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# 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.

## 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 (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 paleoenvironmental 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; Deutz et al., 2001; 2002; Candy et al., 2006; Quade and Cerling, 2007; Brasier et al., 2010; Candy et al., 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; Robinson et al., 2002; Alonso-Zarza and Arenas, 2004), and others have used carbonate isotopic signatures as a record of paleoenvironmental 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.

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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 understand more fully 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 (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 paleoenvironmental 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 (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 paleoenvironmental 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 paleoenvironmental change can also be investigated through the analysis of calcrete oxygen and carbon isotopic composition (Quade and Cerling, 2007; Cerling and Quade (1993); Alam et al. (1997); Achyuthan et al. (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 (Talma and Netterberg (1983); Cerling et al., 1989, 1993; Biedenbender 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