

1 **Pedogenic information from fine-sand. A study in Mediterranean soils.**

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11 *Running title: Fine sand in Mediterranean soils*

12

13 **Summary**

14 The fine sand fraction (50 – 250 µm) of Mediterranean soils from Southern Spain provides
15 valuable information on soil genesis and the origin of their parent materials. ~~The~~This study
16 considers the whole fine sand and heavy fine sand ($\rho > 2.82 \text{ g cm}^{-3}$) of Luvisols, Calcisols
17 and ~~Fluvisols~~Fluvisols which form a chronosequence (ages from 600 to 0.3 ka) of the River
18 Guadalquivir terrace system. Advanced techniques (XRD, ICPms, ICP-AES, VPSEM with
19 EDX system and Raman analysis) were employed. Inheritance is the principal pedogenic
20 process. The whole fine sand consisted of carbonates (calcite and dolomite), tectosilicates
21 (quartz, K-feldspar and plagioclases), phyllosilicates (illite/moscovite, biotite, Na-mica,
22 chlorite, kaolinite, ~~and interstratified~~interstratified vermiculite-chlorite, vermiculite-illite
23 and smectite-illite) and iron oxides (goethite and haematite). The minor minerals (rutile,

24 anatase, ilmenite, zircon, staurolite, monacite, barite, apatite, andalusite, garnet and titanite)
25 are concentrated, also through inheritance, in the heavy fine sand. However, there is also
26 substantiated evidence for neoformation of rutile in these soils, never reported previously.

27 ~~Others original facts are: 1) The~~In addition, we report that (1) the geochemical indices
28 calculated in fine sand (SiO_2/CaO ; Chemical Index of Weathering –CIW-; Weathering Index
29 of Parker –WIP-; Weathering Index –WI-; Base Depletion Index –BDI-; Weathering Ratio
30 –WR-; Sr/Zr) are closely related to soil age, allowing chronofunctions to be established; and
31 (2) geochemical indices ~~also~~ provide information on the origin of ~~the~~ soils and ~~have~~
32 ~~permitted~~ permit the establishment of a ‘critical point’ corresponding to ‘time zero’, that is,
33 the start of pedogenic alteration of the parent material.

34

35 *Keywords: geochemical indices; Raman spectroscopy; rutile neoformation; heavy fine sand;*
36 *soil chronofunction; Guadalquivir River.*

37

38 **Highlights**

- 39 • Mineralogy and geochemistry inform on the provenance of the fine sand
- 40 • Rutile is neoformed in the fine sand and co-exists with the polymorph anatase
- 41 • The properties of the fine sand including geochemical indexes fit chronofunctions
- 42 • Geochemical indices determine a ‘critical point’ related to the start of weathering

43

44 **Introduction**

45 The sand in soil (granulometric fraction 50-2000 µm) has been studied in the recent
46 past (20th century) for a variety of reasons, including as a nutrient reserve in tropical soils
47 (Tamm, 1937) or an indicator of the uniformity of the parent material (Arnold, 1968). More
48 recently, it has been used to study specific pedogenic processes such as quartz dissolution
49 (Martín-García *et al.*, 2004, 2015) and mica alteration (Martín-García *et al.*, 1998; Delgado
50 *et al.*, 2003) and as an indicator of the provenance of materials and the degree of alteration
51 in soil chronosequences (Tejan-Kella *et al.*, 1991a; Farragallah and Essa, 2011; Sulieman *et*
52 *al.*, 2015). Nonetheless, relatively few studies have employed the sand in soils to investigate
53 pedogenesis, and to a lesser extent in Mediterranean soils. This may be due to ~~the~~ sand only
54 being considered useful, historically, for providing information on parent material type and
55 its degree of alteration, since it is assumed to be inherited from the parent material.

56 The use of geochemical indices of evolution/alteration is another method employed in
57 the study of the sand fraction (Garzanti & Resentini, 2016; Liu *et al.*, 2016). These indices
58 generally consider the mobile chemical elements (mainly alkaline and alkaline earth metals)
59 in relation to the least mobile elements (principally silica (Si-), aluminium (Al) and iron
60 (Fe-)). The indices are primarily conditioned by the minerals containing these elements and
61 the resistance of these minerals to alteration. Geochemical indices have been employed in
62 soils to estimate the degree of evolution (Schaetzl & Thompson, 2015), as, during
63 pedogenesis, unstable minerals are eliminated faster than those which are resistant. These
64 indices are also useful in studies on the provenance of materials (Garzanti & Resentini,
65 2016); nonetheless, there is a notable absence of soil studies with these objectiveobjectives,
66 particularly involving the sand fraction.

67 A soil chronosequence is a series of soils which differ in their profile development due
68 to their differences in age, while the other soil-forming factors remain constant ideallyif

69 possible. In the basin of the River Guadalquivir (the most important fluvial system in the
70 Southern Iberian Peninsula), a system of four fluvial terraces and a floodplain, constitute an
71 almost ideal soil chronosequence: Calero *et al.* (2008) found that Harden's PDI and some
72 important soil analytical properties of the fine earth fraction (<2 mm) and field
73 morphological characteristics of soil quantified by optimal scaling fit significant
74 chronofunction equations; furthermore, some SEM-IA fabric morphometric attributes also
75 fit chronofunctions (Calero *et al.*, 2009); the TEM-AEM and XRD studies of mica and
76 smectite in silt (2 – 50 µm) and clay (<2 µm) fractions (Calero *et al.*, 2013) permitted
77 determination, at nanoscale level, of statistically significant logarithmic chronofunctions of
78 the crystallochemical parameters; Martín-García *et al.* (2016) studied some mineralogical
79 (XRD), crystallochemical (DXRD), geochemical (ICP-ms and ICP-AES) and spectroscopic
80 colour (DRS) parameters of the clay fraction of these soils, most of which showed
81 logarithmic chronofunctions with asymptotes at 70-100 ka; and finally, Martín-García *et al.*
82 (2019) established chronofunctions with the contents of lanthanides. But it hasn't been
83 studied the role of fine sand in this chronosequence.

84 Consequently, the aim of the present research, centred on the Mediterranean soils from
85 the River Guadalquivir chronosequence, was to investigate the chemical and mineralogical
86 compositions and morphology at the SEM scale of the soil fine sand fraction.
87 Evolution/alteration indices of fine sand are calculated. An original aspect of this study is
88 the investigation of chronofunctions with the properties measured in the fine sand. All of
89 this is in order to elucidate the pedogenetic applications of fine sand. These themes have
90 scarcely been studied to date.

91

92 **Materials and Methods**

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Comentado [JAJD5]: Please write acronyms in full on first use.

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93 *Setting and soils*

94 The alluvium of the River Guadalquivir (Figure 1a) consists of gravels with some
95 stone-free sandy or silty layers derived from lithologically diverse rocks in the drainage
96 basin: igneous rocks (acids, alkaline, and intrusive rocks) and metamorphic rocks from the
97 Iberian Massif (Larrea *et al.*, 1992, 1994, 1995, 1996; Carracedo *et al.*, 1997; Pin *et al.*,
98 2002; Martínez *et al.*, 2008; Pascual *et al.*, 2008); sedimentary rocks from the External Betic
99 Zones of the Betic Cordilleras (Ortega-Huertas *et al.*, 1991; Martínez-Ruiz, 1994);
100 metasedimentary rocks from the Internal Betic Zones of the Betic Cordilleras (Torres-Ruiz
101 *et al.*, 2003); and quaternary sediments from the Guadalquivir Depression –Cenozoic Basin–
102 (Martínez *et al.*, 2008; Jiménez-Espinosa *et al.*, 2016).

103 The study area is located between the towns of Andújar and Villanueva de la Reina
104 (Figure 1b) in the middle reaches of the Guadalquivir River. Five representative soil profiles
105 (P1 to P5) were selected from a postincisive soil chronosequence on fluvial terraces of the
106 Guadalquivir River (Terrace 1 to Terrace 4 and Flood Plain) (Figure 1b; Table 1). The age
107 of the surfaces ranges from 600 ka to 0.3 ka. Preholocenic terraces are Terrace 1 (600 ka),
108 Terrace 2 (300 ka) and Terrace 3 (70 ka). Holocenic surfaces are Terrace 4 (7 ka) and the
109 Flood Plain (0.3 ka). The soil surface ages were determined by Santos-García (1988),
110 Santos-García *et al.* (1991) and Carral *et al.* (1998). Together with the soil profiles, fresh
111 point bar sediments (PM) of the Guadalquivir River course were also sampled. The climate
112 is Mediterranean (mean annual temperature of 18 °C and total annual precipitation of 650
113 mm). Currently, the soils are mainly used for the cultivation of olives and other crops (mainly
114 wheat and cotton).

115 *Samples and soil-fine sand analyses*

116 The bulk soil samples were air dried and sieved to <2 mm to obtain the fine earth.
117 Subsequently, and after the removal of organic matter with H₂O₂, the fine sand fraction (50
118 – 250 μm) was separated by wet sieving and collected on quartered aliquots for later
119 analysis (these samples are denoted as ‘whole fine sand’ in this study). For some analyses
120 (such as XRD study and ~~VP-SEM~~ Variable Pressure Scanning Electron Microscope (VP-
121 SEM) observations), the whole fine sand fraction was separated gravimetrically with
122 bromoform (ρ = 2.82 g/cm³) in order to concentrate the heavy fraction, denoted as ‘heavy
123 fine sand’.

124 The quantitative mineralogical composition of whole fine sand was determined by
125 XRD (powder method) with a Siemens D5000 X-ray diffractometer (city and country of
126 manufacture) under the conditions: Cu Kα radiation, 35 kV, 15 mA, a step size of 0.05 °2θ.
127 Mineral percentages were estimated by the intensity factor method (Martín-García *et al.*,
128 1997). For selected heavy fine sand samples, a qualitative study was carried out using XRD
129 (same apparatus and conditions).

130 Selected samples of whole fine sand were examined morphologically and analytically
131 using a ~~Variable Pressure Scanning Electron Microscope (VP-SEM)~~ Zeiss SUPRA40VP
132 equipment, (city and country of manufacture), acceleration voltage at between 0.2 and 30
133 kV, in conventional mode, with a backscattered electron detector (AsB images), equipped
134 with an EDX detector, and with a structural and chemical analyzer by Raman spectroscopy
135 inside the measurement chamber of the SEM (SCA-Raman), with two laser excitation lines
136 at 532 and 785 nm. The samples were mounted on aluminium sample holders on double-
137 sided adhesive carbon paper and metallized with carbon. The use of the ~~VPSEM~~ VP-SEM in
138 backscattered electron images mode permitted the detection of minerals with elements of
139 relatively high atomic mass, due to its greater luminosity. In the case of TiO₂ polymorphs,
140 SCA-Raman allowed differentiation of rutile crystals (space group: *P4₂/mnm*) from those of

141 anatase (space group: $I4_1/amd$). In the [VPSEM/VP-SEM](#) studies, at least 50 grains per sample
142 analyzed.

143 Chemical analyses of whole fine sand were carried out at the Natural History Museum
144 laboratories (London, [UK](#)). Following a lithium metaborate fusion and nitric acid digestion,
145 the following were determined: (a) Major oxides, by ICP-AES: SiO_2 , Al_2O_3 , CaO , Fe_2O_3 ,
146 K_2O , MgO , Na_2O , P_2O_5 , TiO_2 ; (b) trace elements by ICPms: Sc, V, Cr, Mn, Co, Ni, Cu, Zn,
147 Ga, Rb, Sr, Y, Zr, Nb, Mo, Sn, Cs, Ba, Hf, Ta, W, Tl, Pb, Th, U. The sum of the lanthanide
148 elements (ΣREE) was taken from Martín-García *et al.* (2019). Several weathering indices
149 were used to estimate the extent of chemical alteration:

150 SiO_2/CaO ,

151 Chemical Index of Weathering (Harnois, 1988): $CIW = 100 \times Al_2O_3 / (Al_2O_3 + CaO + Na_2O)$,

152
153 Weathering Index of Parker (Parker, 1970): $WIP =$
154 $100 \times (CaO_{MOLAR} / 0.7 + MgO_{MOLAR} / 0.9 + 2Na_2O_{MOLAR} / 0.35 + 2K_2O_{MOLAR} / 0.25)$,

155
156 Weathering Index (Vogel, 1975): $WI =$
157 $100 \times (CaO + MgO + Na_2O + K_2O) / (SiO_2 + Al_2O_3 + Fe_2O_3 + CaO + MgO + Na_2O + K_2O)$,

158
159 Base Depletion Index (Jien *et al.*, 2016): $BDI =$
160 $(CaO + MgO + Na_2O + K_2O) / (Al_2O_3 + Fe_2O_3 + TiO_2)$,

161
162 Weathering Ratio (Chittleborough, 1991): $WR = (CaO + MgO + Na_2O) / ZrO_2$,
163 and Sr/Zr (Muhs *et al.*, 2001).

164 Some of these weathering indices were calculated for the clay fraction of these soils
165 by using Martín-García *et al.* (2016)'s data.

166 Statistical analysis was carried out using the IBM SPSS v.22.0 software package.

167

168 **Results**

169 XRD mineralogy

170 The following minerals were identified in the whole fine sand (Table 2): the
171 phyllosilicates K-mica, Na-mica (paragonite), chlorite, kaolinite, and some 2:1 phyllosilicate
172 phases with spacings between 1.23-1.53 nm and 1.0-1.22 nm (identified by Calero *et al.*,
173 2013 as smectite, chlorite and ~~interstratified~~interstratified vermiculite-chlorite, vermiculite-
174 illite and smectite-illite), tectosilicates quartz and feldspars (K-feldspar and plagioclases),
175 iron (hydr)oxides (goethite and haematite) and carbonates (calcite and dolomite).

176 The XRD mineralogy of the heavy fine sand fraction of selected samples (Table 2,
177 Figure 2; supported by Figures 3 and 4) revealed a range of mineral classes (and species):
178 oxides (rutile, anatase, ilmenite, goethite, and haematite), silicates (zircon, staurolite, quartz,
179 K-mica, andalusite, garnet, chlorite, and titanite) and carbonates (calcite and dolomite). This
180 composition (Table 2) is different to that of the whole fine sand, although with a few
181 coinciding mineral species: quartz, K-mica, chlorite, goethite, haematite, calcite and
182 dolomite. The presence of light minerals in ~~our~~the heavy fine sand (Table 2, Figure 2), with
183 densities close to or lower than that of bromoform, 2.82 g cm⁻³ (quartz, calcite, K-mica,
184 chlorite), can be explained by: (1) the polymineral nature of many of the grains (Figure 3b,
185 c, d, e, h, j, l), both heavy and light; (2) the presence of coverings of heavier minerals on the
186 grains (e.g. iron oxides; Figure 3c); and (3) possible small differences in mineral composition
187 (which change it to 'heavy') ~~;) that were~~ undetectable with the techniques used in this study.

188

190 The VPSEMVP-SEM-EDX images (Figure 3) have proved highly informative due to
191 the following: (1) The mineralogy is confirmed for some of the major phases identified with
192 XRD (Table 2): quartz, calcite, dolomite, K-feldspar and chlorite. (2) The mineral species
193 of some of the phases identified with XRD are established: K-mica is both biotite (Figure
194 3f, i) and muscovite-illite (Figure 3b, c, h, i); plagioclase is predominantly albite-type (Na-
195 plagioclase) (Figure 3e, l). (3) The mineralogical inventory is completed with minor species
196 (mainly heavy minerals), which are difficult to detect with XRD due to their low contents.
197 The presence of heavy atoms in the mineral composition is frequently shown in the
198 backscattered electron images (BS in Figure 3) by bright tones close to white. The following
199 minority species were detected: garnet (nesosilicate, variety andradite - $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$ -
200 (Figure 3a), monazite -(Ce,La,Nd,Pr)PO₄- (Figure 3b, h), Titaniumtitanium oxide -rutile or
201 anatase, TiO₂- (Figure 3b, e, j), apatite -Ca₅(PO₄)₃(OH)- (Figure 3c, d), zircon -ZrSiO₄-
202 (Figure 3d, e), ilmenite -FeTiO₃- (Figure 3e, l), barite -BaSO₄- (Figure 3g), staurolite -
203 (Fe,Mg)₂Al₉(Si,Al)₄O₂₀(O,OH)₄- (Figure 3j) and titanite -CaTiSiO₅- (Figure 3k). Iron oxides
204 were also found in many of the grains (Figure 3c, d). Although VPSEMVP-SEM-EDX does
205 not permit mineral species identification, these were either goethite or haematite. The same
206 occurred with the TiO₂ polymorphs, rutile and anatase. However, it was possible to identify
207 these species of Fe and Ti using XRD (Figure 2). 4) Consideration of the mineralogical
208 results derived from Figure 3 together with the XRD results (Table 2, Figure 2) confirms
209 that the fine sand (both whole fine sand and heavy fine sand) is a complex of at least 25
210 different mineral species (20 in horizon 4C2 of P4 alone).

211 Another finding to confirm the usefulness of VPSEMVP-SEM-EDX is the proof that
212 many of the fine sand grains are polymineral (Figures 3b, c, d, e, h, j, l and 4 a) although
213 some are monomineral (Figures 3a, f, g, i, k and 4 e).

214

215 VPSEM-EDX-Raman study of TiO₂ polymorphs in fine sand

216

217 Rutile and anatase (polymorphs of titanium dioxide) were found together in ~~on the~~
218 soils using XRD (Table 2, Figure 2). Using ~~VPSEM~~VP-SEM-EDX, the presence of TiO₂
219 was described (Figure 3a, e, j) without being able to distinguish the grains of the two species,
220 as this is not possible with EDX. Consequently, Raman spectroscopy was used (Figure 4d,
221 f). Rutile showed ~~maxima~~maxima at 143, 236, 447, 612 and 826 cm⁻¹ and anatase at 144,
222 197, 399, 516, 639 cm⁻¹ (Arsov *et al.*, 1991). Rutile, more abundant than anatase, was found
223 in polymineral or even monomineral grains, constituted internally by prismatic crystals.
224 Rutile was also observed (Figure 4a, b, c, d) covering the faces of quartz grains as
225 micrometric acicular and prismatic crystals, which appear to result from pedogenic
226 recrystallization *in situ* (authigenic) of a colloid/gel of ~~titanium oxide~~TiO₂. Two further
227 observations are of interest: the tendency of the acicular and prismatic crystals to cross
228 (Figure 4d), following the typical rutile-law twin (twinning on {011}), and that the crystal
229 support is quartz (Figure 4b) due to the well-known quartz-rutile association (Klein &
230 Dutrow, 2007).

231

232 Major and minor chemical elements

233 The content of SiO₂ varied between 51.68 and 90.36% (Table 3) and was more
234 abundant in pre-Holocene soils (P1, P2, P3) than in Holocene soils (P4, P5) and ~~PM-point~~
235 bar sediments. The content of CaO ranged from 0.06 and 23.60% decreasing dramatically in
236 the pre-Holocene soils.

237 Minor elements (Table 4) exhibited variability between the different soils and terraces.

238 Cr, Mn, Ni, Rb, Sr, Zr, Ba and ΣREE were the only elements to exceed 100 mg kg⁻¹ in at

239 least one sample (Cr and Ni only in Btg2 of P2, where their contents easily exceeded those
240 of the other horizons). The concentrations (means per profile) of some minor elements such
241 as Mn, Sr, Cs, Hf and W showed dependence with the age groups of the soils (pre-Holocene
242 *versus* Holocene): Cs, Hf and W more abundant in pre-Holocene, Mn and Sr in Holocene.
243 The maximum value of Zr (mean per profile) was that of P1.

244

245 **Discussion**

246 *Mineralogy of fine sand*

247 Quartz was the principal constituent in all horizons of the oldest soils—, *i.e.* pre-
248 Holocene— P1, P2 and P3 (between 47 and 78%) (Table 2) so *it* can be assumed to be a
249 resistant phase which is concentrated by inheritance during pedogenesis. In the most recent
250 soils—, *i.e.* Holocene— P4 and P5, the carbonates (calcite + dolomite) were the most abundant
251 (>38%) in most of the horizons. However, in 2Bwk2 of P4 they accounted for only 1%, due
252 to lithological discontinuity. Consequently, quartz and carbonates (calcite+dolomite)
253 contents depend on soil age, and, as major components of these fine sands, their percentages
254 are inversely related ($R^2 = 0.866$; $n = 24$).

255 The pronounced changes in XRD mineralogy (Table 2) confirm the presence of some
256 of the lithological discontinuities already established morphologically and/or
257 granulometrically. Of particular interest are those in horizons 2Bwk2 of P4, 2BCtg of P1
258 (with an increase in quartz and a decrease in K-feldspars) and 4C3 of P5 (with an increase
259 in total phyllosilicates). In none of these examples can the mineralogical changes be
260 explained by the action of pedogenic processes within the soil.

261 The dominant formation process of minerals from the heavy fine sand (Table 2) must
262 be inheritance, since the majority are detrital species and thus originate from the geological
263 materials of the zone. However, there are also other genetic possibilities (see section
264 ‘~~VPSEMVP-SEM-EDX-Raman study of TiO₂ polymorphs in fine sand~~’) since genesis by
265 inheritance of the heavy minerals of the fine sand of the soils, and their subsequent use in
266 chronosequences to study the provenance of materials and their degree of alteration, is not
267 an indisputable paradigm: ~~For example, Tejan-Kella *et al.* (1991a), in soils from a podzol~~
268 ~~chronosequence at Cooloola (Australia),~~ found rutile and zircon grains with different
269 degrees of alteration in the same profile, implying a complex environmental history
270 (different provenances); ~~in soils from a podzol chronosequence at Cooloola (Australia).~~
271 ~~Tejan-Kella *et al.* (1991b), only found a weak tendency towards alteration over time in the~~
272 ~~heavy minerals~~ in Psammets and Orthods from South Australia, developed in sandy
273 sediments of various ages, ~~only found a weak tendency towards alteration over time in the~~
274 ~~heavy minerals;~~ Farragallah & Essa (2011), ~~in soils from different terraces of the River Nile~~
275 ~~near Assiut (Egypt),~~ found that the contents of relatively highly resistant minerals (sphene,
276 rutile, garnet and zircon) followed an irregular distribution in both depth and time sequence;
277 ~~nor did in soils from different terraces of the River Nile near Assiut (Egypt).~~ Sulieman *et*
278 *al.* (2015) did not detect an increase in ultrastable heavy minerals (zircon, tourmaline, rutile)
279 with increasing age of Nile terraces. In the present study, rutile or zircon were found in all
280 profiles (Table 2).

281 The mineralogy of the heavy fine sand (Table 2, Figure 2) also reveals the
282 decarbonatization undergone by the pre-Holocene profiles, since, unlike the Holocene soils
283 and fresh point bar sediments (~~PM~~) of the Guadalquivir river course, they lack carbonate
284 materials. In addition, the notable presence of anatase and rutile in the pre-Holocene soils is
285 shown by the more intense reflections in the XRD diagrams (Figure 2). The high

286 crystallinity, in some cases, of the rutile and anatase reflections could indicate that they are
287 authigenic soil phases (see section '~~VPSEM~~~~VP-SEM~~-EDX-Raman study of TiO₂
288 polymorphs in fine sand').

289 ~~VPSEM~~The ~~VP-SEM~~-EDX analysis of the whole fine sand permitted observation of
290 the ~~subrounded~~sub-rounded shape of some grains, with somewhat polished surfaces,
291 mechanical marking and a degree of sedimentological maturity (Figure 3c, d, e, f, i, j), in
292 accordance with the fluvial origin of the parent material. Superficial features of chemical
293 alteration were also observed in grains of various mineral species (Figure 3b, h, i, j, k).
294 Quartz showed alteration features, even in the fine sands of the less developed soils, such as
295 P5 (Figure 3b), in agreement with our previous results (Martín-García *et al.*, 2004, 2015),
296 which reported alteration features in quartz under Mediterranean climate, even in scarcely
297 evolved soils. Alteration was also observed in the grains of K-mica (Figure 3h), dolomite
298 (Figure 3i), titanium oxides (Figure 3j) or titanite (Figure 3k), from both pre-Holocene (P1,
299 P3) and Holocene soils (P4, P5). These observations give rise to the hypothesis that the
300 alteration features are not necessarily produced in the same soil as that where the grain is
301 currently found, and may be (particularly in less evolved, that is, Holocene soils) inherited
302 from fluvial sediments or from soils from before those giving rise to the sediment. This
303 would, therefore, involve the discussion of aspects such as polycyclism, superimposed
304 features and diverse origins, previously described in zircon by Tejan-Kella *et al.* (1991a),
305 who stated that “the juxtaposition of euhedral, subeuhedral and unetched zircon and rutile
306 grains with highly rounded and etched forms in the same profile indicates diverse
307 provenance”. This genetic complexity would thus imply that the ~~VPSEM~~~~VP-SEM~~-EDX
308 observations of any grain do not provide sufficiently robust information on the effects of the
309 age of the terraces, where the soils are found, on the fine sand grains. This has resulted in

310 further investigation into the problem of the alteration of our fine sands using complimentary
311 geochemical methods (ICPMS).

312

313 *TiO₂ polymorphs*

314 The ~~VPSEMVP-SEM~~-EDX-Raman study of TiO₂ polymorphs in fine sand (Figure 4)
315 imply that pedogenic neoformation of rutile has taken place in the study soils. However, the
316 possibility that some grains of this mineral species, present in our fine sands, may be
317 inherited cannot be ruled out. In no case did the rutile grains show any sign of alteration.
318 Anatase was present in fine sand-sized grains, with some signs of weathering (Figure 4e, f),
319 suggesting possible inheritance from the parent material.

320 The coexistence of the two polymorphs of TiO₂ rutile (neoformed/inherited) and
321 anatase (inherited), shown by ~~VPSEMVP-SEM~~-EDX-Raman, is an original finding,
322 particularly in Mediterranean fluvial terrace soils. Fitzpatrick & Chittleborough (2002)
323 reported that evidence from both laboratory synthesis and field studies indicated that rutile
324 should not necessarily be attributed to high-temperature formation and could also crystallize
325 from an intermediate anatase phase. Rutile neoformation in soils has been assumed by Sun
326 *et al.* (2017), while Cornu *et al.* (1999) showed, in tropical soils, the mobility of Ti and the
327 neoformation of anatase, but never of rutile.

328

329 *Chemical composition*

330 The SiO₂ contents (Table 3) was positively correlated with that of quartz (Table 2) (R^2
331 = 0.851; n = 24). The CaO contents decreased dramatically in the pre-Holocene soils due to
332 ~~decarbonation~~decarbonation and was positively correlated with calcite+dolomite
333 (carbonates) ($R^2 = 0.887$; n = 24), and calcite ($R^2 = 0.854$; n = 24); MgO was correlated with

334 dolomite ($R^2 = 0.775$; $n = 24$), as well as CaO and MgO ($R^2 = 0.762$; $n = 24$). A horizon of
335 interest is 2Bwk2 of P4, with the 'k' showing carbonate accumulation, which has very low
336 percentages of CaO and MgO compared to the other horizons of the profile; the carbonates
337 are found in the silt and clay fraction, as shown by the data of Calero (2005). All assert for
338 CaO content ~~confirm~~ that, as in the case of SiO₂, the CaO amount of the fine sands in our
339 soils contains valuable pedogenic information.

340 Major elements confirm the lithological discontinuity in 2Bwk2 (P4), shown by the
341 XRD mineralogy (Table 2), with visibly higher values of SiO₂, Al₂O₃, Na₂O and K₂O, and
342 lower values of CaO, Fe₂O₃ and MgO. In contrast, the lithological discontinuities of P5 were
343 not accompanied by any notable change in chemical element composition.

344 The concentrations (means per profile) of some minor chemical elements such as Mn,
345 Sr, Cs, Hf and W (Table 4) showed dependence with the age groups of the soils (pre-
346 Holocene *versus* Holocene): Cs, Hf and W more abundant in pre-Holocene, Mn and Sr in
347 Holocene. The maximum value of Zr (mean per profile) was that of P1.

348 The Ba and Zr content can be related to the presence of barite -BaSO₄- and zircon -
349 ZrSiO₄-, respectively (Figure 3d, e, g); as can ΣREE to that of monazite -(Ce,La,Nd,Pr)PO₄-
350 (Figure 3h). The Mn content is related to the presence of ilmenite and andradite (garnet),
351 since, although Mn does not belong to the ideal mineral formulae, it was detected in the
352 ~~VPSEM/VP-SEM~~-EDX spectra (Figure 3a, e, l). Furthermore, the positive correlations
353 between Mn and Fe₂O₃ ($R^2 = 0.777$; $n = 24$) and TiO₂ ($R^2 = 0.726$; $n = 24$) suggest that,
354 together with ilmenite and andradite, Mn may be linked to other Fe- and Ti-bearing minerals
355 detected such as biotite, goethite or haematite.

356 The Rb content positively correlates with total feldspars (K-feldspar + plagioclases;
357 Table 2) ($R^2 = 0.717$; $n = 24$) and consequently shows high relative values (>105 mg kg⁻¹)

358 in the P3 horizons, with maximum values of these minerals (23–38% K-feldspar +
359 plagioclase; Table 2). [The Rb content](#) also positively correlates with K₂O ($R^2 = 0.908$; $n =$
360 24). Hossain *et al.* (2014) showed that Rb isomorphically substitutes for K in feldspars,
361 which would explain our findings. However, Donaire (1995) explained that the significant
362 positive correlation between Rb and K₂O in granitic rocks of the Los Pedroches Batholith
363 (zone of present study) is due to the substitution of Rb by K in the K-mica, as also reported
364 by Feng & Kerrich (1990) and Varga *et al.* (2005). In our fine sands, Rb vs. K-mica showed
365 a positive correlation, albeit low ($R^2 = 0.167$; $n = 24$) and much lower than that of Rb vs.
366 total feldspars ($R^2 = 0.717$; $n = 24$), possibly due to the feldspars being more abundant than
367 K-mica in most of our samples (Table 2).

368 [The Sr content](#) correlates with CaO ($R^2 = 0.863$; $n = 24$) and calcite ($R^2 = 0.815$; $n =$
369 24), which must be due to the well-known isomorphism between Sr and Ca. Cubillas *et al.*
370 (2015) suggested that Sr can be incorporated into the structure of natural and laboratory
371 calcites (and may be a good indicator of the relative supersaturations of Sr *versus* Ca at which
372 the crystals grew).

373 The statistical relationship ($R^2 > 0.811$; $n = 24$) between pairs of elements within groups
374 such as Mn-Ti-Fe, Cr-Ni-Mo, Sr-Ca, Rb-K and Hf-Th-U-REE, must be due to isomorphism
375 (ion substitution in the crystal lattices). This process is regulated by Goldschmidt's rules
376 (Misra, 2012), which postulates ionic substitutions when Δr is small (<15% of the radius of
377 the smallest). The case of the group Mn³⁺, Fe³⁺, Ti⁴⁺ can be considered paradigmatic, since
378 their radii (0.064, 0.064 and 0.068 nm, respectively) have Δr between 0 and 0.004 (never
379 exceeding 7% of the smallest).

380 The chemical element composition (mean values per profile) of the whole fine sand
381 (Tables 3 and 4) differed from that of the clay (Martín-García *et al.*, 2019) in that the former

382 contained lower quantities of major elements Al, Ca, Fe and K, and also lower quantities of
383 most of the minor elements. This may be related, first, to the lower contents of phyllosilicates
384 and, especially, of the (hydr)oxides goethite and haematite, in the fine sand, and, second, to
385 the role of the clay fraction as a scavenger of heavy elements (Martín-García *et al.*, 2016).
386 However, the higher content of Zr in the fine sand (except in [PMpoint bar sediments](#)),
387 possibly due to the presence of zircon mineral (Table 2; Figures 2, 3d, e), should be noted.
388 This mineral species, highly resistant to weathering, would tend to become concentrated
389 through inheritance in the fine sand grains rather than the clay.

390

391 *Geochemical indices*

392 [The SiO₂/CaO ratio](#) of the whole fine sand (Table 5) showed mean values greater than
393 200 (up to 795) in the pre-Holocene soils (P1, P2, P3) and lower than 37 in the Holocene
394 soils (P4, P5, [PMpoint bar sediments](#)), reflecting the effect of soil age on this geochemical
395 index. The presence of these two populations of SiO₂/CaO can be attributed to the two
396 pedogenic processes, which combine and intensify with age: the leaching of carbonates,
397 reducing CaO content, and the relative accumulation of quartz (main source of SiO₂), a
398 mineral with relatively high resistance to alteration. This explains the correlations
399 ‘SiO₂/CaO’ *versus* ‘calcite’ ($R^2 = 0.775$, logarithmic) and ‘SiO₂/CaO’ *versus* ‘quartz’ ($R^2 =$
400 0.777 , logarithmic).

401 The CIW and WIP values also depend on age, ranging from 16.20 ([PMpoint bar](#)
402 [sediments](#)) to 92.58 (P1) for the former and 78.02 (P5) to 17.22 (P1) in the latter. These
403 results are similar to those of Price & Velbel (2003), where CIW grew in parallel with
404 alteration, fresh material being considered as that with CIW ≤ 50 ([PMpoint bar sediments](#)
405 < 20) and with maximum alteration at a value of 100 (P1 ≈ 93). For WIP, Price & Velbel

406 (2003) considered fresh material to have a value >100 with maximum alteration at 0. In the
407 present study, although none of the profiles reached these extreme values, they were within
408 the range 100–0. Ajmone *et al.* (1988) studied the WIP in fine sand of a soil chronosequence
409 from Northwest Italy, where the youngest soil (aged between 10 – 50 ka) showed WIP of
410 41.7, and the oldest (500 – 750 ka), between 16.5 and 18.4, similar WIP and age values to
411 the samples of the present study. Garzanti & Resentini (2016), studying fluvial point bar
412 sands of Taiwanese rivers, reported values of CIW between 48 and 95 and WIP between 18
413 and 65, close to those of our fine sands.

414 The WI and BDI of our whole fine sand (Table 5) persistently showed values related
415 to age. The WI decreased from P1 (2.56) to P5-PMpoint bar sediments (30.49-25.07,
416 respectively); the BDI increased from P1 (0.28) to PMpoint bar sediments (4.66). The BDI
417 was determined by Jien *et al.* (2016) in a soil chronosequence from Taiwan (Arenosol,
418 Cambisol, Lixisol, and Ferralsol), showing values in fine earth (<2 mm) from 0.25 (soils of
419 20 ka) to 0.05 (soils of 80 ka). This tendency of BDI to decrease with age coincided with our
420 results, albeit with very different ranges of values. For example, our P3, with an age of 70
421 ka (Table 1), was comparable to the oldest Taiwanese soils studied by Jien *et al.* (2016), and
422 showed a BDI of 0.59, while that of the equivalent Taiwanese soils was around 0.05. We
423 believe that these divergences are due, in addition to our studying fine sand, to the lower
424 intensity of pedogenic processes in the Mediterranean environment of our fluvial terraces
425 (mean annual temperature 18°C, total annual precipitation 650 mm; soil types Fluvisol,
426 Calcisol and Luvisol) compared to that in the ferralitic soils with tropical oceanic climate of
427 Taiwan (mean annual temperature 23.5 °C, total annual precipitation 2500 mm, soil types
428 Arenosol, Cambisol, Lixisol, Acrisol and Ferralsol).

429 The WR values (Table 5), from 28.9 (P1) to 2447.45 (PMpoint bar sediments), were
430 also related to soil age. This wide range is due to both the relative abundance of Ca in the

431 Holocene soils and [PMpoint bar sediments](#) and to the relative concentration of Zr in the pre-
432 Holocene soils (particularly in P1) (Tables 3, 4). Consequently, the content of carbonates
433 (calcite+dolomite), the main source of CaO, is positively correlated with WR ($R^2 = 0.761$; n
434 = 24). Our values of WR are much higher than those of Chittleborough (1991), which were
435 between 3 and 22, as they were estimated in fine sand of soils lacking calcium carbonates.
436 In the present study, Sr/Zr showed similar tendencies to the other indices, and, since Sr^{2+} is
437 diadochic with Ca^{2+} , and Zr^{4+} increases in pre-Holocene soils, Sr/Zr decreased with age,
438 from [PMpoint bar sediments](#) (6.02) to P1 (0.12) (Table 4).

439 Values of the geochemical indices for whole fine sand were generally similar to those
440 of clay (Table 5). However, there were some cases with pronounced differences, such as
441 WR, which showed lower values in the whole fine sand than in the corresponding clay. This
442 may be due to the higher relative concentration of Zr in the whole fine sand. The trends in
443 the values of the indices with soil age were similar in clay and whole fine sand.

444

445 *Provenance of the soil materials*

446 *Mineralogical evidences*

447 The most abundant mineral species in our fine sands (Table 2): phyllosilicates
448 (muscovite/illite, biotite, paragonite, chlorite, [and](#) interstratified minerals), quartz, feldspars
449 (K-feldspar and plagioclases), iron oxides (goethite and haematite) and carbonates (calcite,
450 [and](#) dolomite) have been described in the rocks of the source area (Ortega-Huertas *et al.*,
451 1991; Larrea *et al.*, 1992, 1994, 1995, 1996; Martínez-Ruiz, 1994; Carracedo *et al.*, 1997;
452 Pin *et al.*, 2002; Torres-Ruiz *et al.*, 2003; Martínez *et al.*, 2008; Pascual *et al.*, 2008; Jiménez-
453 Espinosa *et al.*, 2016). This suggests a potential provenance from the rocks/sediments
454 through the process known as inheritance (Martín-García *et al.*, 1998).

455 Since the mineral contents change over time due to soil evolution, the idea of
456 provenance of soil materials (by comparison between soil materials and rocks of the source
457 area) is only applicable to young soils and ~~PM~~.

458

459 Geochemical evidences

460 The spider diagrams of the chondrite-normalized chemical composition of selected
461 elements in the whole fine sand (Figure 5), again show (sections 'Chemical composition'
462 and Tables 3 and 4) that, due to the effect of time, composition differs between soils.
463 Furthermore, its relationship with all the geological materials of the zone, potential providers
464 of materials, is clear. However, the closest relationships (in all elements, from Fe to Ba) are
465 with the sedimentary rocks (Ortega-Huertas *et al.*, 1991; Martínez-Ruiz, 1994) (Figure 5b).
466 Figure 5 also shows the expected geochemical relationship between the whole fine sand and
467 the clay (Martín-García *et al.*, 2016), although clay contained more Fe and V, and the former
468 more Zr (except in ~~PM~~-point bar sediments).

469 The geochemical indices were used as fingerprints of provenance (Garzanti &
470 Resentini, 2016) by comparing the values of the samples with those of the geological
471 materials (Figure 6). According to CIW (Figure 6a), the fine sands and clays of the pre-
472 Holocene soils (P1, P2, P3) would be related (similar range of values) to the igneous and
473 metasedimentary rocks, while the fine sands and clays of the Holocene soils (P4, P5) and
474 ~~PM~~point bar sediments would be related to the sedimentary rocks. According to WIP (Figure
475 6a), the Holocene soils are in the middle of the range of all the rocks from the source area
476 and the pre-Holocene soils would separate from them. The values of BDI (Figure 6b)
477 reiterate the behaviour of CIW. This once again demonstrates that the values of these indices
478 for our samples depend on age and that the indices are not decisive for determining
479 provenance.

480

481 *Soil fine-sand chronofunctions*

482 In order to better quantify the relationships of the different properties of the whole fine
483 sand with age, chronofunctions were calculated (Table 6). Most were logarithmic ($y =$
484 $a \cdot \ln x + b$) and quadratic ($y = ax^2 + bx + c$) and, to a lesser extent, linear ($y = ax + b$); this can be
485 interpreted as these parameters will reach their steady-state (Schaeletz *et al.*, 1994) and prove
486 the existence of an authentic soil chronosequence, previously demonstrated by other
487 compositional and morphological properties of the soils of the chronosequence (Calero *et*
488 *al.*, 2008, 2009, 2013; Martín-García *et al.*, 2016, 2019). No previous studies of
489 chronofunctions established using the soil fine sand have been found in the bibliography.

490 The equations obtained also provided other information. The curves which decreased
491 with the age of calcite, CaO and Sr (CaO and Sr associated with the carbonates) quantify the
492 process, detected previously, of loss of carbonates through dissolution/alteration over time.
493 This is 0.057% every 1000 years for calcite. The opposite (curve increases with age) occurs
494 in quartz, which accumulates through inheritance in the soil fine sand over time, at a rate of
495 0.065% every 1000 years, similar to the rate of calcite loss.

496 The Zr chronofunction also increases, in this case due to the Zr-bearing mineral zircon,
497 which remains in the fine sand fraction (Figure 3d, e). The same also occurs in Hf, U and
498 REE, which, as elements with low mobility, may be associated with the mineral monazite
499 (Figure 3b, h). The positive chronofunction of the 1.23-1.53 nm phases, indicates the
500 transformation of 2:1 phases, increasing with age, and which was demonstrated using
501 chronofunctions of the nanoparameters of the clay fraction of our soils by Calero *et al.*
502 (2013).

503 The geochemical alteration indices SiO_2/CaO , CIW, WIP, WI, BDI, WR and Sr/Zr

504 mainly exhibited logarithmic fitting in their chronofunction (Table 6), suggesting not only
505 dependence on age but also that the alteration of the fine sands will attain steady-state. The
506 chronofunction $BDI = -0.348 \ln(\text{age in ka}) + 2.659$ (Table 6) implies that, for an age of 600
507 ka (maximum investigated; Table 1) the BDI of the fine sand is 0.43. When this value is
508 interpolated in the chronofunction for fine earth of Taiwanese soils reported by Jien *et al.*
509 (2016): $BDI = 1/(1 + 0.21 \times \text{age in ka})$, the age required to attain this BDI is 6.2 ka. The great
510 difference between 600 ka and 6.2 ka (~100 lower) is due to the Mediterranean climate of
511 our chronosequence being much less pedogenically active than the tropical climate of
512 Taiwan (section ‘Geochemical indices’). Thus, environmental conditions (soil-forming
513 factors) and soil classification must be considered when interpreting alteration indices in soil
514 chronosequences.

515 The chronofunction equations obtained for the alteration indices (Table 6) also permit
516 further discussion regarding the [CPcritical point](#) (Figure 6) and the hypothesis that it
517 represents “time zero” for soil formation or the start of alteration. When the equations are
518 extrapolated to zero (or close to zero) for 0.001 ka (age attributed to [PMpoint bar sediments](#);
519 Table 1) WIP has a value (logarithmic) of 84.56, not only close to 71.34, the WIP value
520 calculated for [PMpoint bar sediments](#) with the analytical data (Table 5) but also very close
521 to those of CP_{WIP} , established in a completely different manner in Figures 6a and 6b: 80.76
522 and 79.39. This confirms an initial WIP of 70 – 80 in our soils and that [CPcritical point](#)
523 represents “time zero”. Furthermore, the BDI values were: $\text{extrapolated}_{(0.001 \text{ ka})} = 5.06$,
524 calculated in [PMpoint bar sediments](#) = 4.66, and $CP_{BDI} = 4.11$, which, due to their relative
525 similarity, confirm an initial BDI value (without alteration) of between 4 and 5, and, once
526 again, that CP represents “time zero”.

527

528 **Concluding remarks**

529 Fine sands are suggested as a granulometric fraction of great pedogenic interest with
530 the advantage of their easiness of extraction and analysis.

531

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541

542 **Data Availability Statement**

543 The data are available on request from the authors.

544

545 **Author contributions:** J.M. Martín-García, J. Calero and R. Delgado have sampled the soils
546 and have separated the fine sand fraction and heavy fine sand fraction. J.M. Martín-García,
547 J. Calero, M. Sánchez-Marañón and R. Delgado have done the XRD study. The ICPms has
548 been done at the Natural History Museum of London, and the results have been interpreted
549 by J.M. Martín-García, A. Molinero-García and R. Delgado. The VPSEM and Raman study
550 has been done by J.M. Martín-García, A. Molinero-García, M.V. Fernández-González and
551 R. Delgado. All authors wrote the manuscript.

552

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734 **Figure Captions**

735 Figure 1 Study area: a) location and geology of the Guadalquivir catchment; b) position of
736 fluvial terrace levels and soil sampling.

737 Figure 2 XRD profiles for selected heavy fine sand ($\rho > 2.82 \text{ g cm}^{-3}$) samples in the angular
738 sector $10 - 43^\circ 2\theta$. Abbreviations: K-m: K-mica; Ch: chlorite; Qz: quartz; Gt: goethite;
739 Hm: haematite; Ca: calcite; Do: dolomite; Ti: titanite; Zr: zircon; Ru: rutile; Ilm:
740 ilmenite; St: staurolite; Ana: anatase; And: Andalusite.

741 Figure 3 Conventional and backscattered (BS) VPSEM images and EDX microanalysis of
742 fine sand-sized mineral grains. a) profile P4, horizon 4C2: monomineral grain of garnet
743 (nesosilicate, variety andradite). Mechanical damage through impacts to edges and
744 corners. Sedimentologically immature and little chemical alteration. Surface
745 reminiscent of 001 crystal (cube) faces viewed from ternary axis. b) profile P5, horizon
746 6C5: polymineral grain of monazite (1), titanium oxide (Tiox) (2), quartz (3) and K-
747 mica (muscovite or illite) (4). Percussion marks, abrasion-smoothing marks and traces
748 of chemical corrosion (notable alteration of quartz) can be observed. Relatively mature
749 and altered grain. c) profile P5, horizon 6C5: monomineral grain of K-mica (muscovite
750 or illite) (1), although with iron oxides adhering to surface (2) (goethite and/or
751 haematite) and apatite (3). Flat, subrounded perimeter due to fluvial activity. Little
752 apparent alteration. d) profile P1, horizon 2BCtg. Polymineral grain of quartz (1) with
753 fissure filled with iron oxides (goethite and/or haematite) and apatite (2). Aggregate of
754 subrounded, laminated quartz crystallites. Monomineral grain of zircon (3) of
755 exceptional size ($> 100 \mu\text{m}$), subrounded and polished by fluvial activity. Detail shows
756 curved percussion marks. e) profile P5, horizon 6C5: polymineral grain consisting of
757 plagioclase (1) (probably albite), ilmenite (2), titanium oxide (Tiox) (3) and zircon (4).
758 Subrounded and polished in zones. Apparently little altered chemically. Some

759 percussion marks also chemically etched. f) profile P3, horizon Bt2: monomineral
760 grain of K-mica (biotite). Flat. Subrounded perimeter, some surface polishing from
761 fluvial activity. Some percussion marks. Incipient chemical alteration. g) profile P1,
762 horizon 2BCtg: monomineral grain of barite. Laminar internal structure: formed by a
763 mosaic of stacks of small laminae (thickness 2 – 5 µm), with different angular
764 orientations. Certain tendency towards subrounding. It shows a large, complex
765 dissolution trace in lower part. h) profile P2, horizon Btg2: polymineral grain of K-
766 mica (muscovite or illite) (1) and monazite (2). Demonstrates presence of monazite.
767 Mica has appearance of being altered, with laminae undergoing exfoliation. Grain is
768 porous, relatively altered. i) profile P4, horizon 4C2; grain of dolomite. Subrounded
769 and polished. Sedimentologically mature. Upper part shows abundant dissolution
770 traces. j) profile P4, horizon 4C2: polymineral grain composed of titanium oxide
771 (TiO₂) (1), staurolite (prism face {110} and pinacoid face {010}) (2) and quartz (3).
772 Subrounded and polished zones with dissolution traces. k) profile P1, horizon 2BCtg:
773 monomineral grain of titanite. Exterior appears relatively immature,
774 sedimentologically, with a pseudopolyhedral silhouette. Interior relatively altered,
775 with abundant corrosion traces (grooves). l) profile P5, horizon 6C5: tabular
776 polymineral grain, consisting mainly of ilmenite (1) with a plagioclase inclusion
777 (albite) (2). Somewhat subrounded and polished, some mechanical effects and
778 corrosion gulfs.

Comentado [AJD7]: Summarise and move descriptions to the Results section.

779 Figure 4 VPSEM/VP-SEM images with EDX and Raman spectra of the whole fine sand of
780 horizon 2BCtg (P1). a, c and e are in conventional mode; b, d and f, in backscattered
781 mode. a) and b): mineral grain of quartz (SiO₂) with “coating” of rutile (TiO₂) on one
782 of its faces, visible in b as a light grey colour. c) and d): detail of a) and b) of rutile
783 coating. c) shows TiO₂ composition, by EDX spectrum. In d) the Raman spectrum

784 confirms the presence of rutile and also shows presence of rutile in a fabric, often
785 interwoven, of acicular crystals (nd) of $3 \times 0.5 \mu\text{m}$ (approx.) with some larger prismatic
786 crystals (pr) of $10 \times 2 \mu\text{m}$. e) and f) grain of anatase. In e), the EDX spectrum shows
787 composition of TiO_2 , while, in f), the Raman spectrum confirms the anatase and that
788 the grain is weathered (w) physically and chemically.

789 Figure 5 Spider diagrams of selected elements, normalized to the composition of chondritic
790 meteorite of McDonough & Sun (1995) of whole fine sand (lines represent mean
791 profiles) compared with (shaded area): (a) acid igneous and magmatic-dike rocks from
792 Iberian Massiff, (b) sedimentary rocks from External and Mean Baetics Zones, (c)
793 alkaline igneous rocks from Iberian Massiff, (d) metasedimentary rocks from Internal
794 Baetics Zone and (e) soil clay fraction ($<2 \mu\text{m}$) from the studied soils (Martín-García
795 *et al.*, 2016).

796 Figure 6 Relationships between geochemical indices CIW vs WIP (a) and WPI vs BDI (b)
797 for soil whole fine sand and soil clay fractions (mean profile values) (Table 5). They
798 include the values for rocks from the Guadalquivir catchment (igneous, sedimentary
799 and metasedimentary). The numbers in the circles correspond to soil profiles, and P to
800 point bar sediment (~~PM~~[point bar sediments](#)). The lines (and adjacent equations)
801 correspond to the straight lines of correlation for the population of samples of soil fine
802 sand (continuous) and soil clay (dots and dashes) fractions. CP indicates the values of
803 the indices at critical intersection points.