant kaolin mineral
381 is kaolinite of perfect pseudo-hexagonal morphology. Tubular halloysite is
382 concentrated in the finer fractions.

383 The geochemical study of the trace elements and REE showed a close
384 relationship between kaolin and associated rocks, and from the geochemical
385 point of view two kaolin types can be differentiated: associated to felsite and
386 associated to metapelite.

387 A felsite hydrothermal auto-metamorphic alteration is suggested for the origin of
388 the kaolin, as an initial kaolinization step. Later a folding of the series led to an
389 apparently chaotic kaolin distribution and a weathering action on the felsite
390 completed the kaolin formation, superimposed on a low-temperature
391 hydrothermal felsite transformation. On the contrary, the occurrence of allophone
392 in some samples point toward a supergene origin of the kaolin. On the other hand,
393 micaschists were also kaolinized by weathering. The kaolin was a plastic
394 incompetent material during the folding, which accumulated in the weaker zones,
395 and was a detachment level for the more competent materials (mainly quartzite
396 and sandstone).

397 The isotopic composition of the nearly pure kaolin is consistent with a supergene
398 origin. The mean $\delta^{18}\text{O}$ and δD values of the $<1\ \mu\text{m}$ fraction indicate that the most
399 likely scenario is formation in equilibrium with meteoric waters at near surface
400 temperatures (between 20 and 36°C). The scenario of a continental weathering
401 followed by a low-temperature hydrothermal episode is therefore plausible.

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402 These new insights into the genesis of the Burela volcanic-hosted kaolin deposit
403 may provide useful information to guide kaolin regional exploration.

404 **ACKNOWLEDGEMENTS**

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410 collaboration during the field research (Figure 10).

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527 **CAPTIONS OF TABLES AND FIGURES**

528

529 **TABLES**

530 Table 1.- Mineralogical and chemical analysis (major elements in %wt) for the
531 representative rocks of the deposit.

532 Table 2.- Chemical analysis (trace elements in mg/kg) for the representative rocks of the
533 deposit.

534 Table 3.- Mineralogical and chemical composition (%wt) for the bulk kaolins.

535 Table 4.- Mineralogical composition (%wt) of the finer fractions.

536 Table 5. Chemical composition (major elements in wt%) of the finer fractions.

537 Table 6. Chemical composition (trace elements in mg/kg) of the bulk samples.

538 Table 7. Chemical composition (trace elements in mg/kg) of the finer fractions.

539 Table 8.- H₂O yields, δ¹⁸O and δ D values of the analyzed <1 μm size fractions, and δ¹⁸O
540 and δ D average values of the separates with the same sizes.

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543 **FIGURES**

544 Figure 1.- Regional geological map of Galicia (NW Spain) after Martinez-Catalán et al.
545 (1997) showing the location of the studied kaolin deposit.

546 Figure 2.- Panoramic view of the kaolin quarries at Ramón-Fazouro and sketch of the
547 sample location in the studied outcrops.

548 Figure 3. a) Micro-photographs of felsite (RF-8) showing feldspars crystals in a
549 microcrystalline matrix composed of plagioclase, quartz, muscovite and
550 biotite; b) micaschist (RF-2) showing oriented micaceous minerals bands
551 alternating with quartz plus feldspars bands; c) quartzite (RF-3) (polygonal
552 quartz grains). PXA, 4x.

553 Figure 4.- a) Halloysite joined to book-like kaolinite aggregate; (b and e) Kaolinite crystals
554 oriented face to face; (c) halloysite crystals in clusters; (d) Halloysite in tubular
555 shape with kaolinite crystals oriented face to face; (f) tubular halloysite crystals
556 and spherical particles which could be allophane.

557 Figure 5.- a) Major chemical composition normalized to felsite; b) normalized to
558 metapelite.

559 Figure 6.- a) Trace elements composition normalized to felsite; b) normalized to
560 metapelite.

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561 Figure 7.- a) Felsite normalized REE distribution pattern of the kaolin samples; b) felsite-
562 normalized REE distribution patterns of different grain-size fractions of the
563 same sample.

564 Figure 8. Cluster analysis.

565 Figure 9. $\delta^{18}\text{O}$ versus δD diagram for the $<1 \mu\text{m}$ fraction of the kaolin. The meteoric
566 water, supergene/hypogene and kaolinite weathering lines (KWL) are given
567 for reference. The dashed line indicates the oxygen and deuterium isotopic
568 composition of water in equilibrium with a kaolinite with the mean isotope ratios
569 ($\delta^{18}\text{O} = 20.4\text{‰}$ and $\delta\text{D} = -74\text{‰}$). Abundances are expressed as parts per
570 thousand relative to Vienna Standard Mean Ocean Water (V-SMOW).

571 Figure 10.- Some pictures realized during the visit of Prof. Haydn Murray to Burela kaolin
572 deposit and Sargadelos Ceramic factory (2005) with some of the authors of
573 this paper.

HIGHLIGHTS

New insights on the genesis the largest kaolin deposit in Spain are presented.

Kaolin consists mainly of kaolinite, tubular halloysite, and spherical allophane.

Geochemical analyses of trace and REE show a close relationship between kaolin and associated rocks.

Two kaolin types can be differentiated: (i) massive, associated to felsite; and (ii) related to metapelite

A temperature average of approximately 28°C was calculated on the basis of the isotopic signatures ($\delta^{18}\text{O}$, δD) for the kaolin materials.

Continental weathering was involved in the kaolin formation, but it was not the only process.

These new insights into the genesis of the Burela volcanic-hosted kaolin deposit may provide useful information to guide kaolin regional exploration.

Table 1.- Mineralogical and chemical analysis (major elements in %wt) for the representative rocks of the deposit.

% wt	Felsic volcanic rocks		Altered felsite	Altered metapelite	Quartzite
	RF-5	RF-6	RF-8	RF-2	RF-3
Quartz	24	33	30	27	97
Feldspars	60	67	35	4	
Mica	15		30	31	3
Clay Minerals	Tr	Tr	<5	38	
MIA	29	33	46	87	100
SiO ₂	73.06	62.33	70.73	65.00	98.86
Al ₂ O ₃	14.64	20.38	16.21	23.10	0.29
Fe ₂ O ₃ (t)	1.46	1.05	1.06	0.44	0.03
MnO	0.01	<0.01	0.01	<0.01	0
MgO	1.20	0.31	0.56	0.38	0.01
CaO	0.03	0.17	0.09	0.04	0.02
Na ₂ O	2.80	4.93	0.57	0.32	0.02
K ₂ O	5.20	6.49	5.69	3.94	0.12
TiO ₂	0.19	0.04	0.16	0.90	0.02
P ₂ O ₅	0.03	0.02	0.03	0.05	0.02
LOI	2.32	3.58	4.92	5.82	0.40
TOTAL	100.94	99.30	100.03	99.99	99.79
CIA	64.58	63.75	71.85	84.31	64.44

Table 2.- Chemical analysis (trace elements in mg/kg) for the representative rocks of the deposit.

mg/kg	Felsic volcanic rocks		Altered felsite	Altered metapelite	Quartzite
	RF-5	RF-6	RF-8	RF-2	RF-3
Sc	0.00	0.00	1.00	12.00	0.00
Be	2.00	1.00	2.00	4.00	0.00
V	0.00	15.41	0.00	79.60	0.00
Cr	0.00	0.00	0.00	106.32	0.00
Ga	20.84	20.30	23.40	28.90	0.00
Ge	1.43	0.00	1.68	0.00	1.14
As	45.17	0.00	26.47	0.00	0.00
Rb	188.80	203.44	240.14	79.49	3.12
Sr	100.39	140.30	55.81	20.07	-4.00
Y	5.91	5.01	43.52	33.02	4.78
Zr	65.72	71.55	76.03	539.03	22.96
Nb	20.40	9.42	26.97	28.91	3.19
Ag	0.00	0.00	0.00	1.15	0.00
Sn	4.67	0.00	4.97	4.62	0.00
Cs	4.35	1.92	11.26	2.39	0.00
Ba	479.43	690.32	140.67	219.77	8.61
W	1.11	0.00	0.00	9.53	0.00
Tl	1.55	1.56	2.25	0.27	0.00
Pb	64.77	43.99	42.54	18.50	0.00
Bi	3.25	1.88	13.67	1.53	0.83
Th	9.25	8.07	10.89	23.38	0.89
U	3.70	2.56	6.11	3.51	0.21
Ta	2.74	2.71	3.41	1.95	0.08
La	24.24	30.92	68.47	85.71	9.89
Ce	35.41	54.11	63.48	159.54	20.41
Pr	3.97	4.04	16.19	16.32	2.04
Nd	14.03	13.83	63.92	57.66	7.24
Sm	3.04	3.02	16.89	10.93	1.30
Eu	0.61	0.56	2.56	1.78	0.24
Gd	2.46	1.83	15.95	7.40	1.27
Tb	0.37	0.28	2.55	1.26	0.21
Dy	1.64	1.15	11.81	6.81	1.13
Ho	0.25	0.16	1.84	1.39	0.20
Er	0.61	0.43	4.85	4.46	0.61
Tm	0.08	0.05	0.67	0.72	0.09
Yb	0.48	0.35	3.76	4.35	0.49
Lu	0.05	0.05	0.47	0.64	0.07
Hf	3.14	3.42	4.03	15.30	1.44

Table 3.- Mineralogical and chemical composition (%wt) for the bulk kaolins.

Samples	RF-1	RF1-05	RF-3-05	RF-5-05	RF-7	RF-12	RF-14	RF-16	RF-17
Quartz	29	30	27	49	36	69	31	22	16
Feldspar	<5	---	<5	28	<5	---	Tr	Tr	---
Kaolin minerals	49	68	56	17	27	22	37	67	74
Mica	17	Tr	13	6	33	9	30	9	9
Others	Sm	Sm	Sm	Sm	Sm	Sm	Sm	Sm	Sm
SiO ₂	65.36	62.23	58.27	71.12	71.24	91.71	76.31	63.28	59.61
Al ₂ O ₃	22.68	25.48	27.37	17.2	17.98	5.28	15.17	23.03	27.26
Fe ₂ O ₃	0.6	0.54	0.54	1.21	0.67	0.07	0.47	0.59	0.56
MnO	0.01	0	0	0.009	0.03	0	0	0.01	0
MgO	0.18	0.07	0.33	0.27	0.36	0.11	0.17	0.13	0.09
CaO	0.04	0.01	0.01	0.03	0.05	0.03	0.05	0.05	0.03
Na ₂ O	0.05	0.03	0.22	0.13	0.16	0.07	0.16	0.07	0.09
K ₂ O	1.82	0.95	3.07	4.84	4.06	0.34	1.37	1.19	0.81
TiO ₂	0.02	0.02	0.78	0.019	0.02	0.162	0.48	0.02	0.02
P ₂ O ₅	0.05	0.02	0.04	0.02	0.02	0.03	0.02	0.04	0.02
LOI	8.37	10.02	8.36	5.71	5.5	2.32	5.29	9.17	11.36
TOTAL	99.18	99.37	98.99	100.56	100.09	100.12	99.49	97.58	99.85
CIA	92.23	96.26	89.24	77.48	80.81	92.31	90.57	94.62	96.7

Table 4.- Mineralogical composition (%wt) of the finer fractions.

<45µm						
Sample	Kaolinite	Halloysite	Illite	Quartz	Feldspar	Others
RF-1	37	30	10	16	7	Sm/ All
RF-1-05	45	45	6	Tr	<5	
RF-5-05	56	11	7	24	Tr	
RF-7	41	21	24	12	<5	Sm
RF-14	42	28	12	10	<5	
RF-16	60	15	12	11	Tr	All
RF-17	74	13	<5	8	Tr	Sm/ All
<2µm						
RF-1	54	34	9	Tr		
RF-1-05	58	36	6			
RF-5-05	63	28	9			
RF-7	54	24	15	<5		Sm
RF-14	32	39	<5	26		
RF-16	49	28	<5	17		
RF-17	38	52	Tr	10		
<1µm						
RF-1	25	65		10		
RF-1-05	32	60		8		
RF-5-05	68	26		6		
RF-7	70	20	5			Sm
RF-14	44	37	13	5		
RF-16	30	64		6		
RF-17	23	70		7		

Tr: traces, Sm: smectites, All: Allophane

Table 5. Chemical composition (major elements in wt%) of the finer fractions

Samples	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	LOI	CIA
RF-1-45µm	56.36	29.22	1.02	0.01	0.24	0.05	0.07	2.12	0.02	0.05	10.83	92.88
RF-2 R <45µm	53.67	30.73	0.64	0.003	0.48	0.04	0.32	4.37	1.266	0.06	8.39	86.66
RF-7-45µm	53.92	29.43	1.05	0.02	0.61	0.07	0.11	3.8	0.02	0.02	10.87	88.09
RF-8-45µm	54.25	26.89	2.42	0.013	0.86	0.14	1.24	4.19	0.024	0.07	9.64	82.84
RF-12-45µm	58.92	27.94	0.26	0	0.38	0.06	0.1	1.4	0.41	0.08	10.3	94.71
RF-14-45µm	49.98	32.21	1.13	0	0.37	0.05	0.17	2.2	1.19	0.04	12.14	93.01
RF-16-45µm	47.03	31.5	0.74	0.01	0.16	0.04	0.07	1.45	0.02	0.05	18.98	95.28
RF-17-45µm	48.42	35.5	0.66	0	0.1	0.04	0.08	1.02	0.02	0.01	14.18	96.89
RF-16<2µm	49.99	33.4	0.85	0.01	0.12	0.09	0.06	1.26	0.02	0.05	13.13	95.95
RF-17<2µm	44.77	36.93	0.4	0	0.05	0.1	0.04	0.1	0.01	0.02	16.79	99.35

Table 6. Chemical composition (trace elements in mg/kg) of the bulk samples.

	RF-1	RF-1-05	RF-3-05	RF-5-05	RF-7	RF-12	RF-14	RF-16	RF-17
Rb	105	59	63	213	164	10	24	84	63
Sr	23	8	25	41	31	6	12	21	4
Ba	50	20	31	119	171	12	125	47	10
Cs	6	6	1	10	6	1	1	7	5
Zr	106	77	223	71	85	300	277	106	68
Hf	5	4	6	4	4	9	8	5	4
Ta	4	3	1	3	4	0	1	4	3
Nb	34	22	19	25	26	8	17	32	20
U	4	2	3	3	3	1	2	2	2
Th	15	14	23	12	12	5	12	16	11
Cr	0	20	90	0	0	0	43	0	0
Pb	52	75	19	3	66	0	0	53	13
Y	31	41	21	16	24	7	13	11	3
Sc	4	5	12	3	3	2	6	3	4
La	36	34	34	12	26	29	29	40	9
Ce	82	51	74	23	46	56	55	70	11
Pr	10	5	7	3	6	6	6	7	1
Nd	42	14	24	13	23	20	20	25	3
Sm	10	3	5	3	6	3	4	5	1
Eu	2	0	1	1	1	1	1	1	0
Gd	9	2	3	3	8	2	3	4	1
Tb	2	0	1	1	1	0	1	1	0
Dy	8	1	3	3	6	2	3	3	1
Ho	1	0	1	0	1	0	1	0	0
Er	3	0	2	1	3	1	2	1	0
Tm	0	0	0	0	0	0	0	0	0
Yb	3	0	2	1	2	1	2	1	0
Lu	0	0	0	0	0	0	0	0	0
ΣREE	209	110	157	65	129	122	124	159	29
ΣHREE	191	108	147	58	116	117	116	152	27
ΣLREE	49	43	31	22	37	12	22	17	5
Eu/Eu*	3	1	1	1	2	1	1	1	0
La/Yb	13	101	14	11	13	27	16	39	24
La/Sm	4	14	7	4	4	9	7	8	10
Gd/Yb	3	5	1	3	4	2	2	4	2
Th/U	4	8	9	4	4	6	6	7	6
La/Th	2	3	2	1	2	5	2	2	1
Sm/Nd	0	0	0	0	0	0	0	0	0

Table 7. Chemical composition (trace elements in mg/kg) of the finer fractions.

	RF-1 <45	RF-7<45	RF-8<45	RF-12<45	RF-14<45	RF-16 <45	RF-17<45	RF-16 <2	RF-17 <2
Rb	129	189	185	32	54	105	75	92	13
Sr	28	23	32	30	15	28	6	34	21
Ba	47	99	72	41	213	63	14	70	25
Cs	7	9	12	3	2	9	7	8	2
Zr	137	172	146	368	605	126	94	142	83
Hf	7	8	8	11	18	6	5	7	4
Ta	6	7	6	1	3	5	4	6	4
Nb	45	44	46	13	46	42	25	39	22
U	5	6	16	2	6	3	2	4	5
Th	20	24	21	19	36	21	13	27	21
Cr	44	0	82	83	332	0	0	30	50
Pb	49	59	28	0	21	57	18	76	43
Y	42	52	77	20	34	14	4	22	6
Sc	8	4	3	12	12	7	4	6	2
La	51	52	108	100	93	54	12	52	30
Ce	116	73	107	192	178	94	15	100	36
Pr	13	11	26	19	18	9	1	10	3
Nd	59	45	100	66	64	32	4	35	9
Sm	15	12	27	11	11	7	1	7	2
Eu	2	2	4	2	2	1	0	1	0
Gd	13	13	25	7	8	5	1	6	2
Tb	2	2	4	1	1	1	0	1	0
Dy	10	11	20	5	7	4	1	5	2
Ho	2	2	3	1	1	1	0	1	0
Er	5	5	8	3	5	2	1	2	1
Tm	1	1	1	0	1	0	0	0	0
Yb	4	4	6	3	5	1	0	2	1
Lu	0	1	1	0	1	0	0	0	0
∑REE	293	235	440	410	396	211	37	222	85
∑HREE	269	209	397	397	374	203	34	212	82
∑LREE	66	78	120	33	56	22	7	32	10
Eu/Eu*	4	3	7	3	3	2	0	2	0
La/Yb	14	12	17	40	18	43	25	33	60
La/Sm	3	4	4	9	8	8	12	7	15
Gd/Yb	4	3	4	3	2	4	2	4	3
Th/U	4	4	1	10	6	7	6	7	4
La/Th	2	2	5	5	3	3	1	2	1
Sm/Nd	0	0	0	0	0	0	0	0	0

Table 8.- H₂O yields, δ¹⁸O and δ D values of the analyzed <1μm size fractions, and δ¹⁸O and δ D average values of the separates with the same sizes.

Sample	H ₂ O (%)	δ ¹⁸ O (‰)	δD (‰)
RF-1	7.3	20.2	-69
RF-7	6.8	20.8	-85
RF-14	7.1	20.2	-84
RF-16	7.7	20.7	-68
RF-17	7.3	20.2	-63
RF-1-05	8.0	21.0	-79
RF-5-05	7.5	19.8	-71
Mean	7.4	20.4	-74

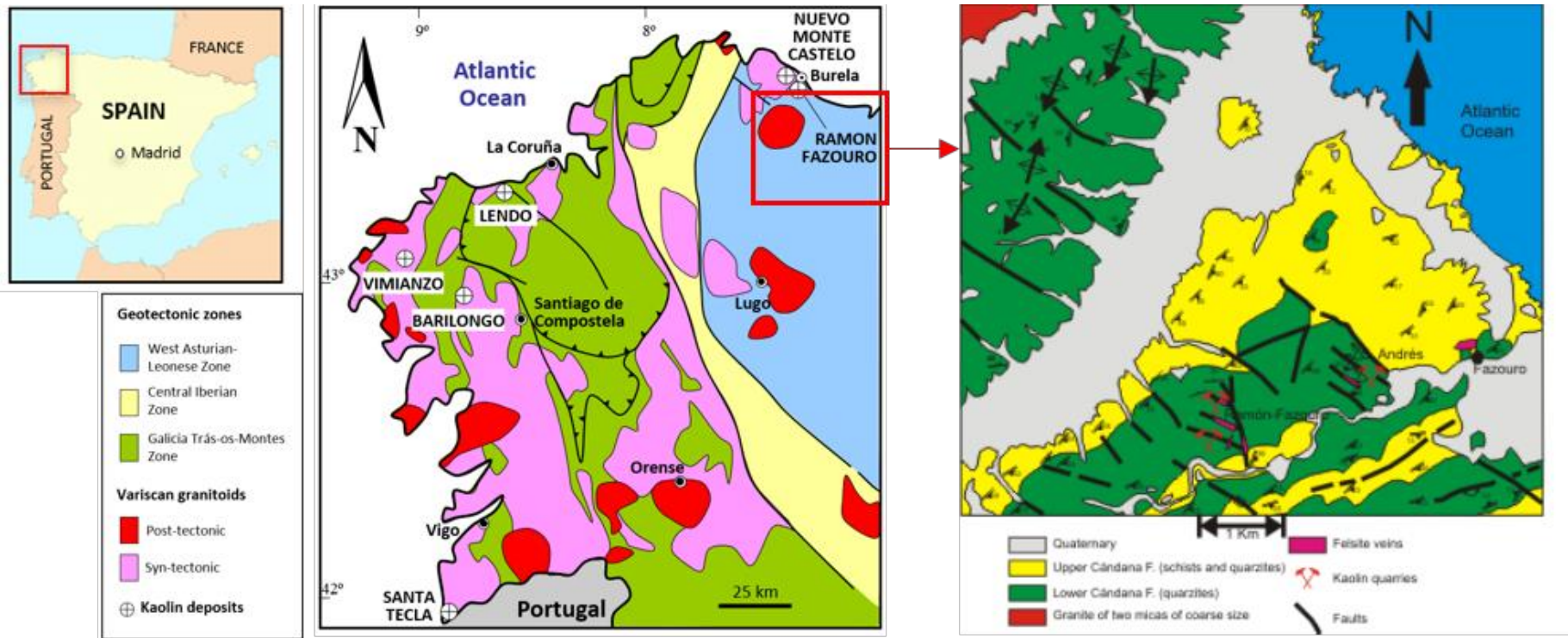


Figure 1.- Regional geological map of Galicia (NW Spain) after Martinez-Catalán et al. (1997) showing the location of the studied kaolin deposit.

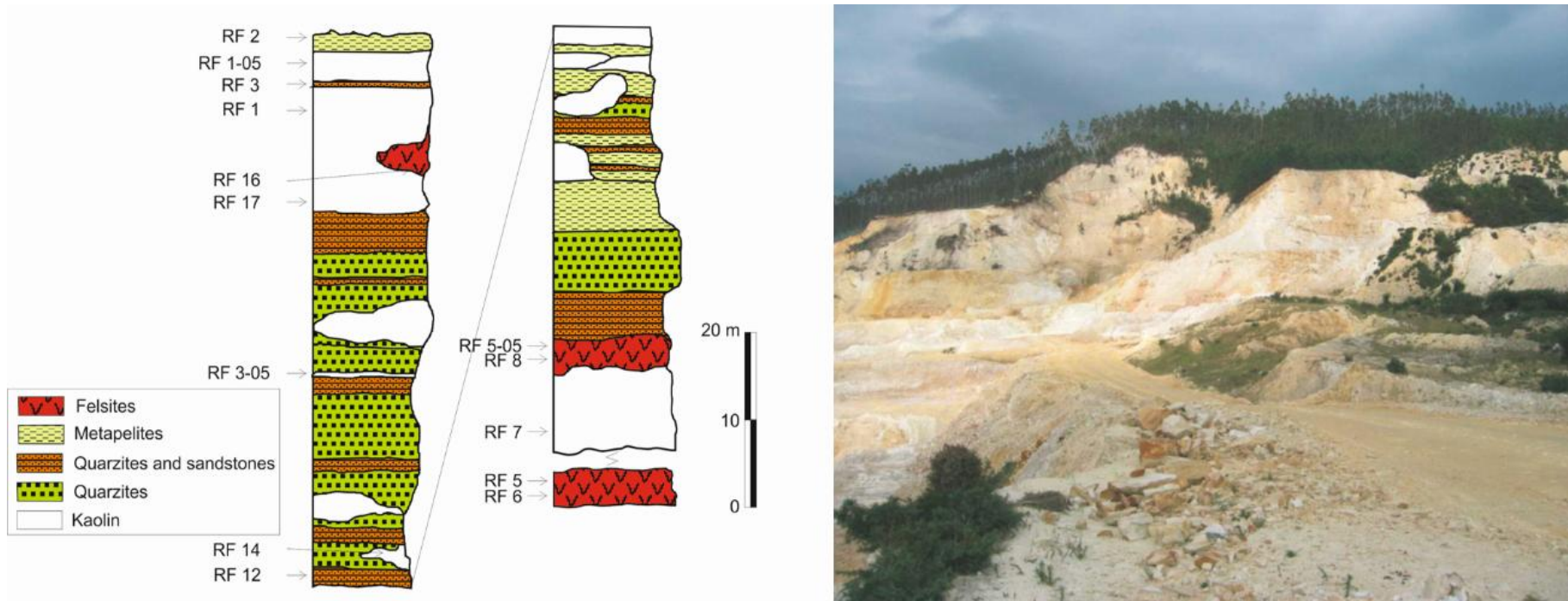


Figure 2.- Panoramic view of the kaolin quarries at Ramón-Fazouro and sketch of the sample location in the studied outcrops.

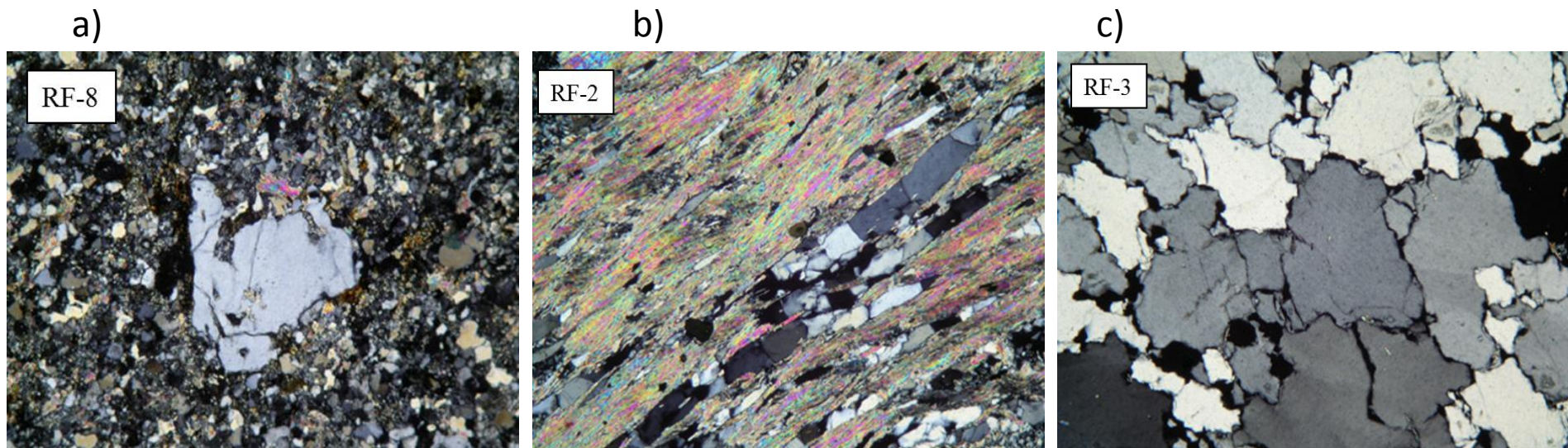


Figure 3. a) Micro-photographs of felsite (RF-8) showing feldspars crystals in a microcrystalline matrix composed of plagioclase, quartz, muscovite and biotite; b) micaschist (RF-2) showing oriented micaceous minerals bands alternating with quartz plus feldspars bands; c) quartzite (RF-3) (polygonal quartz grains). PXA, 4x.

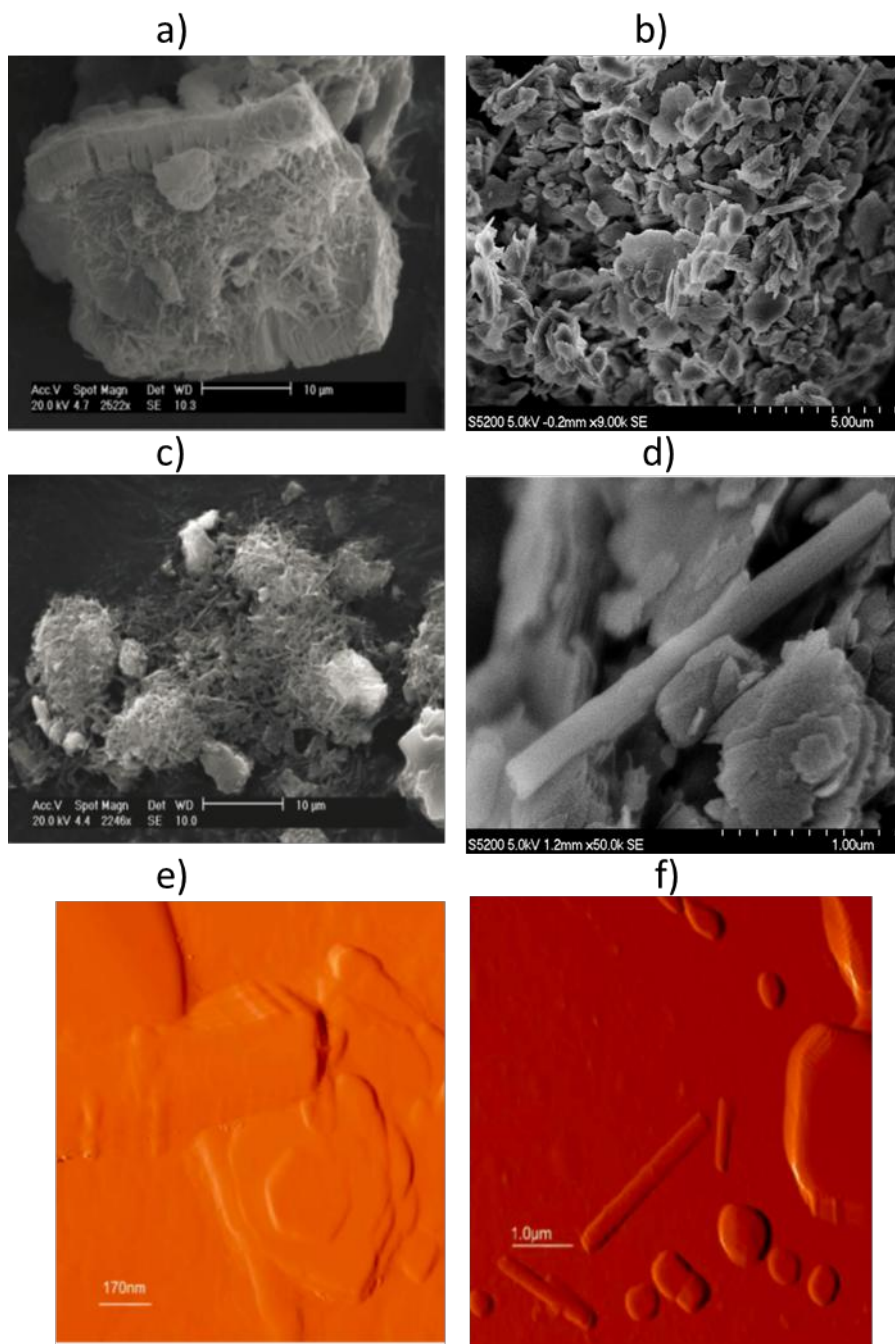
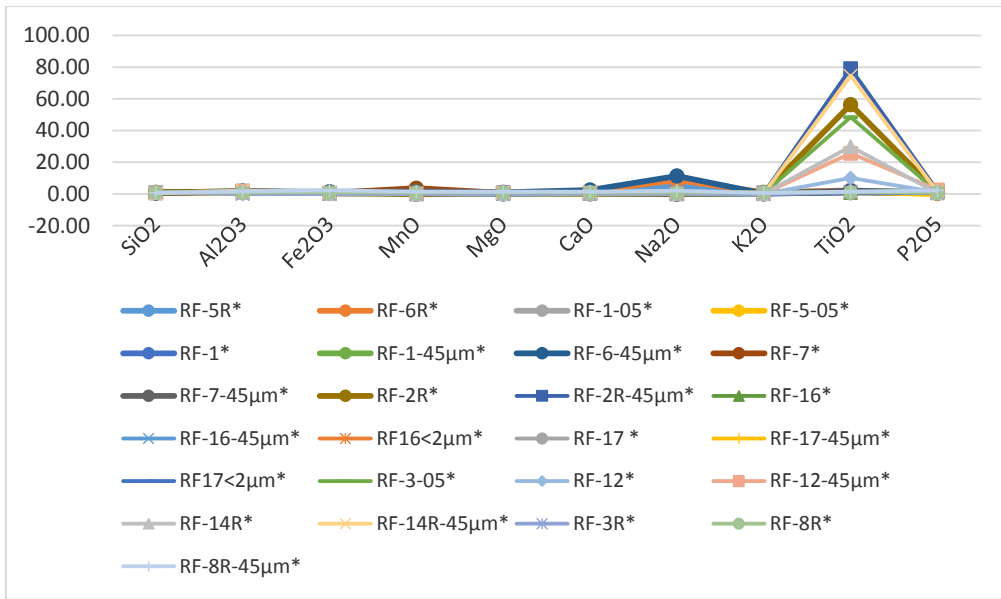


Figure 4.- a) Halloysite joined to book-like kaolinite aggregate; (b and e)Kaolinite crystals oriented face to face; (c) halloysite crystals in clusters; (d) Halloysite in tubular shape with kaolinite crystals oriented face to face; (f) tubular halloysite crystals and spherical particles which could be allophane.

a)



b)

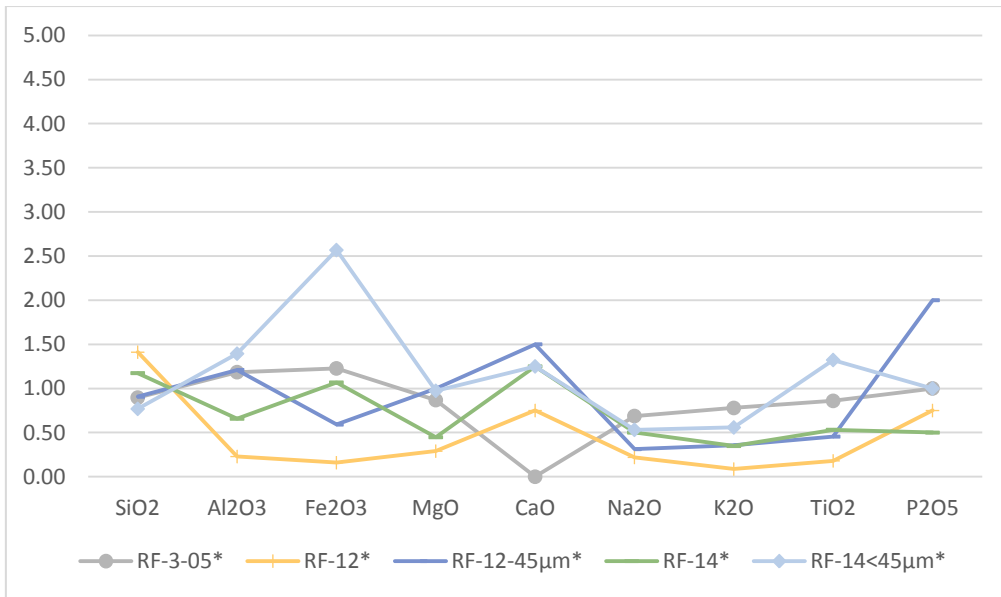
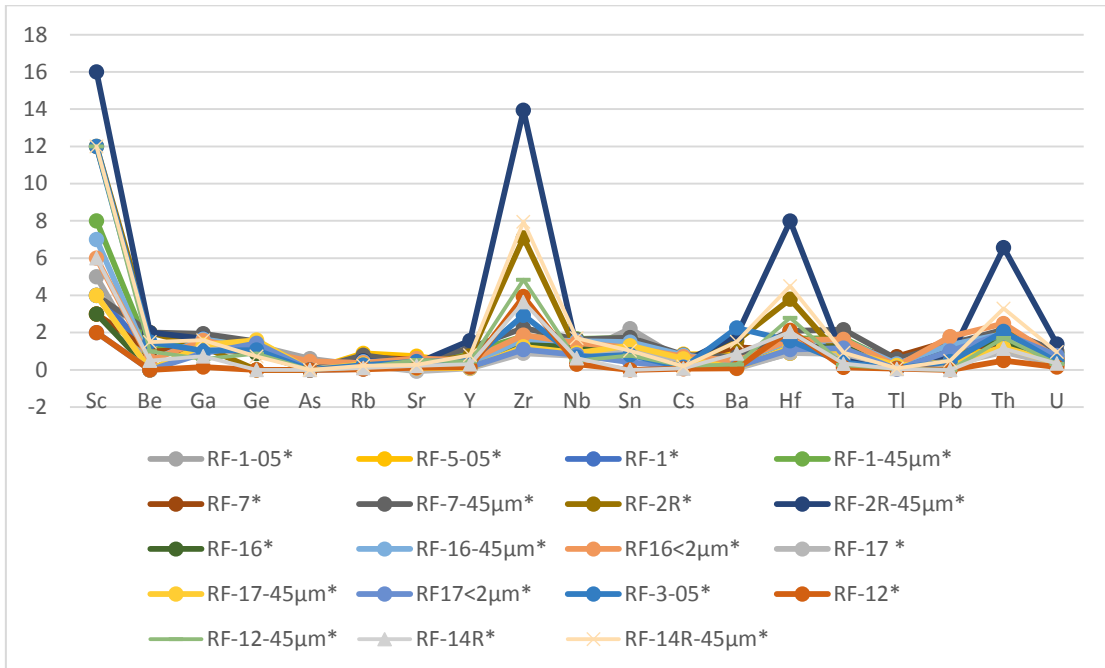


Figure 5.- a) Major chemical composition normalized to felsite; b) normalized to metapelite.

a)



b)

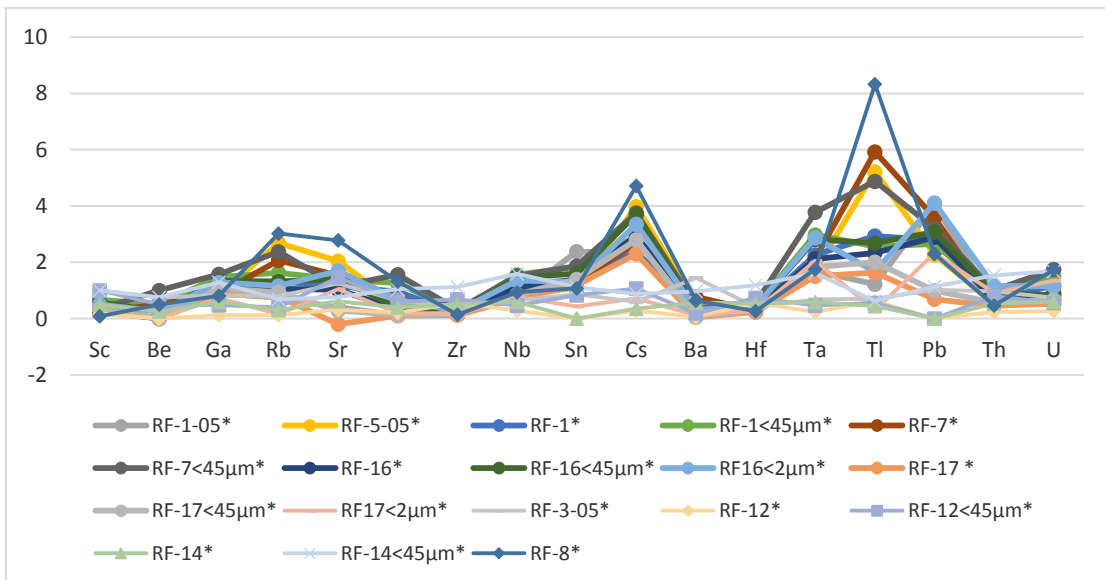
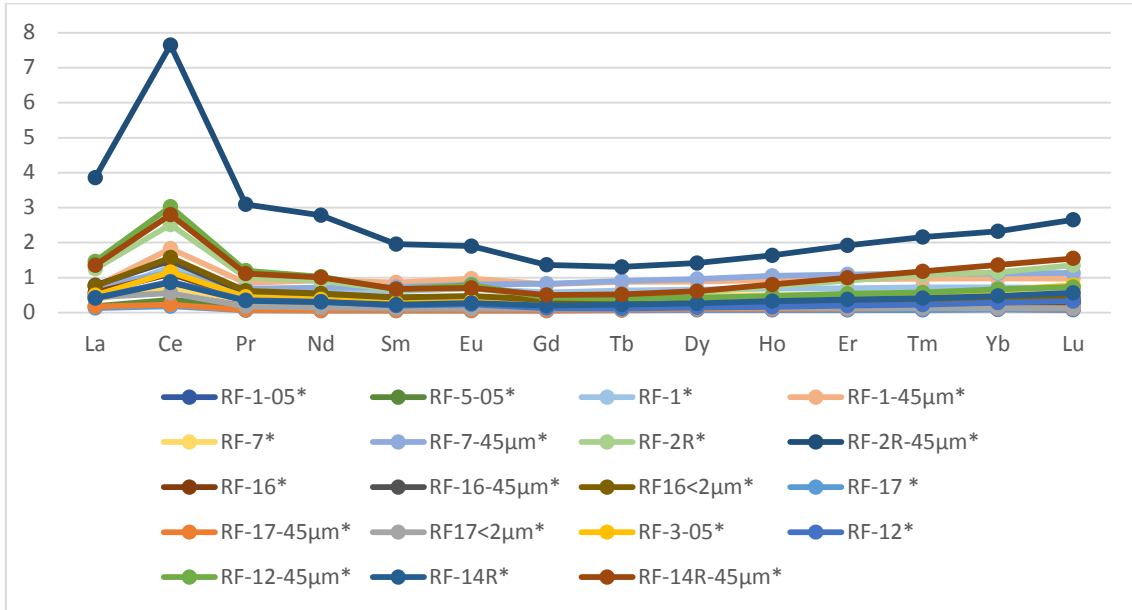


Figure 6.- a) Trace elements composition normalized to felsite; b) normalized to metapelite.

a)



b)

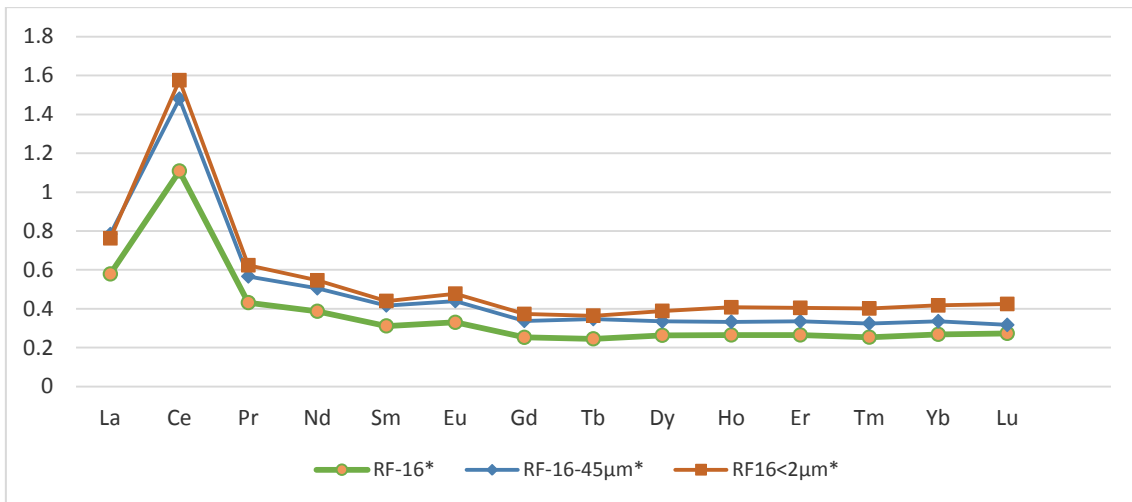


Figure 7.- a) Felsite normalized REE distribution pattern of the kaolin samples; b) felsite-normalized REE distribution patterns of different grain-size fractions of the same sample.

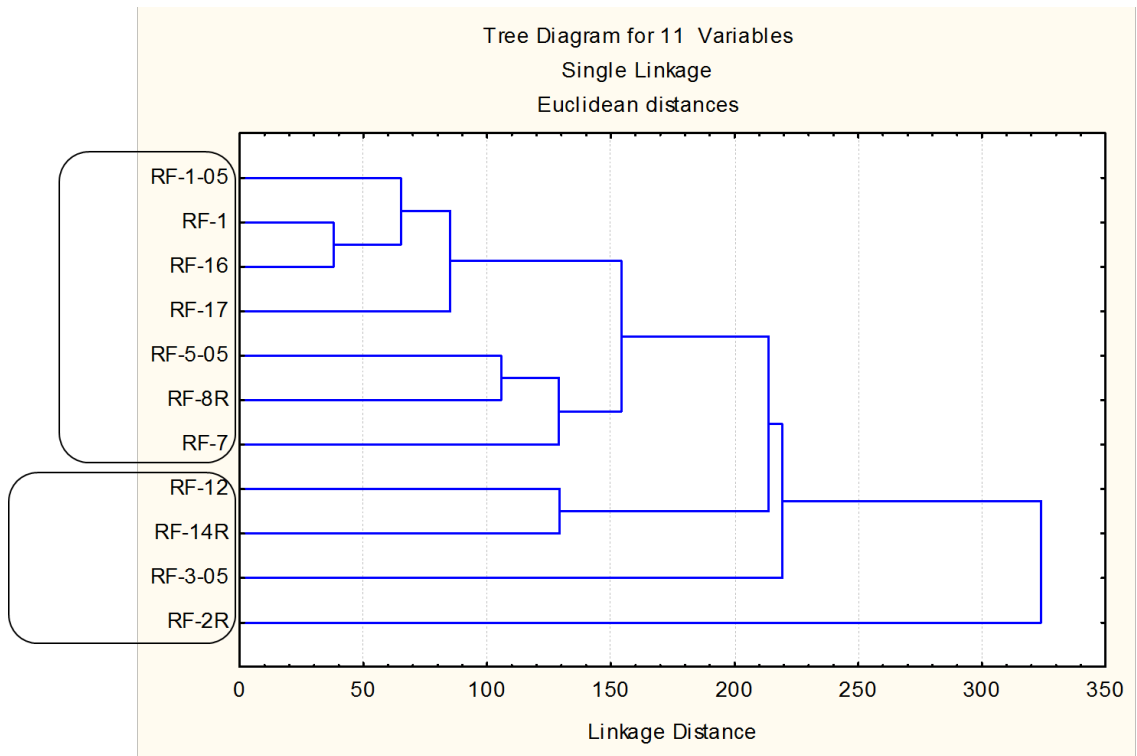


Figure 8. Cluster analysis

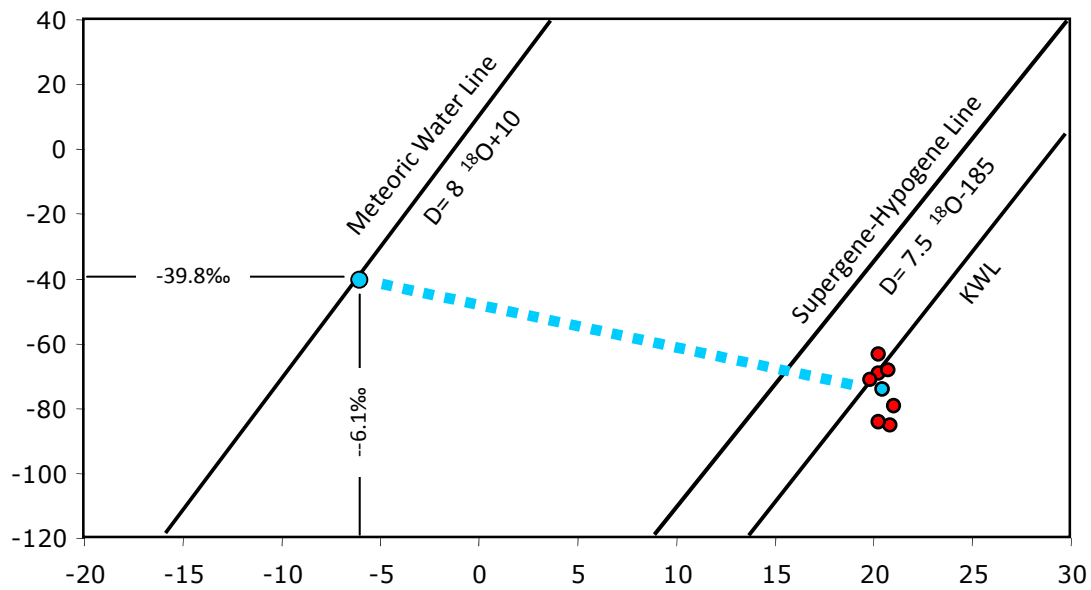


Figure 9. $\delta^{18}\text{O}$ versus δD diagram for the $<1\ \mu\text{m}$ fraction of the kaolin. The meteoric water, supergene/hypogene and kaolinite weathering lines (KWL) are given for reference. The dashed line indicates the oxygen and deuterium isotopic composition of water in equilibrium with a kaolinite with the mean isotope ratios ($\delta^{18}\text{O} = 20.4\text{‰}$ and $\delta\text{D} = -74\text{‰}$). Abundances are expressed as parts per thousand relative to Vienna Standard Mean Ocean Water (V-SMOW).



Figure 10.- Some pictures realized during the visit of Prof. Haydn Murray to Burela kaolin deposit and Sargadelos Ceramic factory (2005) with some of the authors of this paper.

NEW INSIGHTS ON MINERALOGY AND GENESIS OF KAOLIN DEPOSITS: THE BURELA KAOLIN DEPOSIT (NORTHWESTERN SPAIN)

ABSTRACT

The Burela deposit is the largest kaolin deposit in Spain, mined for more than 50 years, the product being mainly used for porcelain. Kaolin is dominantly associated with Lower Cambrian felsites, interbedded with quartzites, micaschists and metapelites (Cándana Series), and was strongly folded during the Hercynian orogeny. Kaolin layers were ductile and incompetent materials among more competent ones, producing many slides with a diastrophic appearance. Consequently, kaolin outcrops are morphologically very variable, - i.e. pockets -, and interlayered between metapelites and/or quartzites, resulting in complication for prospection and mining.

The kaolin consists mainly of kaolinite, tubular halloysite, and spherical allophane along with quartz and minor illite. The content of kaolin minerals reaches up to 90% in the finer fraction (<2 μ m and <1 μ m).

Geochemical analyses of trace and REE show a close relationship between kaolin and associated rocks. Two kaolin types can be differentiated: (i) massive, associated to felsite; and (ii) related to metapelite. A temperature range from 20 to 35°C, with an average of approximately 28°C was calculated on the basis of the isotopic signatures ($\delta^{18}\text{O}$, δD) for the kaolin materials. This scatter suggests that if continental weathering was involved in the kaolin formation on the lower side of the temperatures, it was not the only process, especially for kaolin associate with felsites and metapelites. The higher temperatures are indicative of a hydrothermal auto-metamorphic alteration, followed by a folding of the series that induced an apparently chaotic kaolin distribution with a combined continental weathering superimposed on the previous low-temperature hydrothermal felsite transformation.