Coupled micromorphological and stable isotope analysis of Quaternary calcrete development

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ABSTRACT

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

Keywords: pedogenic calcrete; micromorphology; stable isotopes; palaeoenvironments; Mediterranean

INTRODUCTION

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

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

In this paper, we present a combined morphological, micromorphological, and stable isotopic analysis of pedogenic calcrete profiles from the Quaternary river terrace surfaces of the Rio Alias in southeast Spain (Maher et al., 2007; Maher and Harvey, 2008). We test the potential of using these analyses to more fully understand the impacts of Quaternary environmental change on calcrete formation. The study region was chosen for two reasons. Firstly, the calcrete profiles display a range of morphological maturity. Secondly, the age of the calcretes can be constrained through correlation with the U-series ages of corresponding calcretes in the neighbouring Sorbas Basin, building on the work of previous studies in this region (Candy et al., 2004a and b; 2005; Maher and Harvey, 2008; Candy and Black, 2009). Our coupled analysis means that individual isotope samples can be directly and systematically linked to different morphological types, allowing the relationship between calcrete microfabric and climate conditions to be tested. This study shows that the complexity of calcrete morphology/micromorphology increases with age, and the older and more complex calcrete profiles also show a greater range of carbon ($\delta^{13}C_{carb}$) and oxygen ($\delta^{18}O_{carb}$) isotope values. This implies that they have developed under a wider range of climatic conditions than the younger profiles. The oxygen and carbon isotopic data show a strong degree of co-variance, suggesting that evaporation, and therefore environmental aridity, is a major control on calcrete isotopic composition (see Candy et al., 2012). The paper concludes by discussing the significance of these findings for understanding the role of climate on calcrete formation and for the use of calcrete morphology/micromorphology as a palaeoenvironmental proxy.

BACKGROUND

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

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

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

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

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

Netterberg, 1983; Beidenbender et al., 2004; Schmidt et al., 2006) there is little evidence for a significant role of C_4 vegetation in the western Mediterranean during the Quaternary (Goodfriend, 1999).

STUDY SITE

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

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

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

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

METHODS

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

Calcrete macromorphology

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

Calcrete micromorphology

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

Stable isotope geochemistry

From the microfacies identified using thin section analysis, a total of 77 samples were analysed for stable carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) composition. These reflect the range of cement types and micromorphological features observed within the samples. Isotope samples were extracted from the non-impregnated calcretes using a 500 µm diamond-tipped drill. Approximately 1 µg calcite was analysed simultaneously for stable carbon and oxygen using an IsoPrime mass spectrometer using standard techniques. A 3-standard calibration procedure was employed using one internal (RHBNC) and two external (NBS-19 and LSVEC) standards. All values are reported relative to the Vienna Pee Dee Belemnite (V-PDB) scale. The external precision (1σ) on multiple analyses of the carbonate standards during the sample analysis period was ±0.05‰ for $\delta^{13}C$ and ±0.10‰ for $\delta^{18}O$. The analysed samples yielded mean precision (1σ) of ±0.02‰ and ±0.06‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively, compliant with internationally accepted standards.

RESULTS

Calcrete macromorphology

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

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

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

Calcrete micromorphology

The increasing calcrete maturity from terrace C2 to A is also reflected in the micromorphological complexity (Figs. 3-6). Terraces A and B contain evidence for multiple carbonate precipitation phases. There is a decrease in grain:cement ratio with increasing carbonate age. Terraces C2 and C1 contain c. 50 % detrital grain content, whilst Terraces B and A contain <30 % and <20 %, respectively. Alpha fabrics are closely associated with the microsparitic groundmass of nodular calcretes, while Beta fabrics are most abundant within the micritic cements of hardpan horizons.

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

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

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

Stable isotope geochemistry

The isotopic values indicate that the $\delta^{13}C_{carb}$ 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 $\delta^{13}C_{carb}$ 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 $\delta^{13}C_{carb}$ isotopic range observed within this study (2.89‰), spanning that of all other terraces (Figs. 3-5 and 7).

The $\delta^{18}O_{carb}$ values have a larger range (-6.60 to -2.25‰, range: 4.35‰) than the $\delta^{13}C_{carb}$ 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 ($\delta^{18}O$), and values remain comparatively consistent throughout the profile (-4.73 to -4.30‰, range: 0.43‰) despite the large $\delta^{13}C_{carb}$ range (1.68‰). In contrast, Terrace B yields a broadly heterogeneous $\delta^{18}O_{carb}$ isotopic composition (-5.89 to -4.08‰, range: 1.77‰), and becomes more isotopically depleted with height. Terrace A has the largest $\delta^{18}O_{carb}$ isotopic range (-6.60 to -2.87‰, range: 3.73‰). The $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ 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 $\delta^{18}O_{carb}$ and $\delta^{13}C_{carb}$ compared to Beta microfabrics (Fig. 7d). This is shown through the comparison of the calculated mean $\delta^{13}C_{carb}$ (-6.54‰, -4.24‰) and $\delta^{18}O_{carb}$ (-7.32‰, -5.41‰) values for Alpha and Beta microfabrics, respectively. Non-parametric Mann-Whitney U tests indicate that the $\delta^{13}C$ and $\delta^{18}O$ of both Alpha and Beta fabrics are statistically distinct populations.

DISCUSSION

Patterns of changing calcrete complexity

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

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

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

We infer that the increasing isotopic and morphological complexity of the Rio Alias calcretes can be explained by; 1) their different ages, and 2) the implication of these different ages for the number of climatic cycles to which each profile has been exposed. The U-series ages for the A and B terrace surfaces in the Sorbas basin suggest that their counterparts in the Rio Alias basin began to form prior to MIS 6, with the B terrace being at least as old as MIS 7 (207 ± 11 ka) and the A terrace being at least as old as MIS 9 (304 ± 26 ka) (Candy et al., 2005). Both terrace surfaces have therefore been exposed to at least two full glacial/interglacial cycles and the associated changes in moisture availability, carbonate supply, biological activity, vegetation, and landscape stability; all of which would affect calcrete formation (Wright and Tucker, 1991; Candy and Black, 2009). The role of Quaternary glacial/interglacial cycles on calcrete development in the western Mediterranean has been discussed more fully by Candy and Black (2009). The age of the C terrace carbonates in the Sorbas basin (77.7 ± 4.4 ka) implies that the C1 and C2 terrace calcretes of the Rio Alias formed during, or since, MIS 5a (Candy et al., 2005). This means that they have developed primarily under "glacial" climates with only the last 11,500 years of their history being "interglacial". This has resulted in calcretes forming under much less variable environmental conditions, which explains the smaller range in isotopic and morphologic variability. Although the current interglacial has persisted for 11,500 years it is unclear, due to the impact of human induced soil erosion (Gilman and Thornes, 1985) and the short duration of the Holocene humid period in the Mediterranean, whether calcrete formation was possible during much of the Holocene (Jalut et al., 2000; Magny et al., 2002). If the Holocene period was unsuitable for calcrete genesis then it is possible that much of the C1 and C2 terrace calcrete profiles formed entirely during the last glacial stage (MIS 4 to 2), resulting in physical and isotopic characteristics that are conditioned by "glacial" climates alone.

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

Quaternary palaeoenvironmental records from the Mediterranean provide evidence for alternations between "humid" interglacial stages and "semi-arid/arid" glacial stages (Prentice et al., 1992; Harrison and Digerfeldt, 1993). Whether these shifts in climatic conditions reflect changes in the absolute amount of annual precipitation or a change in the duration of the late spring/summer moisture drought is unclear (Prentice et al., 1992). However, shifts in moisture availability are clearly seen in multiple Mediterranean pollen records (Pons and Reille, 1988; Allen et al., 1999; Tzedakis et al., 2001; 2006). The closest long-pollen record to the study site comes from Padul in the Granada basin. This archive shows the expansion of woodland (dominated by *Quercus*) during interglacials and an increase in non-arboreal taxa (notably *Artemisia*, *Asteraceae*, *Chenopodiaceae,* and *Cyperacea*) during the last cold stage (Pons and Reille, 1988). Although temperatures have also varied during glacials/interglacials in the Mediterranean, much of the palaeoclimate record of this region is dominated by changing moisture regimes. It is therefore anticipated that the $\delta^{13}C$ and $\delta^{18}O$ values of Mediterranean calcretes also reflect changes in moisture conditions. Candy et al. (2012) have shown that in the semi-arid regions of the Mediterranean the $\delta^{13}C$ and $\delta^{18}O$ value of calcrete is driven by evaporation, resulting in co-variance between the two isotopic groups. In regions where temperature is the primary control on the $\delta^{18}O$ value of calcrete, Candy et al. (2012) have argued that co-variance between $\delta^{13}C$ and $\delta^{18}O$ values should be minimal.

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

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

The wide range of $\delta^{18}O$ values seen in this dataset (4.35‰) is consistent with the magnitude of isotopic shifts that occurs in association with a full glacial to interglacial transition in meteoric carbonates from elsewhere in the Mediterranean (Bar-Matthews et al., 2003). However, it is not certain that the full range of $\delta^{18}O$ values associated with the shift from full glacial to full interglacial conditions is recorded in the carbonate dataset. This uncertainty is partly due to the inherent randomness of sampling which means that facies that precipitated under the extremes of either glacial or interglacial climates may not have been sampled. It is also possible that calcretes do not form under the extremes of Quaternary climate cycles (see Candy and Black, 2009). This may be because interglacial maxima are too humid, resulting in the formation of red Mediterranean soils but not calcretes (Federoff, 1997; Yaalon, 1997), or because glacial minima are too arid or generate landscapes that are too unstable for pedogenesis to occur (Günster et al., 2001; Candy and Black, 2009). It is clear, however, that calcretes that have experienced the greatest number of glacial/interglacial cycles, have the greatest range of $\delta^{13}C$ and $\delta^{18}O$ values.

Calcrete microfabrics as indicators of palaeoenvironmental change

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

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

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

Wider significance

Pedogenic calcretes are sensitive to Quaternary climate change as their formation is controlled by a range of environmental conditions. Consequently, they can be important indicators of climate dynamics. However, their main limitation is that this palaeoenvironmental information is contained within a narrow horizon at the landsurface, often with no clear stratigraphic order. This study has shown that by systematically combining morphological, micromorphological, and stable isotopic analysis and applying this approach to calcrete profiles of a range of ages it is possible to develop a clearer understanding of changing patterns of calcrete development and palaeoenvironmental conditions. In particular, the comparison between a mature calcrete profile that has formed under multiple glacial/interglacial cycles with immature calcrete profiles that have formed under a single glacial episode allows the morphological/micromorphological and stable isotopic characteristics of "humid" (interglacial) and "semi-arid/arid" (glacial) calcretes to be identified. This study has focused on pedogenic calcretes, but groundwater carbonates are also widespread in arid and semi-arid regions, including southeast Spain (e.g. Nash and Smith, 1998). This approach may provide opportunities to explore in detail the relationships between groundwater calcretes and palaeoenvironmental conditions. Although the data shown here are predominantly applicable for understanding palaeoclimatic change in southeastern Spain, the methodology may significantly enhance our understanding of climate variability in other dryland regions of the world where palaeoecological data are absent but calcrete profile chronosequences are abundant.

CONCLUSION

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

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

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

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