

1 **Characterisation of clays from Alicante province (SE Spain) for use in**
2 **the recovery of degraded soils**

3 **J.D. Jordá^{a,b}, J.E. Tent-Manclús^{a,c}, M. Cerdán, A. Sánchez-Sánchez^b, P. Jaramillo^b**
4 **M.M. Jordán^{d,*}**

5 a Institute for Environmental Studies Ramon Margalef. University of Alicante. Carretera
6 de S. Vicente del Raspeig s/n, 03080. Alicante Spain

7 b Department of Agrochemistry and Biochemistry. University of Alicante. Carretera de
8 S. Vicente del Raspeig s/n, 03080. Alicante Spain

9 c Department of Earth Sciences. University of Alicante. Carretera de S. Vicente del
10 Raspeig s/n, 03080. Alicante Spain

11 d Environmental Soil Science Group (GEA in Spanish) Department of Agrochemistry
12 and Environment, Miguel Hernández University, Avenida de la Universidad s/n, 03202-
13 Elche, Alicante, Spain

14 *corresponding author

15 **Abstract**

16 The goal of this paper is the characterisation of seven clays of the province of Alicante
17 (SE Spain) and their possible use to improve the fertility, water absorption and
18 contaminant retaining capacity of degraded soils. Three soils affected by the dumping of
19 construction debris were also studied to diagnose the problems and possible recovery
20 strategies. Several physicochemical properties were measured, such as the water holding
21 capacity, soil organic matter, lime, pH, EC and CEC. A high correlation between
22 mineralogical and elemental composition was obtained. Illite was present in all clays and
23 soils. Some of the samples also contained kaolinite and significant amounts of lime. The
24 CEC, as expected, was more closely related to the organic matter content. Soil organic
25 matter was detected in the second derivative of the FTIR spectra by the signals of the CH₂
26 groups at 2850 and 2919. This way, the FTIR spectrum for the soils of the area would
27 make it possible to estimate both the organic matter content and the CEC. Despite their
28 origin, soils did not show heavy metal pollution, however salinization risk seemed to be
29 the most probable cause of degradation. According to the organic matter, lime and illite

30 content, two clays were selected as the most suitable for soil degradation recovery.
31 Furthermore, organic matter additions may help to improve the self-depurative ability of
32 the soil.

33

34 **Keywords:** Soils, pollution, clays, FTIR, XRF.

35

36 **Introduction**

37 The pollution of soils over time following the repeated addition of high doses of biosolids
38 in the agricultural land of the provinces of Alicante and Murcia (Spain) had a different
39 impact, depending on the physical characteristics and chemical properties of soils, which
40 affect the fixation and evolution of polluting elements in the soils. Soil is a barrier that
41 filters, retains, transforms and degrades some contaminants. But the self-purification
42 power of soils is not unlimited, and their self-recovery ability is highly variable depending
43 on the soil characteristics and the amount of pollutant (Plekhanova, 2017). The variability
44 of soils in polluted areas is a key element for their recovery. Thus, surveying soils is
45 essential for any decontamination project. The main soil properties that condition the
46 vulnerability of soils to pollution are: texture, permeability, porosity, water dynamics,
47 pH, ion exchange capacity, carbonate contents, salts, clay mineralogy, organic matter and
48 microorganisms, among others (Alamgir, 2016; Lundy et al., 2017). In the south-east of
49 Spain, the soils that present a higher capacity to retain heavy metals and prevent the
50 contamination of water and plants are those with clayey texture, poor drainage, high water
51 holding capacity, basic pH, high cation exchange capacity and high amounts of organic
52 matter, salts, carbonates and clay minerals mainly 2:1 type clays. Clay minerals tend to
53 adsorb heavy metals, in their exchange positions, especially at mid pH values; whereas at
54 higher pH values, the main reactions are precipitation and the formation of inner sphere

55 complexes with the clays (Echeverria et al., 2002). On the other hand, sandy soils lack
56 the fixation capacity for heavy metals, which can quickly pass through to the subsoil and
57 may contaminate groundwater. The pH is a very important parameter to define the
58 geochemical stability of heavy metals and other cations (Hou et al., 2019). Heavy metals
59 are generally dissolved at extremely acidic pH values (mobilisation), whereas at neutral
60 and basic pH values they tend to precipitate (immobilisation). At very high pH values
61 they can be mobilised again as soluble anions or through the formation of hydroxi-
62 complexes (Se, As, Cr) (Masindi and Muedi, 2018; Namieśnik and Rabajczyk, 2010).
63 Likewise, the higher the CEC, the greater the capacity of the soil to fixate pollutants. Soil
64 lime favours basic soils, neutralises acidic spills and is able to fixate heavy metals.

65 The presence of salts in the soil may be positive regarding heavy metal pollution as it is
66 an indicator of barely washed media, and usually of basic pH levels. However, the rise in
67 salinity can increase the mobilisation of heavy metals by two mechanisms. Firstly, the
68 cations linked to salts (Na, K) can replace heavy metals in soil adsorption centres.
69 Secondly, the chloride anions can form stable soluble complexes with heavy metals such
70 as Cd, Zn and Hg (Darban et al., 2000; Luendy et al., 2017).

71 The 2:1 clay minerals such as smectites and vermiculites present a high cation exchange
72 capacity (CEC). On the contrary, 1:1 clay minerals such as kaolinite show lower CEC
73 values. However, the adsorption of divalent metals in kaolinite improves properties such
74 as flocculation, plasticity, porosity and the hydraulic conductivity of the clay, and
75 increases metal retention (Miranda-Treviño and Cole, 2003; Muththalib and Baudet,
76 2019). This effect has also been observed in 2:1 clays. The Ca^{2+} ion increased the
77 interlayer space of bentonite, improving its capacity to retain water (Castrillo et al., 2018).
78 The ion exchange capacity of organic matter is even higher than that of clays.

79 Furthermore, organic matter may form organometallic complexes. If metals react with
80 organic compounds of low molecular weight, the resulting complexes can migrate more
81 easily through the profile (Darban et al., 2000; Masindi and Muedi, 2017), but they are
82 retained if the reaction with organic compounds of high molecular weight occurs.

83 Agriculture has been practiced for a long time in Mediterranean regions. Intensive
84 agriculture and irrigation have been developed. Nowadays, these regions are suffering
85 from the abandonment of these traditional activities and the consequent soil degradation.
86 The studied area, situated in the Mediterranean basin, has been long cultivated with
87 cereal, almonds, and olive trees, among others (Navarro-Pedreño et al., 2018). However,
88 soils are being abandoned and degraded because of poor agricultural and economic
89 returns. The landscape is changing, and sustainable dry agriculture may be a great
90 opportunity to rehabilitate the area based on the maintenance or to increment organic
91 matter levels in the soils and improve soil quality (Navarro-Pedreño et al., 2018).

92 The main objective focuses on characterising clays of different geological origin and age
93 from the Alicante province located in abandoned ceramic clay pits in order to understand
94 their physical, chemical and mineralogical properties. This will make it possible to select
95 the most suitable ones to be used in degraded and contaminated soil recovery projects in
96 the region, improving soil environmental and agronomical quality. These soils are very
97 common in the area, and cause severe environmental damage. The characteristics of three
98 soils from an area that is degraded due to the dumping of construction debris were also
99 studied, in order to detect critical points in the recovery of these soils.

100 **Materials and methods**

101 To conduct the research, the area of study was first examined in order to take one-off samples
102 that were representative of the clayey material. Then, the sampling areas in Alicante province
103 were selected (Fig. 1). A total seven clay samples were taken and placed in duly labelled
104 airtight containers. The gathered samples and their corresponding codes are listed in Table 1.
105 Points were chosen from the sampling areas at random, visually delineating the most suitable
106 spots where to find the clayey material. Soil samples were also taken from an area adjacent
107 to the University of Alicante, which in the past was used as a debris dump and which is
108 currently partially covered with vegetation adapted to dry and/or salinized environments (Fig.
109 1). The outcrops sampled can be assigned to the southern Alicante Prebetic depositional
110 sector of the Prebetic domain (Ruiz-Ortiz et al., 2019), that correspond to the southeastern
111 Iberian plate paleoplatform. The rock sediments correspond to a marine outer platform
112 transition to the slope environment except the Triassic keuper clays that were sedimented in
113 a continental tropical environment. . The soils had a massive structure, with areas completely
114 devoid of vegetation (Table 1).

115 The samples were dried at room temperature. After that, each sample was crushed with a
116 mortar, sieved through a 2 mm mesh, and stored in plastic containers. A standard
117 decanting process was carried out in clays, in order to remove the thicker particles.

118 The organic matter content (SOM), was measured by the loss of weight after heat
119 treatment at 550 °C. Lime content was measured by calcimetry. The water holding
120 capacity (WHC) was determined using the gravimetric method. The cation exchange
121 capacity (CEC) of the soil was measured using the method of Bower et al. 1952, based
122 on displacing change cations with sodium.

123 The mineralogical and elemental characterisation of the samples was conducted using
124 instrumental techniques such as ATR-Fourier-transform infrared spectroscopy (ATR-
125 FTIR) and X-ray fluorescence (XRF). For the ATR-FTIR analysis, fine 0.1 mm sieved

126 soil/clay powder was used. Potassium ferricyanide ($K_3Fe(CN)_6$) at 50% was added to the
127 samples as a reference (Reig et al., 2002), without any additional treatment. The
128 potassium ferricyanide band at 2116 cm^{-1} did not interfere with any other band of the soil
129 spectra and made it possible to measure relative intensities of the FTIR signals which are
130 related to concentration. A BRUKER IFS 66/S spectrometer was used to conduct the
131 analysis. The spectra were normalised using the signal of the second derivative of the
132 ferricyanide. The minerals contained in each clay/soil were identified by comparing the
133 FTIR spectra with the FTIR spectra of pure mineral samples from the mineral collection
134 at the University of Alicante and the Ruff database (Lafuente et al., 2015). The use of the
135 second derivative also helped to identify and interpret some of the signals (Jordá et al.,
136 2015). The equipment used for the elemental analysis was an X-ray sequential
137 spectrometer (PHILIPS MAGIX PRO), equipped with a Rh tube and a Be window. As La
138 was not detected in any of the samples during the qualitative analysis, it was used as an
139 internal reference to quantify the elemental concentrations in the soil. To do so, 9.000 g
140 of clay were weighed, and 0.1000 g of La_2O_3 were added. The samples were analysed
141 again using XRF. As we knew the percentage of La present in the sample and the relative
142 proportion of each element with respect to La, it was possible to calculate the percentage
143 of each element present in the clay/soil samples soil mass.

144

145 Regression analyses were conducted using the SPSS[®] 26 software. This software was also
146 used for the principal component analysis (PCA), which was performed on the FTIR
147 spectra of the studied samples and a kaolinite sample from Guadalajara (Spain). The
148 partial correlations between the different properties of the clays and soils and the
149 spectroscopic and laboratory data were all drawn from the correlations extracted for each
150 component of the PCA analysis.

151

152 **Results**

153

154 **Elemental analysis of the clays/soil samples**

155 The results obtained in the elemental analysis are shown in Table 2. The presence of
156 elements that are specific to clays such as Si, Al and K were observed in all samples, as
157 well as substantial Ca concentrations in some of them, and variable amounts of Fe, Sr and
158 Ti. There were merely unrepresentative percentages of other elements present in all
159 samples. Even though, none of the soils contained significant amounts of heavy metals,
160 sample S1 contained higher amounts of Na and Cl than the rest of the samples. There was
161 a strong positive relationship between the concentrations of Si and Al, especially, but
162 also with K, Fe and Ti, meaning that these elements were related to clays and they did not
163 occur in free forms as salts or oxides. K, Fe and Mg were especially related (Table 3). As
164 we will see later on, Ca, whose correlation with Si was negative (Table 3), was related to
165 lime, and Sr, which appears in small amounts in all samples, was also correlated to Ca.
166 Mn was not correlated with Si or Al, meaning that it must be found, at least in some
167 samples, as oxides and not included in clay formulae. Similar results were obtained for
168 the rest of trace elements. They are usually detected in soils of the Alicante province
169 (Navarro-Pedreño, 2018; Sánchez-Sánchez et al. 2019). Copper occurrence in these soils
170 has been related to human action (Micó et al. 2008)

171

172 **Physicochemical properties of the clays and soils samples**

173 The results of the different physicochemical properties of the samples are shown in Table
174 4. Several samples contained high amounts of lime, sometimes surpassing 50 % and thus
175 explaining the high amounts of Ca in these samples, as noted in the previous section. As

176 a result, the pH values both in water and in KCl (1M) were high. The concentration of H⁺
177 extracted with KCl correlated very strongly with the lime content (R = -0.918; sig. 0.001)
178 for clays with lime amounts greater than 25 %. The KCl pH values also correlated to the
179 SOM content (R = 0.686; sig. 0.02), but specially significant was the relationship
180 between CEC and SOM (R= 0.909; sig. > 0.0001), verifying the known fact that organic
181 matter contributes more than clays to the CEC of soils, and suggesting that the origin of
182 the H⁺ exchanged for K⁺ was mainly from organic acid groups. These H⁺ may be partially
183 neutralised by lime. The CEC of the samples was not too high however, as it was in the
184 range between 1 and 10 cmol_c/kg. On the contrary, the EC values were high in a majority
185 of samples, and especially for S1 and C3.

186 No differences were observed between the water holding capacity of clays and soils,
187 despite the latter being poor in clay, according to the low Si and Al levels observed in the
188 elemental analysis (Table 2).

189 In general, better correlations were obtained using the values of elemental concentration
190 per clay/soil mass using La₂O₃ oxide as a reference, than using the values of percentage
191 of oxides obtained directly from the traditional XRF analysis.

192

193 **Mineralogical analysis by ATR-FTIR**

194 All clays were similar in mineralogical composition. Quartz and illite (signals at ~775
195 and 798 (double band) and 1164 cm⁻¹ for quartz, and at 900 and 3620 for illite) were
196 observed in all samples. Calcite was also present in a majority of the samples (bands at
197 711, 845 and 871 cm⁻¹) and was usually linked to the presence of kaolinite (bands at 1025
198 and 3696 cm⁻¹). As an example, the characteristic spectra of clay C1, composed almost
199 exclusively of illite, and soil S1, rich in calcite and kaolinite and some illite, can be seen
200 in Fig. 1.

201

202 The principal component analysis explained 83 % of the variance with just two
203 components (Fig. 3). Clay C8, composed almost exclusively of kaolinite, in accordance
204 with its FTIR spectrum and its elemental analysis (data not shown), was included in the
205 analysis for comparative purposes. Component PC1 was related to the illite content, i.e.
206 samples with a high value of this component were rich in this clay mineral, whereas those
207 with a low value also showed lower concentrations of illite, either because they were rich
208 in calcite or because they contained kaolinite. Component PC2 was related to the kaolinite
209 content, although in this case a low or even negative value represents an abundance of
210 this mineral, whereas higher values entail its absence, either due to the presence of illite
211 or calcite. Thus, the points representing the soil samples and C5 are located in Fig. 3 in
212 the top left quadrant due to their concentration of carbonates. Although C5 was almost
213 exclusively composed of illite and calcium carbonate, it had a high PC2 value, whereas
214 the PC2 value for S1, S2 and S3 containing both clays and calcium carbonate is near zero
215 value.

216 A strong correlation was observed between these two components and the elemental
217 composition of the clays and soils, especially regarding the majoritarian elements, Al, Si
218 and Ca, and lime (Table 5). For K, Fe, Ti, CEC and SOM, the correlation was only
219 observed with PC1 (Table 6). Illites are rich in K, meaning it is foreseeable for this
220 element to correlate with a component linked to the concentration of illite. The high
221 relationship with Fe and Ti also suggested that both elements were related to this
222 mineral. In fact, C1 and C2, the clays that have the most illite, are also the richest in Fe
223 and Ti. Although not in such a clear way, clays rich in illite tended to contain more organic
224 matter and therefore more CEC.

225 Strong correlations between individual signals of the spectrum and some
226 physicochemical characteristics of the clay/soil samples were observed. The intensity of
227 bands 711 (second derivative) and 1400 cm^{-1} , as expected, correlated to lime or Ca, and
228 the 3620 cm^{-1} (second derivative) band correlated to Si or Al. The bands at 2850 and 2919
229 (second derivative) which correspond to CH_2 both correlated to SOM, which made it
230 possible to estimate the amount of organic matter and therefore of CEC of the samples
231 through the ATR-FTIR spectra ($R = 0.789$, sig. 0.007 for the signal at 2919, second
232 derivative). These signals were clearly visible in the main spectrum of some samples (Fig.
233 4). The signals of the carboxyl groups that could be more directly related to the CEC are
234 hard to detect, especially in the presence of large amounts of lime. Despite the fact that
235 water provides very clear signals in the FTIR spectrum, it was not possible to find a link
236 between the spectra and the water holding capacity.

237

238 **Discussion**

239 Our results showed the ability of the ATR-FTIR mineralogical analysis using $\text{K}_3\text{Fe}(\text{CN})_6$
240 as a reference to describe not only the elemental composition of the samples, but also
241 other important physicochemical characteristics related to the dynamics of metals in soils
242 such as CEC, or lime, which limits the release of H^+ via exchange. There are numerous
243 references that consider that high amounts of organic matter and lime in the soil favours
244 the retention of heavy metals (de Matos et al., 2001; Takáč et al., 2009), although soluble
245 organic molecules could facilitate the dissolution of elements such as Cu (Campillo-Cora
246 et al., 2020). Conversely to what could be expected, because of the dumping that took
247 place for years on soils S1, S2 and S3, no heavy metal pollution was observed, and the
248 metals present seemed to be related to clays, mainly to illite. Because of the lime content,
249 EC, pH and considering the role of organic matter, it seems more probable for there to be

250 a salinisation risk, especially in soil S1. Soils with high amounts of clays have high EC
251 values because clay charge (Jung et al., 2005; Choo et al., 2016), but there is no risk of
252 salinisation, due to K which is especially abundant in illite, is strongly retained by the
253 clay. However, sample S1 stood out due to its high NaCl content. It is possible that the
254 area where the soil was located was more exposed than samples S2 and S3 to winds which
255 drag marine spray, as the distance to the coast is merely six kilometres. Its recovery could
256 thus be more complicated. The salinisation problem made this soil more susceptible to
257 mobilise heavy metals (Darban et al., 2000).

258 Regarding the water holding capacity, it was not affected by the presence of lime or
259 kaolinite in several samples, despite the smaller interlayer space in kaolinite compared to
260 illite. This can be due to the absorption of Ca by kaolinite, which increases its interlayer
261 space (Miranda-Treviño and Cole, 2003; Muththalib and Baudet, 2019). Maybe other
262 properties related to soil water as the wilting point or the rate of water loss would be more
263 adequate to understand the differences in water dynamics in clays and degraded soils.

264

265 **Conclusions**

266 The organic matter of the clay/soil samples is responsible for the CEC and the potential
267 pH of the soils. Carbonate counteracts this H⁺ release, thus decreasing the risk of
268 contamination with heavy metals in the future. The presence of kaolinite in some samples
269 as well as calcite does not seem to affect the water holding capacity, as the presence of
270 Ca could increase the interlayer space in several mineral clays. In this regard, clay C2,
271 rich in illite, with moderate amounts of lime and high amounts of organic matter, has the
272 highest water holding capacity, and could be used in degraded soils to improve both CEC
273 and soil water. Clay C6, with more lime but also rich in organic matter and a high CEC,

274 could be a good candidate in the case of heavy metal spills. Furthermore, organic matter
275 additions could be of great help to improve the self depurative ability of soils.

276

277 **Declaration**

278

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281 material: Data available on request from the authors.

282 Code availability: No application.

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284 validation: J. Jordán and A. Sánchez; formal analysis and data curation: P. Jaramillo, M.
285 Cerdán and J.E Tent; writing—original draft preparation J.E. Tent, J. Jordá and M.M.
286 Jordán; writing—review and editing: M.M. Jordán; supervision: J. Jordá.

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369 **FIGURE CAPTIONS**

370

371 Figure 1. Sampling points of the studied clays and soils.

372 Figure 2. ATR-FTIR spectra of illitic clay C1 and soil S1.

373 Figure 3. PCA of the clay and soil samples. Sample C8 corresponds to a kaolinite
374 standard.

375 Figure 4. CH₂ signals in clay C3.

376

377 **TABLES CAPTIONS**

378

379 Table 1. Sampled clays and soils.

380 Table 2. Elemental analysis of clay and soil samples (wt %).

381 Table 3. Linear relations between the different elements of the studied samples.

382 Table 4. Physicochemical properties of the clay and soil samples.

383 Table 5. Correlations between components PC1 and PC2, lime and the majoritarian elements in
384 the samples.

385 Table 6. Correlations between the CEC, om and different elements and component PC1.

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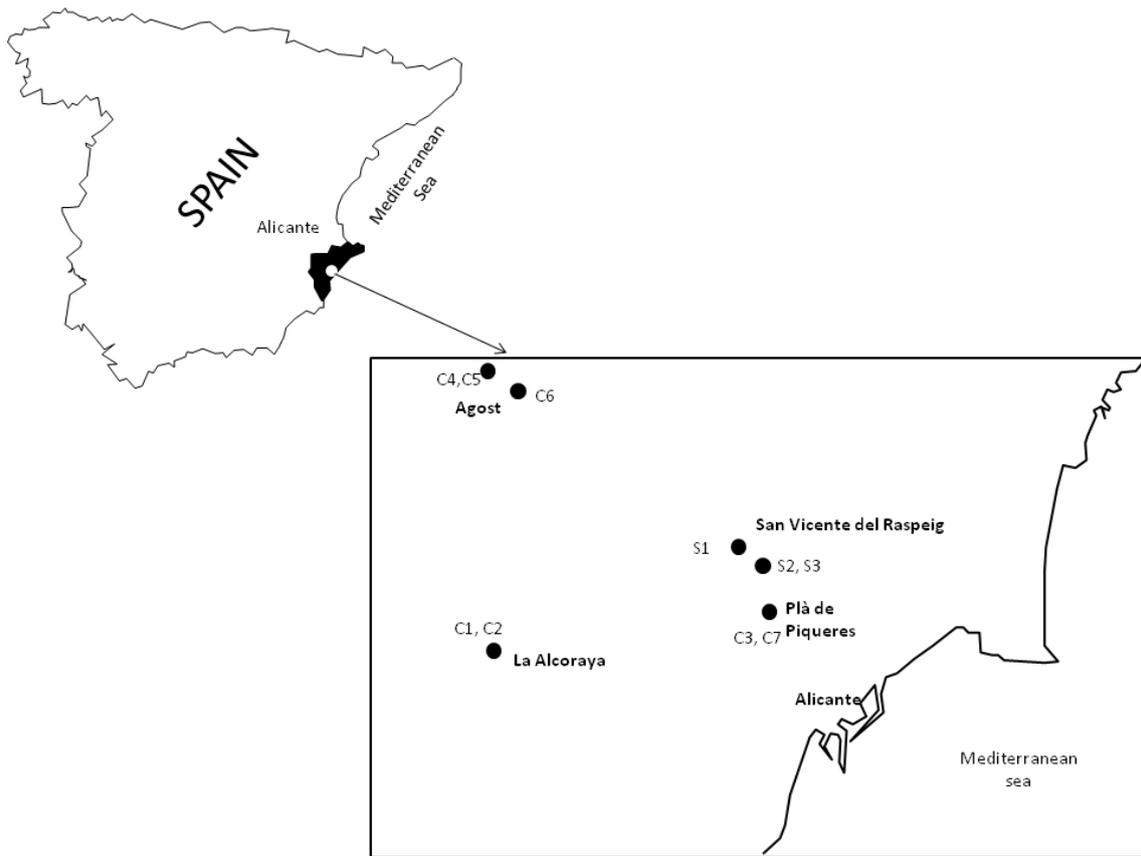
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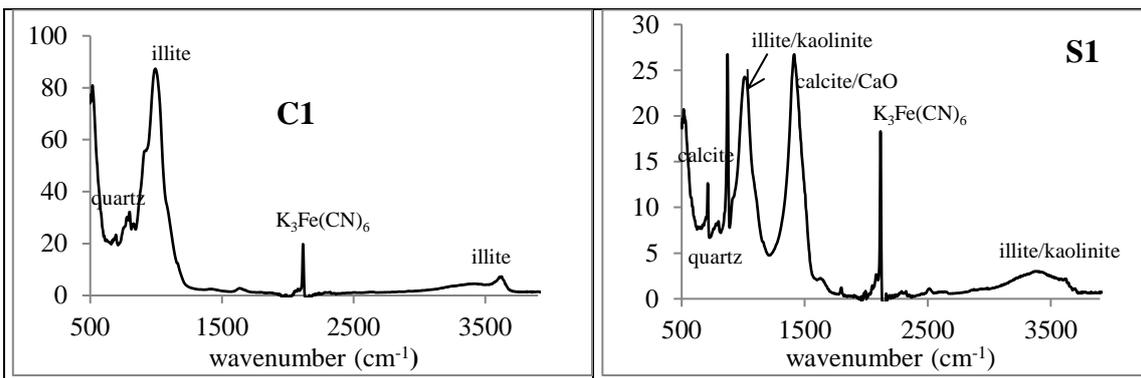
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403 Fig. 1. Sampling points of the studied clays and soils

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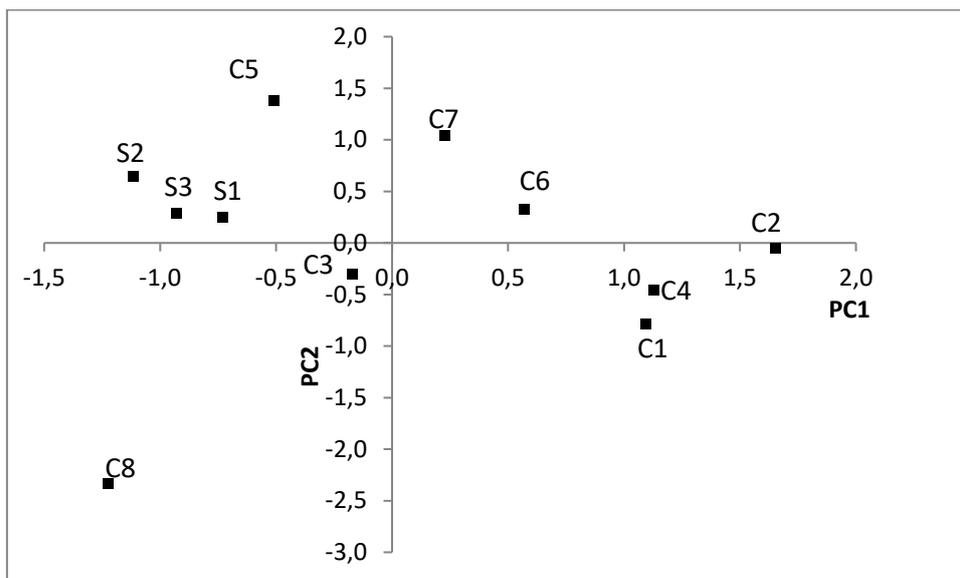
407 Figure. 2. ATR-FTIR spectra of illitic clay C1 and soil S1

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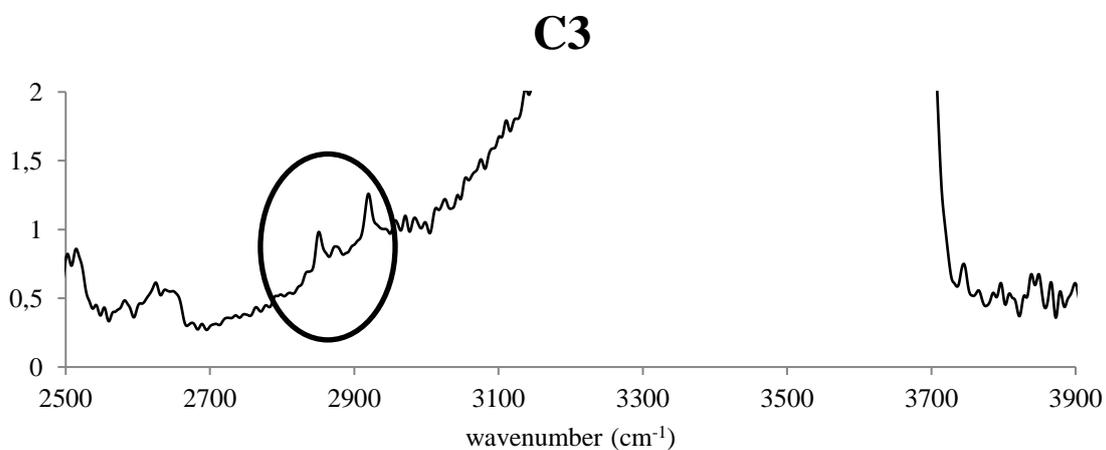
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413 Fig. 3. PCA of the clay and soil samples. Sample C8 corresponds to a kaolinite standard

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418 Fig.4. -CH₂ bands in clay C3. ATR-FTIR spectrum

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422 Table 1. Sampled clays and soils

clay	code
Keuper 1 red La Alcoraya	C1
Keuper 1 green La Alcoraya	C2
Albiense "Fondo de Piqueres" Alicante	C3
Eocene Agost	C4
Paleocene Agost	C5
Albiense Agost	C6
Albiense "Fondo Piqueres" Alicante (oxydized sample)	C7
Technosol	S1
Technosol	S2
Technosol	S3

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424 Table 2. Elemental analysis of clay and soil samples

element % soil	clay and soil samples									
	C1	C2	C3	C4	C5	C6	C7	S1	S2	S3
Na	0.3	0.5	0.2	0.2	0.1	0.2	0.3	2.9	0.2	0.3
Mg	1.8	2.6	1.3	1.6	0.9	1.0	1.7	1.3	0.9	1.8
Al	13	14	7.8	9.5	2.9	8.5	5.7	3.2	2.5	5.9
Si	32	29	18	23	9	19	14	10.3	7.4	16.4
P	0.04	0.1	0.02	0.04	0.1	0.04	0.1	0.1	0.04	0.1
S	0.1	0.9	0.2	0.1	0.1	0.2	0.8	0.1	0.2	0.2
Cl	0.05	0.06	0.05	0.03	0.02	0.03	0.2	3.4	0.05	0.2
K	6.2	6.9	1.7	2.8	0.5	1.9	1.9	1.4	0.9	2.2
Ca	1.1	14	23	15	41	24	28	34	34	44
Ti	0.8	0.9	0.4	0.6	0.2	0.5	0.4	0.3	0.2	0.4
V		0.04								
Cr	0.02	0.02		0.02						
Mn	0.02	0.5	0.02	0.04	0.1	0.02	0.03	0.02	0.02	0.05
Fe	6.7	7.5	2.9	4.0	1.1	3.2	2.7	1.9	1.5	3.4
Ni	0.01	0.01								
Cu		0.02	0.01		0.01	0.01		0.01		
								0.01		
Rb	0.03	0.04	0.02	0.02		0.02	0.02	0.01	0.01	0.02
Sr	0.03	0.07	0.1	0.05	0.1	0.09	0.1	0.1	0.1	0.1
Y	0.01	0.01	0.003	0.003		0.01	0.004			0.004
Zr	0.03	0.02	0.03	0.03	0.02	0.02	0.02	0.04		0.02
Ba	0.1	0.1		0.03	0.2				0.03	
Nb							0.2			
Ce	0.04									
W	0.03	0.06	0.03	0.03	0.03	0.03	0.03	0.04		0.05

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427 Table 3. Linear relationships between the different elements of the studied samples

	R	F	sig
Al-Si	0.984	252	<0.0001
K-Si	0.921	45	0.0002
Fe-Si	0.957	86	<0.0001
Ti-Si	0.971	132	<0.0001
Ca-Si	-0.973	142	<0.0001
Ca-Sr	0.895	32	0.0005
Na-Cl	0.993	553	<0.0001
Mg-Fe	0.850	21	0.002
K-Fe	0.989	345	<0.0001
Ti-Fe	0.978	175	<0.0001

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430 Table 4. Physicochemical properties of the clay and soil samples

sample	WHC %	CEC cmolc/kg	SOM %	lime %	pH KCl	pH H ₂ O	EC dS/m
C1	47	7	2.8	2.9	7.51	8.25	946
C2	59	8	4.4	17.7	7.51	8.23	637
C3	51	9	4.4	44	7.29	7.71	1738
C4	48	8	4.5	26	7.13	7.9	771
C5	49	7	3.5	79	7.6	8.44	660
C6	45	10	4.6	43	7.21	7.97	815
C7	46	9	3.8	54	7.28	8.14	877
S1	51	1	2.4	60	7.35	7.77	1710
S2	45	1	1.4	69	7.74	8.05	351
S3	51	2	1.9	58	7.52	7.76	464

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433 Table 5. Correlations between components PC1 and PC2, lime and the majoritarian
434 elements in the samples

	R	F	sig
lime	0.977	199	<0.0001
Ca	0.924	20	0.001
Al	0.953	35	<0.0001
Si	0.946	29	<0.0001

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438 Table 6. Correlations between the CEC, SOM and different elements and component PC1

	R	F	sig
CEC	0.687	7	0.028
SOM	0.695	7	0.026
K	0.799	14	0.006
Ti	0.896	33	<0.0001
Fe	0.825	17	0.003

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