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1 Coupled micromorphological and stable isotope analysis of Quaternary 2 calcrete development

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11 12 ABSTRACT

13
14 Pedogenic calcretes are widespread in arid and semi-arid regions. Using calcrete profiles from four
15 river terraces of the Rio Alias in southeast Spain, this study explores the potential of using detailed
16 micromorphological and stable isotopic analysis to more fully understand the impacts of Quaternary
17 environmental change on calcrete development. The four profiles increase in carbonate complexity
18 with progressive age, reflecting calcretisation over multiple glacial-interglacial cycles since MIS 9 (c.
19 300 ka). Calcrete profiles contain a mixture of Alpha (non-biogenic) and Beta (biogenic)
20 microfabrics. Alpha fabrics have higher $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. The profiles contain a range of crystal
21 textures, but there is little difference between the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of spar, microspar, and micrite
22 cements. Strong positive covariance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ suggests that both isotopes are responding
23 to the same environmental parameter, which is inferred to be relative aridity. The study reveals that
24 the detailed co-analysis of calcrete micromorphology and stable isotope signatures can allow patterns
25 of calcrete formation to be placed into a wider palaeoclimatic context. This demonstrates the potential
26 of this technique to more reliably constrain the palaeoenvironmental significance of secondary
27 carbonates in dryland settings where other proxy records may be poorly preserved.

28
29 **Keywords:** pedogenic calcrete; micromorphology; stable isotopes; palaeoenvironments;
30 Mediterranean

31 32 33 INTRODUCTION

35 Pedogenic carbonates (calcretes) have been widely used as proxy records of Quaternary
36 environmental change within semi-arid and arid regions such as the Mediterranean (Alonso-Zarza,
37 2003; Candy and Black, 2009; Candy et al., 2012). Calcretes form at a land surface due to the
38 dissolution and reprecipitation of calcium carbonate (CaCO_3) within a soil profile (Wright and
39 Tucker, 1991). Calcrete formation is governed by a range of environmental factors, including:
40 carbonate supply, water availability, evaporation, vegetation dynamics, and landscape stability
41 (Wright and Tucker, 1991; Rossinky and Swart, 1993; Jiménez-Espinosa and Jiménez-Millán, 2003;
42 Wright, 2007; Candy and Black, 2009). Because many of these factors are controlled by prevailing
43 climate conditions, climate change, over long or short timescales, can produce complex calcrete
44 macromorphologies (see Gile et al., 1965; 1966; Netterberg, 1969; Goudie, 1983; Machette, 1985;
45 Alonso-Zarza, 2003; Candy and Black, 2009). This complexity is also expressed in the
46 micromorphology, where different calcrete microfabrics record different mechanisms of carbonate
47 precipitation, which may in turn reflect changing environmental conditions (e.g. Calvet and Julià,
48 1983; Wright and Tucker, 1991; Bain and Foos, 1993; Alonso-Zarza et al., 1998; Andrews et al.,
49 1998; Robinson et al., 2002; Alonso-Zarza and Arenas, 2004).

50

51 Aside from carbonate morphology, the stable isotopic composition of Quaternary calcretes can
52 provide valuable records of palaeoenvironmental change. Oxygen and carbon isotopic signatures are
53 indicative of the temperature, aridity, or vegetation conditions that existed during calcrete formation
54 (Cerling, 1984; Cerling and Quade, 1993; Andrews et al., 1998; Candy et al., 2006; 2011; 2012).
55 Many studies have investigated Quaternary calcrete morphology (e.g. Calvet and Julià, 1983; Wright
56 and Tucker, 1991; Bain and Foos, 1993; Alonso-Zarza et al., 1998; Andrews et al., 1998; Deutz et al.,
57 2001; 2002; Robinson et al., 2002; Alonso-Zarza and Arenas, 2004; Brasier et al., 2010), and others
58 have used carbonate isotopic signatures as a record of palaeoenvironmental change (i.e. Andrews et
59 al., 1998; Candy et al., 2006; 2012), but few have applied both analyses simultaneously. Combining
60 these techniques is important as $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values provide an environmental proxy that can allow
61 changing carbonate processes to be placed into a climatic framework. Such co-analysis will allow us
62 to establish more reliably whether changes in calcrete morphology and micromorphology directly
63 reflect oscillations in environmental conditions.

64

65 In this paper, we present a combined morphological, micromorphological, and stable isotopic analysis
66 of pedogenic calcrete profiles from the Quaternary river terrace surfaces of the Rio Alias in southeast
67 Spain (Maher et al., 2007; Maher and Harvey, 2008). We test the potential of using these analyses to
68 more fully understand the impacts of Quaternary environmental change on calcrete formation. The
69 study region was chosen for two reasons. Firstly, the calcrete profiles display a range of
70 morphological maturity. Secondly, the age of the calcretes can be constrained through correlation with

71 the U-series ages of corresponding calcretes in the neighbouring Sorbas Basin, building on the work
72 of previous studies in this region (Candy et al., 2004a and b; 2005; Maher and Harvey, 2008; Candy
73 and Black, 2009). Our coupled analysis means that individual isotope samples can be directly and
74 systematically linked to different morphological types, allowing the relationship between calcrete
75 microfabric and climate conditions to be tested. This study shows that the complexity of calcrete
76 morphology/micromorphology increases with age, and the older and more complex calcrete profiles
77 also show a greater range of carbon ($\delta^{13}\text{C}_{\text{carb}}$) and oxygen ($\delta^{18}\text{O}_{\text{carb}}$) isotope values. This implies that
78 they have developed under a wider range of climatic conditions than the younger profiles. The oxygen
79 and carbon isotopic data show a strong degree of co-variance, suggesting that evaporation, and
80 therefore environmental aridity, is a major control on calcrete isotopic composition (see Candy et al.,
81 2012). The paper concludes by discussing the significance of these findings for understanding the role
82 of climate on calcrete formation and for the use of calcrete morphology/micromorphology as a
83 palaeoenvironmental proxy.

84
85

86 **BACKGROUND**

87

88 Following the classic calcrete morphological framework outlined by Netterberg (1969) and Machette
89 (1985), pedogenic calcrete profiles develop in a continuum from: discrete carbonate nodules (Stage I
90 development) to coalesced, indurated hardpan horizons, often characterised by overprinting,
91 brecciation, and re-cementation (Stage VI). It is the complex Stage VI calcretes that typically exhibit
92 evidence for environmental change. As carbonate development is related to climatic regime, moisture
93 availability, timescale of development, and landsurface stability, the cyclical patterns of Quaternary
94 environmental change are likely to form complex calcrete profiles (see Candy and Black, 2009). This
95 is not to overlook, however, the impact that taphonomic factors such as diagenesis (Wright and
96 Tucker, 1991) and neomorphism (Flügel, 2004) may have on calcrete form.

97

98 Calcrete microstructures also reflect the environmental conditions that have influenced calcrete
99 development. Microfabrics record variations in climatic and vegetation conditions, duration of
100 carbonate formation, and characteristics of the host sediment (Alonso-Zarza and Arenas, 2004). Two
101 microfabric end members (Alpha and Beta fabrics) have been identified, although profiles typically
102 contain a combination of the two (Wright and Tucker, 1991). Alpha microfabrics (the K fabrics of
103 Gile et al., 1965; 1966) are associated with carbonate precipitation by physical (typically evaporative)
104 processes under arid environmental regimes (Watts, 1978; Wright and Tucker, 1991). Alpha fabric
105 microstructures include: bladed calcite coronas, voids, fractures and cracks, floating and etched
106 grains, exploded grains, and crystallaria (Braithwaite, 1983; Wright, 1990; Wright and Tucker, 1991).

107 Beta microfabrics develop through biogenic carbonate precipitation associated with macro- and
108 microorganisms (Wright, 2007). Microstructures include: rhizocretions, pedotubules, calcified root
109 hairs, laminated crusts, peloids, pelleted micrite, microcodium, needle fibre calcite, bioclasts and
110 coated grains (Calvet and Julià, 1983; Bain and Foos, 1993; Alonso-Zarza et al., 1998; Andrews et al.,
111 1998; Robinson et al., 2002). These fabrics are indicative of root activity and microbial processes
112 within the overlying soil horizons and are linked to wetter climate conditions than Alpha fabrics.
113 Vegetation expansion during temperate phases of the Quaternary, for example, would have led to an
114 increase in the biogenic precipitation of secondary carbonates (Martín-Algarra et al., 2003). Calcite
115 cements, in both Alpha and Beta environments, range in crystal size from micrite (smallest), to
116 microspar, and spar (largest). Different crystal sizes are not necessarily diagnostic of different climatic
117 regimes, and crystal size should be analysed alongside microfabric characteristics to ensure reliable
118 palaeoenvironmental interpretations (Calvet and Julià, 1983; Drees and Wilding, 1987; Bain and
119 Foos, 1993; Alonso-Zarza et al., 1998; Andrews et al., 1998; Robinson et al., 2002; Nash and
120 McLaren, 2003).

121

122 The relationship between carbonate formation and palaeoenvironmental change can also be
123 investigated through the analysis of calcrete oxygen and carbon isotopic composition (Cerling and
124 Quade, 1993; Alam et al., 1997; Achyuthan et al., 2007; Quade and Cerling, 2007). A range of
125 environmental factors can control the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of calcretes, making the isotopic signature
126 potentially difficult to interpret. Candy et al. (2012) have argued, however, that, in regions where
127 there is a strong co-variance in the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of calcretes it is likely that aridity is the
128 primary environmental factor. This is suggested because progressive evaporation of soil moisture
129 leads to the preferential removal of the “lighter” H_2^{16}O , resulting in relatively higher ^{18}O values in the
130 remaining soil moisture, and consequently, in the resulting carbonate (Dever et al., 1987; Quade et al.,
131 1989; Ufnar et al., 2008). Equally, the gradual reduction in the volume of water results in the
132 degassing of $^{12}\text{CO}_2$ and leads to a relatively higher $\delta^{13}\text{C}$ value of dissolved inorganic carbon (DIC) in
133 the soil moisture (Ufnar et al., 2008). This effect may be enhanced by lower biological productivity
134 during more arid conditions resulting in a greater contribution of atmospheric CO_2 to the soil zone,
135 which typically has a higher $\delta^{13}\text{C}$ value than soil CO_2 (Candy et al., 2012).

136

137 In regions such as the Mediterranean, increasing aridity should result in an increase in the $\delta^{18}\text{O}$ and
138 $\delta^{13}\text{C}$ values of calcretes, whilst a reduction in aridity should result in a decrease in the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$
139 values of calcretes. It is likely that, in such regions, although temperature may have a minor effect on
140 calcrete $\delta^{18}\text{O}$ values, this is minimal compared to the effect of evaporation. Furthermore, although
141 there is a significant body of literature on the role of plants using the C_3 and C_4 photosynthetic
142 pathways in controlling the $\delta^{13}\text{C}$ values of soil carbonate (Cerling et al., 1989; 1993; Talma and

143 Netterberg, 1983; Beidenbender et al., 2004; Schmidt et al., 2006) there is little evidence for a
144 significant role of C₄ vegetation in the western Mediterranean during the Quaternary (Goodfriend,
145 1999).

146

147

148 **STUDY SITE**

149

150 The Rio Alias drainage system lies within the Sorbas and Almeria Neogene sedimentary basins of the
151 Betic Cordillera, southeast Spain (36°59'28", -1°58'22") (Fig. 1). High-grade metamorphic lithologies
152 (e.g. amphibole mica schist, tourmaline gneiss, and graphite mica schists) dominate in the Sierra de
153 los Filabres, and lower grade metamorphic lithologies (e.g. meta-carbonates and mica schists) are
154 present in the Sierra Alhamilla and Cabrera (Maher et al., 2007). The Rio Alias drains from its
155 headwaters in the Sorbas basin, south and eastwards across the Sierra Alhamilla/Cabrera (Maher et
156 al., 2007). Six well-defined river terraces have been mapped in detail (Harvey and Wells, 1987;
157 Maher et al., 2007; Fig. 1): Terrace A (50 m above the modern channel) is the highest, and oldest,
158 terrace; Terrace B (c. 30 m); Terraces C1 and C2 (c. 15-20 m); Terrace D (c. 10 m), and Terrace E (c.
159 5 m). Terraces contain interbedded fluvial gravels (granules-pebbles) and sands, often capped by fine
160 grained (coarse sand-silt) colluvium. Fluvial aggradational phases are associated with glacial/stadial
161 events and quiescent or incisional periods are correlated to interglacial/interstadial phases (Maher et
162 al., 2007). A major river capture at c.70 ka (Candy et al., 2005) diverted drainage from the Sorbas
163 basin eastwards towards the Vera basin, beheading the Rio Alias through a 70% loss in drainage area
164 (Maher et al., 2007). Consequently, terraces A – C and D – E (outlined by Harvey and Wells, 1987;
165 Fig. 1) are attributable to pre- and post-capture development, respectively (Maher et al., 2007).

166

167 The A-C river terraces of the Rio Alias contain pedogenic calcrete profiles similar to those of the
168 Sorbas basin (Candy et al., 2003). The D terrace contains only weak calcrete development. Carbonate
169 profiles in this part of southeast Spain are morphologically complex (Harvey et al., 1995; Alonso-
170 Zarza et al., 1998) and probably formed continuously throughout glacial and interglacial periods
171 (Candy et al., 2004a and b; 2005). This contrasts with the generic model of episodic carbonate
172 formation, in which carbonate formed chiefly during interglacial periods (Candy and Black, 2009).
173 'Simple' and 'complex' carbonate profiles are routinely observed in the Aguas/Alias drainage basins.
174 Complex profiles can be further refined to Type 1 and 2 carbonates (Candy et al., 2003). Type 1
175 profiles contain multiple carbonate horizons, separated by unconsolidated sediment, and are
176 characterised by Alpha microfabrics. Type 2 profiles are composite, often overprinted, carbonates
177 containing Alpha and Beta microfabrics.

178

179 Although not directly dated, the Rio Alias terraces have been mapped as a continuous sequence from
180 the Sorbas basin through the lower Feos valley (Maher et al., 2007). On the basis of detailed terrace
181 sedimentology, mineralogy, pedogenic carbonate, and soil development analysis a clear correlation
182 between the Sorbas and Alias systems has been established. These analyses are discussed in detail by
183 Maher et al. (2007). Their correlation allows extrapolation of the Sorbas U-series chronology to the
184 Alias terraces (Kelly et al., 2000; Candy et al., 2005) (Table 1). The U-series framework provides
185 minimum ages of calcrete development, and therefore terrace formation, of: 304 ± 26 ka (Terrace A);
186 207 ± 11 ka (Terrace B); 77.7 ± 4.4 ka (Terrace C); 30 ± 3.3 ka (Terrace D); and the Holocene
187 (Terrace E). Terrace C1 of the Alias sequence is stratigraphically correlated with Terrace C of the Rio
188 Aguas (Maher et al., 2007; Maher and Harvey, 2008; Candy et al., 2005) and predates Terrace C2.
189 The C2 terrace is a localised phase of development, and there is no direct equivalent in the Sorbas
190 basin. Terrace D is preserved throughout the Rio Alias reaches and correlates with terrace D of the
191 Rio Aguas (Maher and Harvey, 2008; Candy et al., 2005). The U-series ages indicate that the oldest
192 calcrete profile in the Rio Alias may have developed during the period spanning MIS 9-1. This means
193 that the Rio Alias calcretes have been exposed to multiple glacial/interglacial cycles (Table 1):
194 Terrace A, 3 cycles; Terrace B, 2 cycles; Terraces C1/C2, 1 cycle; Terrace D has formed during the
195 transition from MIS 4-2 to 1; and Terrace E during the Holocene.

196

197 The well-developed carbonate profiles of the Rio Aguas terraces have been the focus of a number of
198 studies (e.g. Harvey et al., 1995; Kelly et al., 2000; Candy et al., 2003; Candy et al., 2005), but those
199 associated with the Rio Alias terraces have not yet been analysed in detail. Calcrete profiles from
200 terraces A, B, C1 and C2 are widespread, and these form the focus of this investigation. In the
201 youngest terraces, D and E, calcrete profiles are weakly developed or absent, making them unsuitable
202 for analysis in this study. Four calcrete profiles were selected for analysis (Fig. 1). Terraces A
203 ($37^{\circ}01'24''$, $-2^{\circ}04'42''$) and B ($37^{\circ}01'05''$, $-2^{\circ}04'17''$) are located on the Rio Alias upstream of the
204 Rambla de los Feos junction and the C1 ($36^{\circ}59'49''$, $-1^{\circ}58'35''$) and C2 ($36^{\circ}59'48''$, $-1^{\circ}58'29''$)
205 terraces are situated downstream of the capture site where the Rio Alias crosses the Carboneras Fault
206 Zone. This sequence provides an important opportunity to investigate the influence of Quaternary
207 climate change on calcrete development over multiple glacial-interglacial cycles.

208

209

210 **METHODS**

211

212 This study investigates calcrete development at three spatial scales using carbonate
213 macromorphology, micromorphology, and stable isotopic composition. This co-analysis ensured that
214 the isotopic dataset could be securely tied to the macro- and micromorphological analyses.

215

216 *Calcrete macromorphology*

217 Sediments were exposed in road cuttings and stream cut sections. Profiles from each terrace were
218 logged using standard sedimentological field descriptions. Units were defined on the basis of calcrete
219 morphology using the six-stage calcrete macromorphological classification outlined by Netterberg
220 (1969) and Machette (1985). This framework follows a progression from the unconsolidated host
221 sediment (Stage I) to indurated hardpan and laminar calcrete horizons (Stage VI). Where carbonate
222 formation was absent, standard sedimentological field logging techniques were used to define the
223 sediment matrix. Calcrete samples were extracted from each carbonate unit using a geological
224 hammer. This ensured that the entire stratigraphic progression of calcrete development within each of
225 the four terrace profiles was captured. A total of 39 samples were collected and prepared for thin
226 section and stable isotope analysis.

227

228 *Calcrete micromorphology*

229 The 39 calcrete samples were divided into two: one half was impregnated with resin and prepared for
230 thin section analysis; the second half was retained for stable isotope analysis. This ensured that
231 calcretes prepared for isotope analysis were not contaminated by the isotopic signature of the resin.
232 Thin section slides were analysed using a petrographic microscope. Micromorphological features (e.g.
233 groundmass and fabrics) were quantified following the examples outlined by Alonso et al. (2004) and
234 Wright (2007), among others. Groundmass statistics were generated by visual estimates of the
235 percentage areal cover of cement type (micrite, microspar, and spar) and grain content following the
236 methodology of Kemp (1985).

237

238 *Stable isotope geochemistry*

239 From the microfacies identified using thin section analysis, a total of 77 samples were analysed for
240 stable carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) composition. These reflect the range of cement types and
241 micromorphological features observed within the samples. Isotope samples were extracted from the
242 non-impregnated calcretes using a 500 μm diamond-tipped drill. Approximately 1 μg calcite was
243 analysed simultaneously for stable carbon and oxygen using an IsoPrime mass spectrometer using
244 standard techniques. A 3-standard calibration procedure was employed using one internal (RHBNC)
245 and two external (NBS-19 and LSVEC) standards. All values are reported relative to the Vienna Pee
246 Dee Belemnite (V-PDB) scale. The external precision (1σ) on multiple analyses of the carbonate
247 standards during the sample analysis period was $\pm 0.05\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.10\text{‰}$ for $\delta^{18}\text{O}$. The analysed

248 samples yielded mean precision (1σ) of $\pm 0.02\text{‰}$ and $\pm 0.06\text{‰}$ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively,
249 compliant with internationally accepted standards.

250

251

252 **RESULTS**

253

254 *Calcrete macromorphology*

255 The Rio Alias calcrete profiles follow the morphological framework of Machette (1985), and progress
256 with terrace age from discrete nodules (glaebules) in the youngest terraces, to complex
257 hardpan/laminar horizons and boulder calcretes (Stages I to VI) in the oldest terraces. Multiple
258 carbonate accumulation phases are evident within each terrace profile, indicative of ‘complex’
259 carbonate development (Fig. 2). The C2 terrace contains small (c.1 cm diameter) calcrete glaebules
260 set within fine-grained, matrix supported, colluvium (silty-sand). Three units (C i, ii, and iii) are
261 identified, each of increasing carbonate complexity from Carbonate Stages I and II of Machette
262 (1985). Terrace C1 contains five sedimentological/carbonate morphological units that progress from
263 Stage II to V of the Machette (1985) carbonate development index. The stage V carbonate is
264 represented by an incipient laminar carbonate horizon at the terrace surface.

265

266 Terrace B contains more complex calcretes than the lower terraces and comprises seven units. Units B
267 i and B iii are identified as weathered, red palaeosols (5YR 4/6). There is limited evidence of
268 translocated material from their previously associated A horizons, which is indicative of *in-situ*
269 weathering of mica schist and consequent development of Bw horizons. These palaeosols are
270 separated by calcrete horizons containing dissolution features (B ii), which suggest overprinting of
271 multiple calcrete formation phases. The profile is capped by a succession of Stage IV/V hardpan
272 accumulations (Fig. 2).

273

274 Three profiles were recorded at Terrace A to reflect the lateral variation in carbonate development at
275 this exposure (Fig. 5). All profiles contain a progression from Stage II to Stage VI carbonates. The
276 upper horizons, which contain a series of thick, laterally discontinuous, laminar calcretes, display
277 extensive brecciation and recementation features. These are indicative of Stage VI (boulder) calcretes,
278 which have been overprinted during successive calcretisation phases. The sequence is discontinuously
279 overlain by an unbrecciated Stage V hardpan and laminar crust.

280

281 *Calcrete micromorphology*

282 The increasing calcrete maturity from terrace C2 to A is also reflected in the micromorphological
283 complexity (Figs. 3-6). Terraces A and B contain evidence for multiple carbonate precipitation

284 phases. There is a decrease in grain:cement ratio with increasing carbonate age. Terraces C2 and C1
285 contain c. 50 % detrital grain content, whilst Terraces B and A contain <30 % and <20 %,
286 respectively. Alpha fabrics are closely associated with the microsparitic groundmass of nodular
287 calcretes, while Beta fabrics are most abundant within the micritic cements of hardpan horizons.
288

289 Terrace C2 contains uniform micromorphological profiles, with both micritic and microsparitic
290 cements (Fig. 3). Etched grains are abundant within all microfacies (frequently $n \geq 50$), as well as
291 numerous desiccation fractures and crystallaria. ‘Exploded’ grain structures, which are considered
292 indicative of the physical expansion of the grain-matrix, and etched grains (e.g. Figure 6B) are also
293 present. Small rhizcretions (<375 μm) are found throughout, but other biogenic evidence is limited,
294 indicating a dominantly Alpha fabric environment. Terrace C1 contains heterogeneous microfabrics,
295 with frequent to dominant microsparitic cements within the lower, nodular horizons. The upper
296 hardpan units contain micritic/microsparitic cements with increasing evidence of Beta microstructures
297 (peloids, alveolar septal structures, and pisoids). These are set within broadly Alpha-dominated
298 microfacies (Fig. 3). Cutans are also common on some grains. Rhizcretions are often larger than
299 those present in Terrace C2 (up to 1,000 μm) whilst voids and fractures are of similar dimensions.
300 There is no significant evidence of cement overprinting or neomorphism.
301

302 Terrace B contains microsparitic cements within the lower, nodular, Alpha fabric horizons (Fig. 4).
303 Thin sections taken across the glaebular-hardpan interface (Samples 25 and 26i) display a shift from
304 Alpha- to Beta-dominated microfabrics at the terrace surface (cutans, pelleted micrite, pisoids, and
305 alveolar septal structures, Fig. 6C) and an increase in microfabric complexity when compared to the
306 underlying horizons.
307

308 Thin sections from Terrace A show a decrease in grain size (typically below 2,000 μm), and a
309 reduction in the abundance of etched grains, when compared to Terrace C1 and C2. The basal,
310 nodular calcrete unit (Unit Ai) contains microsparitic cement with associated Alpha fabrics (notably
311 bladed calcite coronas, voids, and fractures; Fig. 6A). As the glaebules coalesce, there is a clear
312 transition from Alpha- to Beta-dominated microfacies (Fig. 5). The groundmass becomes increasingly
313 well-cemented throughout the hardpan units, and there is an abundance of peloids, rhizcretions, and
314 large pisoids (frequently >2,250 μm), as well as alveolar septal fabric (Fig. 6F) throughout. These
315 features are associated with biogenic/root activity, and are also observed in Terrace B (Fig. 6C-F).
316 The presence of Alpha microstructures within a predominantly Beta environment is considered
317 indicative of multiple calcretisation phases.
318

319 *Stable isotope geochemistry*

320 The isotopic values indicate that the $\delta^{13}\text{C}_{\text{carb}}$ values occupy a relatively narrow range (-8.28 to -5.30‰, range: 2.98‰) with limited variation both within and between calcrete profiles (Appendix A, Figures 3-5, 7, Appendix A). Calcite from terrace C2 becomes enriched in $\delta^{13}\text{C}_{\text{carb}}$ towards the terrace surface (range: 1.19‰), whilst Terrace C1 carbonates becomes progressively depleted (range: 1.68‰). These terraces do not occupy the same isotopic envelope. Terrace B, which is significantly older than C1, also occupies a narrow isotopic range (1.62‰) but demonstrates little isotopic variation with profile height. Terrace A presents the largest $\delta^{13}\text{C}_{\text{carb}}$ isotopic range observed within this study (2.89‰), spanning that of all other terraces (Figs. 3-5 and 7).

328

329

330 The $\delta^{18}\text{O}_{\text{carb}}$ values have a larger range (-6.60 to -2.25‰, range: 4.35‰) than the $\delta^{13}\text{C}_{\text{carb}}$ data. Each terrace unit possesses a distinct isotopic signature, and there is a progressive increase in the range of values with increasing calcrete age. Terrace C2 contains the most isotopically enriched values (-3.69 to -2.25‰, range: 1.44‰). Terrace C1 is significantly more depleted in the heavier isotope ($\delta^{18}\text{O}$), and values remain comparatively consistent throughout the profile (-4.73 to -4.30‰, range: 0.43‰) despite the large $\delta^{13}\text{C}_{\text{carb}}$ range (1.68‰). In contrast, Terrace B yields a broadly heterogeneous $\delta^{18}\text{O}_{\text{carb}}$ isotopic composition (-5.89 to -4.08‰, range: 1.77‰), and becomes more isotopically depleted with height. Terrace A has the largest $\delta^{18}\text{O}_{\text{carb}}$ isotopic range (-6.60 to -2.87‰, range: 3.73‰). The $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ biplots (Fig. 7) indicate that values from all terraces display a positive and strongly linear relationship, becoming, on average, increasingly strongly positive with decreasing age from Terrace A to C2. The isotopic signal of individual microtextures is displayed in Figure 7. Micritic and microsparitic cements have similar isotopic ranges (Fig. 7c). Alpha fabrics, however, are enriched in both $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ compared to Beta microfabrics (Fig. 7d). This is shown through the comparison of the calculated mean $\delta^{13}\text{C}_{\text{carb}}$ (-6.54‰, -4.24‰) and $\delta^{18}\text{O}_{\text{carb}}$ (-7.32‰, -5.41‰) values for Alpha and Beta microfabrics, respectively. Non-parametric Mann-Whitney U tests indicate that the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of both Alpha and Beta fabrics are statistically distinct populations.

346

347

348 **DISCUSSION**

349 *Patterns of changing calcrete complexity*

350

351 In the Rio Alias system, the complexity of calcrete morphology and variability in stable isotopes increase with terrace age. The A terrace surface contains evidence for multiple phases of hardpan and laminar calcrete development separated by periods of calcrete brecciation, i.e. a stage VI calcrete profile (Gile et al. 1965; 1966; Machette, 1985). The complexity is not simply a reflection of multiple

355 phases of soil development occurring at the same land-surface but evidence for accumulation and
356 erosion of the surface over time. This is indicated by the occurrence of multiple hardpans and laminar
357 crusts at different levels, probably in association with episodes of erosion and deposition on the
358 terrace surface (Candy and Black, 2009). It is likely that these erosional-depositional cycles reflect
359 colluvial rather than alluvial processes because the river would have incised, and therefore ceased to
360 impact, the A terrace during the formation of the calcrete profile (Candy et al., 2003). The B terrace
361 calcrete profile is less complex than that of the A terrace, but it is still characteristic of a stage VI
362 calcrete. This terrace contains two hardpan calcretes, each overlain by a laminar crust, superimposed
363 on top of each other. The morphology of this calcrete profile suggests an initial phase of calcrete
364 formation, generating a hardpan and laminar crust, followed by a phase of erosion and calcrete
365 brecciation over which a second hardpan and laminar crust formed.

366 The C1 and C2 terrace profiles are much more basic, particularly the C2 terrace which contains
367 discrete, but locally coalescing nodules, i.e. a Stage I to II calcrete profile. The C1 terrace profile
368 contains two discrete calcrete hardpans separated by a unit of unaltered sediments. This sequence is
369 likely to be a product of: 1) a phase of calcrete genesis producing a lower hardpan horizon; 2) a phase
370 of colluvial sedimentation that buries this horizon; and 3) a second phase of landscape stability during
371 which the upper calcrete hardpan is formed. The C1 profile therefore reflects the complex interaction
372 of landscape stability and instability that has been recorded elsewhere in this region in the form of
373 Type I calcrete profiles (Candy et al., 2003; Maher and Harvey, 2008; Candy and Black, 2009). The
374 difference in calcrete morphology between the C2 and C1 terraces supports the evidence presented by
375 Maher et al. (2007) that these are discrete landforms, and that the C1 terrace is older than the C2
376 terrace.

377 The A terrace calcrete profile displays the most complex macromorphology and the most diverse
378 range of microfeatures. The combination of Alpha and Beta microfabrics, as well as micrite,
379 microspar, and spar cements, suggests that these sediments were exposed to a wide variety of calcrete
380 forming processes, possibly in response to major variations in environmental conditions. This
381 suggestion is indicated by the A terrace $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, which show the largest isotopic range
382 of any of the four profiles. In comparison, the C1 and C2 terraces show a relatively restricted range of
383 microfeatures and $\delta^{13}\text{C}/\delta^{18}\text{O}$ values. The C1 and C2 calcrete profiles are dominated by Alpha fabrics
384 with minimal evidence for biological activity. Both profiles show a narrow range of $\delta^{18}\text{O}$ values (C1 =
385 0.20‰; C2 = 1.44‰), when compared to the older A and B profiles.

386 We infer that the increasing isotopic and morphological complexity of the Rio Alias calcretes can be
387 explained by; 1) their different ages, and 2) the implication of these different ages for the number of
388 climatic cycles to which each profile has been exposed. The U-series ages for the A and B terrace

389 surfaces in the Sorbas basin suggest that their counterparts in the Rio Alias basin began to form prior
390 to MIS 6, with the B terrace being at least as old as MIS 7 (207 ± 11 ka) and the A terrace being at
391 least as old as MIS 9 (304 ± 26 ka) (Candy et al., 2005). Both terrace surfaces have therefore been
392 exposed to at least two full glacial/interglacial cycles and the associated changes in moisture
393 availability, carbonate supply, biological activity, vegetation, and landscape stability; all of which
394 would affect calcrete formation (Wright and Tucker, 1991; Candy and Black, 2009). The role of
395 Quaternary glacial/interglacial cycles on calcrete development in the western Mediterranean has been
396 discussed more fully by Candy and Black (2009). The age of the C terrace carbonates in the Sorbas
397 basin (77.7 ± 4.4 ka) implies that the C1 and C2 terrace calcretes of the Rio Alias formed during, or
398 since, MIS 5a (Candy et al., 2005). This means that they have developed primarily under “glacial”
399 climates with only the last 11,500 years of their history being “interglacial”. This has resulted in
400 calcretes forming under much less variable environmental conditions, which explains the smaller
401 range in isotopic and morphologic variability. Although the current interglacial has persisted for
402 11,500 years it is unclear, due to the impact of human induced soil erosion (Gilman and Thornes,
403 1985) and the short duration of the Holocene humid period in the Mediterranean, whether calcrete
404 formation was possible during much of the Holocene (Jalut et al., 2000; Magny et al., 2002). If the
405 Holocene period was unsuitable for calcrete genesis then it is possible that much of the C1 and C2
406 terrace calcrete profiles formed entirely during the last glacial stage (MIS 4 to 2), resulting in physical
407 and isotopic characteristics that are conditioned by “glacial” climates alone.

408

409 *Calcrete $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values as evidence for palaeoenvironmental change*

410 Quaternary palaeoenvironmental records from the Mediterranean provide evidence for alternations
411 between “humid” interglacial stages and “semi-arid/arid” glacial stages (Prentice et al., 1992;
412 Harrison and Digerfeldt, 1993). Whether these shifts in climatic conditions reflect changes in the
413 absolute amount of annual precipitation or a change in the duration of the late spring/summer
414 moisture drought is unclear (Prentice et al., 1992). However, shifts in moisture availability are clearly
415 seen in multiple Mediterranean pollen records (Pons and Reille, 1988; Allen et al., 1999; Tzedakis et
416 al., 2001; 2006). The closest long-pollen record to the study site comes from Padul in the Granada
417 basin. This archive shows the expansion of woodland (dominated by *Quercus*) during interglacials
418 and an increase in non-arboreal taxa (notably *Artemisia*, *Asteraceae*, *Chenopodiaceae*, and
419 *Cyperaceae*) during the last cold stage (Pons and Reille, 1988). Although temperatures have also
420 varied during glacials/interglacials in the Mediterranean, much of the palaeoclimate record of this
421 region is dominated by changing moisture regimes. It is therefore anticipated that the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
422 values of Mediterranean calcretes also reflect changes in moisture conditions. Candy et al. (2012)
423 have shown that in the semi-arid regions of the Mediterranean the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ value of calcrete is

424 driven by evaporation, resulting in co-variance between the two isotopic groups. In regions where
425 temperature is the primary control on the $\delta^{18}\text{O}$ value of calcrete, Candy et al. (2012) have argued that
426 co-variance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values should be minimal.

427 If the Rio Alias $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ dataset is considered as a whole, the strong positive linear relationship
428 between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, suggests that, over Quaternary time, both carbon and oxygen isotopes
429 are responding to the same environmental driver. Together with existing palaeoenvironmental
430 evidence from the Mediterranean (Prentice et al., 1992; Allen et al., 1999; Tzedakis et al., 2001,
431 2006), we suggest that calcrete isotopic values are responding to changing degrees of aridity. In such
432 a model, calcretes with the highest $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values would have formed under the driest climates,
433 whilst those that have the lowest values would have formed under the most humid environments.

434

435 If the whole isotopic dataset is divided by terrace then two basic patterns are apparent; 1) the A
436 terrace values span the range of almost the entire Rio Alias dataset (although the mean is closer to the
437 lower end of the whole dataset), and 2) the isotopic data from the youngest two terraces, C1 and C2,
438 contain some of the highest $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. If it is accepted that the Mediterranean
439 palaeoclimate is characterised by humid interglacials and semi-arid/arid glacials, and that the co-
440 variance in the isotopic dataset is driven by changing aridity, then these two patterns can be explained
441 in the following way. Firstly, that the wide range of isotopic values derived from the A terrace
442 suggests that this calcrete profile has formed under the widest range of climatic settings, from most
443 “arid” (highest values) through to most “humid” (lowest values). This is consistent with the degree of
444 morphological and micromorphological maturity/complexity seen in the A terrace profile and the MIS
445 9 minimum age of this terrace surface. Secondly, that the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the C1/C2 terrace,
446 which are restricted to the higher end of the dataset, imply that the calcretes from these two terraces
447 have only formed under the “driest” climates that this region has experienced.

448

449 The wide range of $\delta^{18}\text{O}$ values seen in this dataset (4.35‰) is consistent with the magnitude of
450 isotopic shifts that occurs in association with a full glacial to interglacial transition in meteoric
451 carbonates from elsewhere in the Mediterranean (Bar-Matthews et al., 2003). However, it is not
452 certain that the full range of $\delta^{18}\text{O}$ values associated with the shift from full glacial to full interglacial
453 conditions is recorded in the carbonate dataset. This uncertainty is partly due to the inherent
454 randomness of sampling which means that facies that precipitated under the extremes of either glacial
455 or interglacial climates may not have been sampled. It is also possible that calcretes do not form under
456 the extremes of Quaternary climate cycles (see Candy and Black, 2009). This may be because
457 interglacial maxima are too humid, resulting in the formation of red Mediterranean soils but not
458 calcretes (Federoff, 1997; Yaalon, 1997), or because glacial minima are too arid or generate
459 landscapes that are too unstable for pedogenesis to occur (Günster et al., 2001; Candy and Black,

460 2009). It is clear, however, that calcretes that have experienced the greatest number of
461 glacial/interglacial cycles, have the greatest range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values.

462

463 *Calcrete microfabrics as indicators of palaeoenvironmental change*

464 The value of calcrete microfabrics as an indicator of palaeoenvironmental conditions has been debated
465 in the literature (Drees and Wilding, 1987; Wright and Tucker, 1991; Nash and McLaren, 2003;
466 Wright, 2007). For example, cement crystal size, such as micrite and microspar, may be indicative of
467 moisture availability. The dominance of Beta (biological) fabrics over Alpha (inorganic) fabrics may
468 also provide evidence of increased wetness and enhanced biological/organic activity (Drees and
469 Wilding, 1987; Nash and McLaren; Wright, 2007). This study has developed systematic links
470 between microfabric description and stable isotope analysis, and these ideas can be tested within the
471 Rio Alias sequence.

472

473 Figure 7c shows the Rio Alias isotopic dataset plotted by groundmass, based on micrite or microspar
474 crystal size. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of both groups overlap and there is no statistical difference
475 between each groundmass type; the mean values and range of both datasets are almost identical and U
476 scores calculated by the Mann Whitney test implies that both datasets are part of the same population.
477 Consequently, there is no isotopic evidence in the Rio Alias calcretes to suggest that calcrete crystal
478 size is controlled by prevailing environmental conditions.

479

480 Figure 7d shows the Rio Alias isotopic dataset plotted by Alpha and Beta fabrics. Although there is a
481 degree of overlap between the two groups of isotopic data, Beta fabrics are characterised by lower
482 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values than Alpha fabrics. The mean $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of Alpha fabrics are 0.78‰
483 and 1.17‰ higher than Beta fabrics, respectively. Furthermore, U scores calculated through the Mann
484 Whitney test indicate that these differences are significant enough to suggest that these two datasets
485 are from different populations. Given the palaeoenvironmental interpretation of the isotopic dataset
486 outlined above, this would imply that, in the Rio Alias region, Beta fabrics form under more humid
487 conditions than Alpha fabrics. Although based on a small dataset, this investigation indicates that
488 variations between Alpha and Beta fabrics within other calcrete profiles may also have the potential of
489 providing valuable sedimentary/petrographic evidence for palaeoenvironmental change.

490

491 *Wider significance*

492 Pedogenic calcretes are sensitive to Quaternary climate change as their formation is controlled by a
493 range of environmental conditions. Consequently, they can be important indicators of climate
494 dynamics. However, their main limitation is that this palaeoenvironmental information is contained
495 within a narrow horizon at the landsurface, often with no clear stratigraphic order. This study has

496 shown that by systematically combining morphological, micromorphological, and stable isotopic
497 analysis and applying this approach to calcrete profiles of a range of ages it is possible to develop a
498 clearer understanding of changing patterns of calcrete development and palaeoenvironmental
499 conditions. In particular, the comparison between a mature calcrete profile that has formed under
500 multiple glacial/interglacial cycles with immature calcrete profiles that have formed under a single
501 glacial episode allows the morphological/micromorphological and stable isotopic characteristics of
502 “humid” (interglacial) and “semi-arid/arid” (glacial) calcretes to be identified. This study has focused
503 on pedogenic calcretes, but groundwater carbonates are also widespread in arid and semi-arid regions,
504 including southeast Spain (e.g. Nash and Smith, 1998). This approach may provide opportunities to
505 explore in detail the relationships between groundwater calcretes and palaeoenvironmental conditions.
506 Although the data shown here are predominantly applicable for understanding palaeoclimatic change
507 in southeastern Spain, the methodology may significantly enhance our understanding of climate
508 variability in other dryland regions of the world where palaeoecological data are absent but calcrete
509 profile chronosequences are abundant.

510

511

512 CONCLUSION

513

- 514 • Calcrete profiles from river terraces of the Rio Alias, southeastern Spain have been used to
515 develop a combined analysis of calcrete macromorphology, micromorphology, and stable
516 isotope geochemistry. This analysis has been used to test the impacts of palaeoenvironmental
517 change on calcrete development.
- 518 • The oldest calcrete profile (from the A terrace) shows the greatest complexity with respect to
519 the variety of morphological and micromorphological features and the range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
520 values. The youngest calcrete profile (from the C terrace) shows the least complexity with
521 negligible variability with respect to both morphological and micromorphological features
522 and the range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values.
- 523 • This pattern is interpreted as being an expression of the impact of glacial/interglacial cycles
524 on calcrete development. Older terrace profiles have experienced multiple climate cycles, and
525 contain more complex morphologies and isotopic signatures than the younger terrace profiles
526 that may have developed during a single glacial.
- 527 • The covariance of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values suggests that aridity is the main environmental
528 control on the isotopic values of these calcrete profiles. Carbonates that formed solely during
529 the last glacial (Terrace C1 and C2) have high “arid” $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. The oldest
530 calcrete profiles (Terrace A) display a wide range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, suggesting that

531 carbonate has accumulated under both “humid” (low values) and “arid” (high values)
532 conditions.

- 533 • This study shows that by combining sedimentological, petrographic, and isotopic analysis of
534 calcrete profiles a better understanding of the climatic history of a region and the interaction
535 of the role of environmental change on calcrete development may be developed. This
536 technique may provide important insights into palaeoclimatic change in dryland regions
537 where palaeoecological records are scarce, but calcrete profiles are well-developed.

538

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