



Invited review

# Pedogenic carbonates: Forms and formation processes



Kazem Zamanian <sup>a,\*</sup>, Konstantin Pustovoytov <sup>b</sup>, Yakov Kuzyakov <sup>a,c</sup>

<sup>a</sup> Department of Soil Science of Temperate Ecosystems, Georg August University of Goettingen, Buesgenweg 2, 37077 Goettingen, Germany

<sup>b</sup> Institute of Soil Science and Land Evaluation (310), University of Hohenheim, Schloss Hohenheim 1, 70599 Stuttgart, Germany

<sup>c</sup> Department of Agricultural Soil Science, University of Goettingen, Buesgenweg 2, 37077 Goettingen, Germany

ARTICLE INFO

Article history:

Received 6 September 2015  
 Received in revised form 19 January 2016  
 Accepted 10 March 2016  
 Available online 22 March 2016

Keywords:

Pedogenic carbonate  
 CaCO<sub>3</sub> recrystallization  
 Diagenesis  
 Paleoenvironment reconstructions  
 Radiocarbon dating  
 Inorganic carbon sequestration

ABSTRACT

Soils comprise the largest terrestrial carbon (C) pool, containing both organic and inorganic C. Soil inorganic carbon (SIC) was frequently disregarded because (1) it is partly heritage from soil parent material, (2) it undergoes slow formation processes and (3) has very slow exchange with atmospheric CO<sub>2</sub>. The global importance of SIC, however, is reflected by the fact that SIC links the long-term geological C cycle with the fast biotic C cycle, and this linkage is ongoing in soils. Furthermore, the importance of SIC is at least as high as that of soil organic carbon (SOC) especially in semiarid and arid climates, where SIC comprises the largest C pool. Considering the origin, formation processes and morphology, carbonates in soils are categorized into three groups: geogenic carbonates (GC), biogenic carbonates (BC) and pedogenic carbonates (PC). In this review we summarize the available data and theories on forms and formation processes of PC and relate them to environmental factors. After describing the general formation principles of PC, we present the specific forms and formation processes for PC features and the possibilities to use them to reconstruct soil-forming factors and processes. The following PC are described in detail: earthworm biospheroliths, rhizoliths and calcified roots, hypocoatings, nodules, clast coatings, calcretes and laminar caps.

The second part of the review focuses on the isotopic composition of PC: δ<sup>13</sup>C, Δ<sup>14</sup>C and δ<sup>18</sup>O, as well as clumped <sup>13</sup>C and <sup>18</sup>O isotopes known as Δ<sub>47</sub>. The isotopic signature of PC enables reconstructing the formation environment: the dominating vegetation (δ<sup>13</sup>C), temperature (δ<sup>18</sup>O and Δ<sub>47</sub>), and the age of PC formation (Δ<sup>14</sup>C). The uncertainties in reconstructural and dating studies due to PC recrystallization after formation are discussed and simple approaches to consider recrystallization are summarized.

Finally, we suggest the most important future research directions on PC, including the anthropogenic effects of fertilization and soil management. In conclusion, PC are an important part of SIC that reflect the time, periods and formation processes in soils. A mechanistic understanding of PC formation is a prerequisite to predict terrestrial C stocks and changes in the global C cycle, and to link the long-term geological with short-term biological C cycles.

© 2016 Elsevier B.V. All rights reserved.

Contents

1.	Introduction: inorganic carbon in soil and pedogenic carbonates . . . . .	2
1.1.	Relevance of soil inorganic carbon . . . . .	2
1.2.	Soil inorganic carbon: worldwide distribution . . . . .	2
1.3.	Soil inorganic carbon pools, classification and definitions . . . . .	2
1.4.	Pedogenic carbonate within soil inorganic carbon pools and its relevance . . . . .	3
2.	Formation of pedogenic carbonate . . . . .	3
2.1.	General principle of pedogenic carbonate formation . . . . .	3
2.2.	Formation mechanisms of pedogenic carbonates . . . . .	4
2.3.	Morphology of pedogenic carbonates . . . . .	4
2.4.	Factors affecting pedogenic carbonate accumulation in soil . . . . .	7
2.4.1.	Climate . . . . .	8
2.4.2.	Soil parent material . . . . .	8
2.4.3.	Soil properties . . . . .	9

\* Corresponding author.  
 E-mail address: [kzamani@gwdg.de](mailto:kzamani@gwdg.de) (K. Zamanian).

2.4.4.	Topography, soil position in the landscape and soil age	9
2.4.5.	Local vegetation and soil organisms	9
3.	Carbon and oxygen in pedogenic carbonates	10
3.1.	Sources of carbon, oxygen and calcium in pedogenic carbonates	10
3.2.	Isotopic composition of carbon ( $\delta^{13}\text{C}$ , $\Delta^{14}\text{C}$ ) and oxygen ( $\delta^{18}\text{O}$ ) in pedogenic carbonates	10
4.	Implications of PC in paleoenvironmental and chronological studies	11
5.	Recrystallization of soil carbonates	11
5.1.	Uncertainties of paleoenvironmental reconstructions based on pedogenic carbonates	12
5.2.	Evidence of pedogenic carbonate recrystallization after formation	12
6.	Conclusions and outlook	13
6.1.	Conclusions	13
6.2.	Future research directions	13
	Acknowledgements	14
	References	14

## 1. Introduction: inorganic carbon in soil and pedogenic carbonates

### 1.1. Relevance of soil inorganic carbon

Soils with 2,470 Pg C (Eswaran et al., 2000) are the largest terrestrial C pool and are the third greatest C reservoir in the world after oceans with 38,725 Pg (IPCC, 1990) and fossil fuels with 4000 Pg (Siegenthaler and Sarmiento, 1993) containing organic and inorganic C (Eswaran et al., 2000). Plant litter, rhizodeposits and microbial biomass are the main sources of the soil organic carbon (SOC) pool. The SOC pool comprises 697 Pg C in 0–30 cm and 1500 Pg C in 0–100 cm depths (IPCC, 2007). Intensive exchange of organic C with the atmosphere, especially connected with anthropogenic activities, led to a very broad range of studies related to the organic C cycle in soil and these have been summarized in many reviews (e.g. IPCC, 2007; Kuzyakov, 2006a).

In contrast to organic C, the exchange of soil inorganic carbon (SIC), i.e. various soil carbonate minerals (mostly calcite), with the atmosphere and the involvement of SIC in biotic C cycles is much slower (mean residence time of 78,000 years (Schlesinger, 1985)). Additionally, the distribution depth of SIC is opposite to that of SOC: most stocks are located deeper than one meter (Díaz-Hernández et al., 2003; Wang et al., 2010). These two reasons explain why much fewer studies focused on SIC than on SOC (Drees et al., 2001; Rawlins et al., 2011). Nonetheless, large stocks of SIC – 160 Pg C in 0–30 cm (Nieder and Benbi, 2008), 695–748 Pg C in 0–100 cm depth (Batjes, 1996) and 950 Pg C up to 2 m (Lal, 2012) – reflect its importance especially over the long term. The SIC content in first 2 m of soil in semi-arid regions could be 10 or even up to 17 times higher than SOC (Díaz-Hernández et al., 2003; Emmerich, 2003; Shi et al., 2012). Furthermore, a much longer mean residence time of SIC – millennia (Schlesinger, 1985) – shows its greater role in the global C cycle compared with SOC (few hours to centuries) (Hsieh, 1993; Qualls and Bridgham, 2005). SIC also links SOC with short residence times to the long-term geological C cycle (Liu et al., 2010). Soils of arid and semi-arid regions with usually alkaline pH (>8.5) and richness in Ca and/or Mg (>0.1%) may enhance the SIC content following organic fertilization and increase the respired  $\text{CO}_2$  (Bugchio et al., 2016; Wang et al., 2015).

Changes in environmental properties such as soil acidification because of N fertilization, N fixation by legumes or intensification of rewetting cycles due to irrigation could release great amounts of SIC and increase  $\text{CO}_2$  emissions (Eswaran et al., 2000; Shi et al., 2012). Such effects, though driven by natural processes, are well known in our planet's history, e.g. between the Pleistocene and Holocene, when around 400–500 Pg C were released from SIC and strongly intensified global warming over a short period (Adams and Post, 1999). The formation and accumulation of carbonate minerals in soils, in contrast, can directly mitigate the increase of atmospheric  $\text{CO}_2$  (Landi et al., 2003; Xie et al., 2008) if calcium ( $\text{Ca}^{2+}$ ) ions have been released to the soil via sources

other than carbonate-containing minerals, for instance from weathering of igneous rocks, decomposition of organic matter or dissolved  $\text{Ca}^{2+}$  in rainwater (Boettinger and Southard, 1991; Emmerich, 2003; Monger et al., 2015). This calls for investigating SIC stocks, forms and their dynamics to understand the role of SIC in the C cycle at regional and global scales, the fast and slow processes of C cycling, as well as the link between biotic and abiotic parts of the C cycle.

### 1.2. Soil inorganic carbon: worldwide distribution

Large SIC stocks are mostly found in regions with low water availability (i.e. arid, semi-arid and sub-humid regions) (Fig. 1) (Eswaran et al., 2000). Low precipitation and high potential evapotranspiration strongly limit the dissolution and leaching of carbonates from soil (Eswaran et al., 2000; Royer, 1999). Accordingly, the highest SIC content – around 320 to 1280 Mg C  $\text{ha}^{-1}$  – is accumulated in soils of arid regions with mean annual precipitation (MAP) below 250 mm such as middle east, African Sahara and west USA (Fig. 1). As MAP increases, the SIC content decreases and <40 Mg C  $\text{ha}^{-1}$  may accumulate at MAP exceeding 1000 mm for example in Amazonian forests and monsoonal forests in south-east Asia. However, partial eluviation and redistribution of carbonates may concentrate SIC deeper in the soil profile (Díaz-Hernández et al., 2003; Wang et al., 2010).

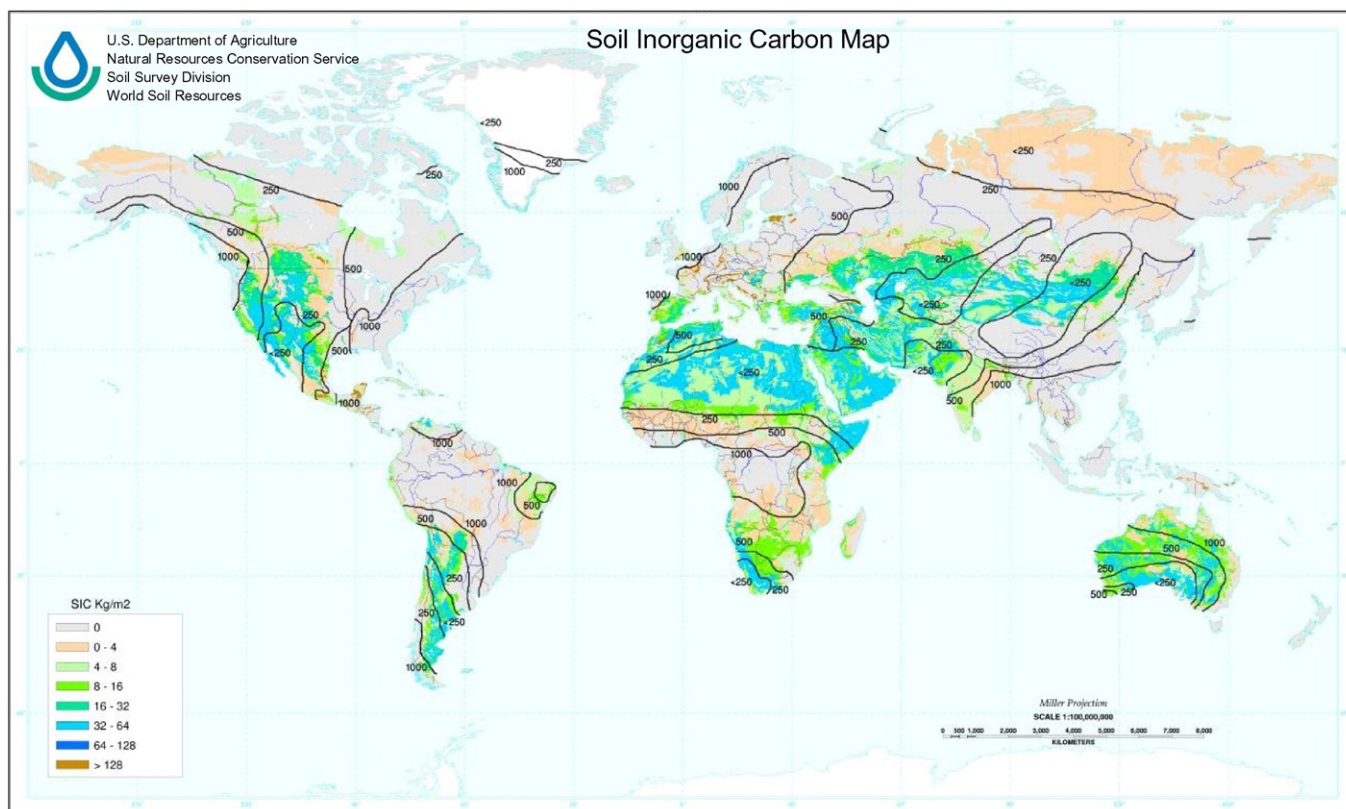
### 1.3. Soil inorganic carbon pools, classification and definitions

Based on origin, formation processes and morphology, the SIC can be subdivided into three large groups:

1. Geogenic carbonates (GC)<sup>1</sup>: carbonates which have remained or are inherited from soil parent materials such as limestone particles or allocated onto the soil from other locations by calcareous dust or landslides etc.
2. Biogenic carbonates (BC)<sup>1</sup>: carbonates formed within terrestrial or aquatic animals and plants as part of their skeleton, for example shells, bones and calcified seeds, or released from or within certain organs such as the esophageal glands of earthworms.
3. Pedogenic carbonates (PC): carbonates formed and redistributed in soils via dissolution of the SIC pool (i.e. geogenic, biogenic or previously formed pedogenic carbonates) and re-precipitation of dissolved ions in various morphologies such as carbonate nodules.

This review focuses solely on the origin, morphology and processes of PC formation. The GC and BC are mentioned only if relevant for PC formation.

<sup>1</sup> Here we do not review the forms and formation of geogenic and biogenic carbonates in soil.



**Fig. 1.** World SIC distribution in the top meter of soils (USDA-NRCS, 2000) and its correlation with areas of lower mean annual precipitation. The isolines of mean annual precipitation (mm) are from (FAO, 1996). Only the isolines of precipitation <1000 mm are presented. Note the exponential scale of SIC content. Most SIC is located in areas with precipitation <500 mm and SIC stocks above  $32 \text{ kg C m}^{-2}$  ( $320 \text{ Mg C ha}^{-1}$ ) are located in areas with precipitation <250 mm.

#### 1.4. Pedogenic carbonate within soil inorganic carbon pools and its relevance

PC originates during soil formation from GC or BC and/or former PC by recrystallization and redistribution in soil (see Section 2). PC accumulation affects the physical, chemical and biological properties of soil (Nordt et al., 1998) and thus affects plant growth and soil productivity.

PC accumulation can plug soil pores (Baumhardt and Lascano, 1993; Gile, 1961), increasing bulk density and reducing root penetration, water migration and oxygen supply (Baumhardt and Lascano, 1993; Geogren et al., 1991).

Fine PC crystals (i.e. micrite <4  $\mu\text{m}$ ) are more active in chemical reactions than large particles of GC (such as for example limestone). The availability of phosphorus and some micro-nutrients such as iron, zinc and copper for plants is therefore extremely reduced in the presence of PC (Becze-Deák et al., 1997). Accordingly, the presence of PC, their localization and forms in soil modify the water budget and fertilizer management.

Considering the effect of PC on plant growth and soil productivity, the layers or horizons containing PC have been defined quantitatively (e.g. amounts of carbonate, layer thickness) as diagnostic materials, diagnostic properties or diagnostic horizons in many soil classification systems such as World Reference Base, Soil Taxonomy, Russian and German systems especially in higher levels, i.e. major soil groups (WRB, 2014) orders and sub-orders (Soil Survey Staff, 2010).

In this review we focus on 1) the general mechanisms of PC formation, 2) the most common morphological forms of PC and their specific formation processes and 3) environmental factors affecting the rate of PC accumulation in soils. We then discuss 4) the importance and applications of PC in environmental sciences and mention 5) the

uncertainties because of recrystallization and 6) evidence of PC recrystallization. Finally, we suggest 7) directions of further studies.

## 2. Formation of pedogenic carbonate

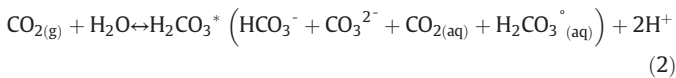
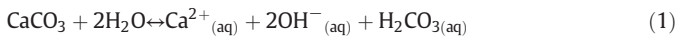
### 2.1. General principle of pedogenic carbonate formation

The general process of PC formation consists of three steps: 1) dissolution of SIC pools,<sup>2</sup> 2) movement of dissolved ions within pores, through soil profiles as well as landscapes and 3) re-precipitation.

- (1) Dissolution of SIC pools: The dissolution of SIC – mostly of  $\text{CaCO}_3$  – considering the solubility product ( $K_{sp} \approx 10^{-6} - 10^{-9}$ ) in distilled water (Robbins, 1985) is comparatively low (Eq. (1)). The dissolution rate is strongly controlled by soil pH and dissolved  $\text{CO}_2$ . The dissolution rate of  $\text{CO}_2$  and concentration of dissolved inorganic carbon (DIC) species (i.e.  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}_2\text{CO}_3$  and  $\text{CO}_2$ ), however, is controlled by the partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) in the soil atmosphere (Andrews and Schlesinger, 2001; Karberg et al., 2005).  $\text{CaCO}_3$  solubility in pure  $\text{H}_2\text{O}$  at 25 °C is  $0.013 \text{ g L}^{-1}$ , whereas in weak acids such as carbonic acid, the solubility increases up to five times (Aylward, 2007). The acidity produced by  $\text{CO}_2$  dissolution removes  $\text{OH}^-$  ions and shifts the Eq. (1) to the right, leading to further dissolution of  $\text{CaCO}_3$ . The

<sup>2</sup> This is the general formation mechanism of PC. If Ca ions are provided by sources other than SIC, such as weathering of Ca-bearing silicates, PC may also form (See Section 2.4., parent material).

increase of  $p\text{CO}_2$  in the soil air increases the solubility of  $\text{CaCO}_3$ , otherwise the pH will drop.



- (2) Movement of dissolved ions: the dissolved  $\text{Ca}^{2+}$  ions and DIC species are translocated by water movement in various directions: i.e. diffusion, capillary rise (unidirectional), water percolation (mainly downwards) or evaporation (upward). The transportation occurs over multiple spatial scales from mm to km: within and between microaggregates, macroaggregates, soil horizons, landscapes and even from terrestrial to aquatic ecosystems. The dissolved ions, however, may remain without significant translocation if soil permeability is very low, e.g. at the top of hard bedrock. Despite downward and upward migration of water, the upward migration of  $\text{Ca}^{2+}$  ions and DIC species is strongly restricted. Because  $p\text{CO}_2$  in the soil air strongly decreases close to the surface,  $\text{CaCO}_3$  solubility declines, the solution becomes supersaturated and  $\text{CaCO}_3$  precipitates. The rare cases of upward  $\text{CaCO}_3$  migration are possible only from continuously evaporating groundwater (e.g. in calcretes, see Section 2.3.), or in the case of a higher  $\text{CO}_2$  concentration in the topsoil versus subsoil, e.g. due to high microbial and root respiratory activities.
- (3) Re-precipitation: if soil solution becomes supersaturated with  $\text{CaCO}_3$ , the solutes precipitate. Supersaturation of soil solution in respect to  $\text{CaCO}_3$  may take place for two reasons: 1) decreasing soil water content mainly connected with evapotranspiration and 2) decreasing  $p\text{CO}_2$  (Robbins, 1985; Salomons and Mook, 1976). Considering changes in precipitation rates due to environmental properties (see Section 2.4) however, various morphologies may form.

## 2.2. Formation mechanisms of pedogenic carbonates

Considering the water movement during PC formation and the morphology of accumulated PC, various theories and mechanisms have been proposed for PC formation. These can be classified into four groups (adapted from (Monger, 2002)):

- (1) *Perdescendum* models: dissolution of GC, BC or PC in the topsoil, downward leaching and re-precipitation in subsoil because of water consumption. This is the main process of PC redistribution and accumulation in soil horizons (Gile et al., 1966; Machette, 1985; Royer, 1999). Lateral movement of solutes in this model also explains PC formation in various positions of a landscape (Monger, 2002).
- (2) *Perascendum* models: PC forms by upward water movement due to capillary rise or fluctuations of shallow groundwater. Dissolution occurs in the subsoil, and upward movement of the solution (after soil dryness because of evaporation, or drop in  $\text{CO}_2$  concentration) accumulates PC near or even at the soil surface (Khadkikar et al., 1998; Knuteson et al., 1989; Miller et al., 1987; Monger and Adams, 1996; Suchý, 2002). This model also includes the dissolution of SIC in higher landscape elevations and carbonate migration with groundwater with subsequent evaporation in soils at lower landscape elevations.
- (3) *In situ* models: dissolution of SIC pool and re-precipitation of dissolved  $\text{CaCO}_3$  take place without significant movement through

the soil profile (Monger and Adams, 1996; Rabenhorst and Wilding, 1986; West et al., 1988). This process commonly redistributes carbonates within the soil aggregates and pores of one horizon.

- (4) Biological models: biological activities increase the concentration of  $\text{Ca}^{2+}$  ions inside the organisms (e.g. plant cell-walls, plant vacuoles, fungi hyphae) or close to the organisms (e.g. along roots due to water mass flow towards the root, below termite nests because of their characteristic residual collectivity). Further calcification of Ca-bearing organs or supersaturation of soil solution at such sites forms PC (Alonso-Zarza, 1999; Becze-Deák et al., 1997; Elis, 2002; Monger and Gallegos, 2000; Verrecchia et al., 1995).

Depending on the prevalence of one or more of these mechanisms and their localization, the accumulation of re-precipitated carbonate generates various morphological forms of PC.

## 2.3. Morphology of pedogenic carbonates

Around 10 main PC forms are differentiated based on their morphology, properties and formation mechanisms (Table 1). These PC forms are classified based on the contribution of biotic and abiotic processes to their formation as well as PC formation rates.

- A) Earthworm biospheroliths: calciferous glands or esophageal glands of earthworms produce carbonate features, which are excreted in earthworm casts (Fig. 2) (Becze-Deák et al., 1997). Despite the primary biogenic origin of earthworm biospheroliths, they frequently provide an initial nucleus for further spherical accumulation of other forms of PC. The presence of earthworm biospheroliths in soils is an indication of stable conditions, i.e. absence of erosion or deposition (Becze-Deák et al., 1997). Earthworm biospheroliths occur frequently in loess-paleosol sequences (Becze-Deák et al., 1997) and can be used for  $^{14}\text{C}$  dating (Pustovoytov et al., 2004). The formation rate of earthworm biospheroliths is fast – within a few days (Lambkin et al., 2011).
- B) Rhizoliths are formed by mass flow of water with soluble  $\text{Ca}^{2+}$  towards the root and precipitation of  $\text{CaCO}_3$  along the root (Fig. 3 top). Because  $\text{Ca}^{2+}$  uptake is much lower than the water uptake, the remaining  $\text{Ca}^{2+}$  ions precipitate with  $\text{CO}_2$  from rhizomicrobial respiration as  $\text{CaCO}_3$ , thus forming the rhizoliths (Callot et al., 1982; Hinsinger, 1998; Lambers et al., 2009). The other but rare possibility is the release of  $\text{HCO}_3^-$  instead of  $\text{H}^+$  by roots to compensate for the uptake of anions such as  $\text{NO}_3^-$ . Increasing soil pH by released  $\text{HCO}_3^-$  induces  $\text{CaCO}_3$  precipitation around the root (Klappa, 1980). Rhizolith formation is common for shrubs and trees, but is not relevant for grasses because of their short life cycle.  $\text{CaCO}_3$  accumulation increases with root age over decades to centuries (Gocke et al., 2011a) and may form huge rhizolith landscapes, e.g. in Western Australia. In strongly calcareous soils, plants may reduce  $\text{Ca}^{2+}$  toxicity by  $\text{CaCO}_3$  precipitation in vacuoles of root cortical cells. This leads to calcification of the root cortex and formation of another type of rhizoliths termed calcified roots (Jaillard, 1987) (Fig. 3 bottom).
- C) Hypocoatings or pseudomycels are formed by penetration of percolating water through the soil matrix and rapid precipitation of  $\text{CaCO}_3$  around large and medium soil pores (Fig. 4). Rapid precipitation is common because of the strong  $p\text{CO}_2$  decrease in these pores compared to the micro-pores. Hypocoatings may also be formed by a fluctuating water table (Durand et al., 2010). Because of fast precipitation, this form of  $\text{CaCO}_3$  is young, potentially forming within weeks to months.
- D) Nodules (Fig. 5) are formed *in situ* by impregnation of soil matrix with  $\text{CaCO}_3$  at specific locations (Durand et al., 2010). This

**Table 1**  
Characteristics of the most common pedogenic carbonate features in soils<sup>1</sup>.

PC features	Characteristics					Formation <sup>5</sup> category	Formation time scale
	Shape	Size	Density <sup>2</sup>	Porosity <sup>3</sup>	Impurities <sup>4</sup>		
<i>PC features mostly related to biotic controls</i>							
Earthworm biospheroliths <sup>A</sup>	Spheroidal	Few mm	High	Moderate	Moderate	4	Days
Calcified root cells <sup>B</sup>	Branch shape structures	Less than mm in diameter and up to few cm length	Low	High	Low	4	Weeks to months
Rhizoliths <sup>B</sup>	Cylindrical structures	Up to several cm in diameter and up to several meters length	High	Moderate	Low to high outward root center	4	Months to years
Needle fiber calcite	Microscopic needle shape crystals	Some $\mu\text{m}$	Very high	Very low	Very low to pure calcite	4 or could be even not pedogenic	Days
Pseudomorph calcite after gypsum	Microscopic lenticular crystals	Some $\mu\text{m}$	Very high	Very low	Very low to pure calcite	Not clear, probably 4	Not clear
<i>PC features mostly related to abiotic controls</i>							
Soft masses	Diffuse powder	Visible powder	Low	High	Low	probably 3	Weeks
Hypocoatings <sup>C</sup>	Laminated carbonate inside soil matrix and along soil pores	Few mm thickness with diffuse boundary into soil matrix	High	Low	High	2	Weeks to months
Nodules <sup>D</sup>	Spheroidal	Few mm to few cm in diameter	Low to very high	Low to very high	High	3	Decades
Clast Coatings <sup>E</sup>	Laminated carbonate beneath (or at the top of) clasts	Few mm to few cm thickness, the same length as related clast	High	Low	Moderate	1, (2) <sup>6</sup>	Centuries to millennia
Calcretes <sup>F</sup>	Cemented horizon <sup>7</sup>	At least 10 cm	Very high	Very low	High	2, (1, 3, 4)	Millennia
Laminar caps <sup>G</sup>	Laminated horizon <sup>7</sup>	Few mm to even meter	Very high	Very low	Very low	1, (4)	Millennia

<sup>1</sup> The information for pedogenic carbonate features were inferred considering data in: Alonso-Zarza, 1999; Amundson et al., 1997; Barta, 2011; Becze-Deàk et al., 1997; Brock and Buck, 2005; Candy et al., 2005; Durand et al., 2010; Gile et al., 1966; Gocke et al., 2011a; Khormali et al., 2006; Klappa, 1980; Kovda et al., 2003; Pustovoytov and Leisten, 2002; Rabenhorst and Wilding, 1986; Verrecchia and Verrecchia, 1994; Versteegh et al., 2013; Villagran and Poch, 2014; Wieder and Yaalon, 1982.

<sup>2</sup> Low: 1.5–1.6, moderate: 1.6–1.7, high: 1.7–1.8, very high: 1.8–> 2 g cm<sup>-3</sup>.

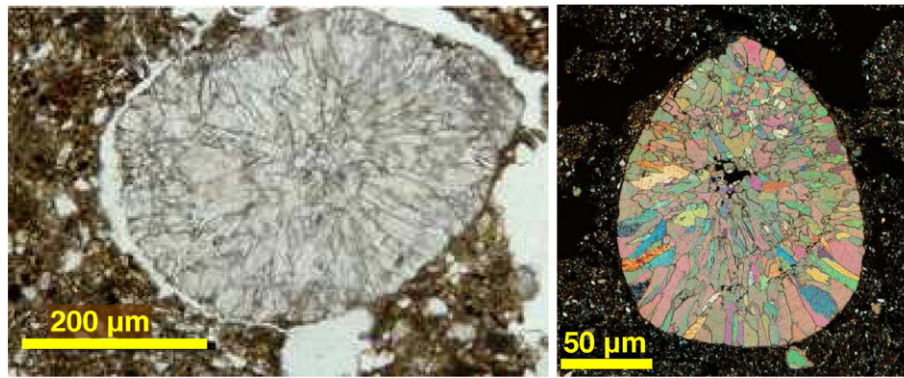
<sup>3</sup> Very low: <5, low: 5–20, moderate: 20–30, high: >30%.

<sup>4</sup> Very low: <10, low: 10–30, moderate: 30–50, high: >50% (minerals or particles other than calcite).

<sup>5</sup> See Section 2.2. (Formation mechanisms of pedogenic carbonate).

<sup>6</sup> In parentheses: probable mechanism(s) other than the main one.

<sup>7</sup> Calcretes and laminar caps are new soil horizons which are formed by cementation.



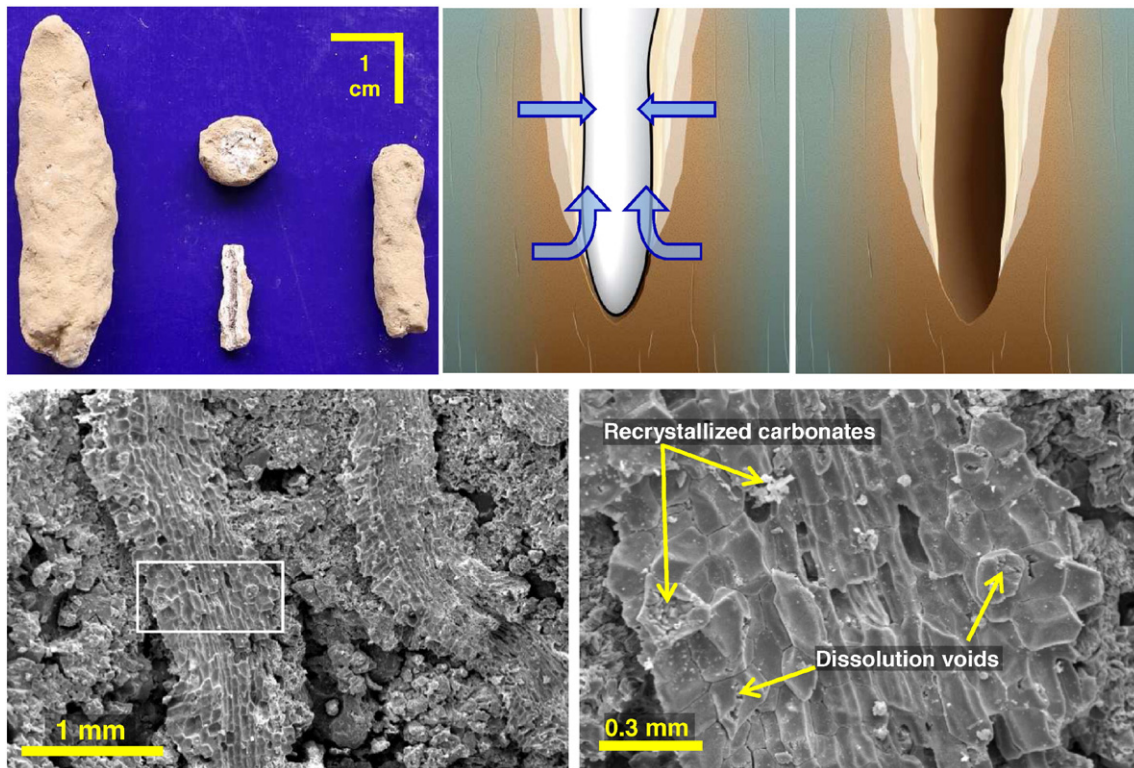
**Fig. 2.** Earthworm biospheroliths. Left: Plain Polarized Light; PPL (Verrecchia, 2011); Right: Cross Polarized Light, XPL (courtesy O. Ehrmann). Earthworm biospheroliths are produced by earthworms' calciferous glands, which release  $\sim 0.8 \text{ mg CaCO}_3 \text{ earthworm}^{-1} \text{ day}^{-1}$  (Lambkin et al., 2011). The thin section of biospherolith (right) is kindly provided by Dr. Otto Ehrmann (Bildarchiv Boden, <http://www.bildarchiv-boden.de>).

impregnation creates the diffuse and gradual outer boundaries of the nodules, and the internal fabric of the nodules remains similar to the host soil (Durand et al., 2010). Although nodules are one of the most common forms of PC, the formation processes and localization of nodules remain unclear. The  $\text{CaCO}_3$  accumulation probably initially begins around a nucleus, e.g. mineral particles, organic remnants, particles of GC or biospheroliths. Sometimes, nodules have a sharp outer boundary as well as a dissimilar fabric as does the host soil (Fig. 5). This probably reflects soil turbation or translocation of nodules from other horizons or other parts of the landscape by means of deposition (Kovda et al., 2003).

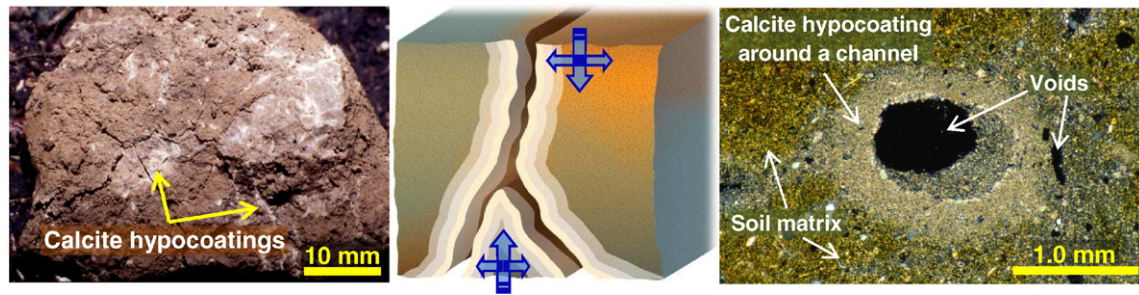
E) Coatings on clasts are formed by slowly percolating water becoming trapped on the bottom of clasts such as stone particles.

Subsequent desiccation by evaporation or water uptake by roots supersaturates the trapped water with  $\text{CaCO}_3$ .  $\text{CaCO}_3$  then precipitates in microlayers on the bottom of clasts (Fig. 6). The microlayers usually have light and dark colors, reflecting the presence of impurities. The light-colored microlayers are mostly comprised pure calcite, but the darker one may contain organic compounds and/or minerals other than  $\text{CaCO}_3$  (Courty et al., 1994; Durand et al., 2010). The formation period of coatings is centuries to millennia. Therefore, radiocarbon dating and the stable isotope composition ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) of microlayers represent an informative chronological and paleoenvironmental proxy (Fig. 6 left) (Pustovoytov, 2002).

The formation mechanism of clast coatings, however, is not always similar to that of stalactites. The presence of cracks



**Fig. 3.** Rhizoliths (top) and calcified roots (bottom). Top left: Rhizoliths formed in loess deposits, Nussloch, south-west Germany (© Zamanian), Top middle and right: Rhizolith formation stages by soil solution mass flow towards the roots by water uptake (top middle) leading to  $\text{Ca}^{2+}$  accumulation and  $\text{CaCO}_3$  precipitation in the rhizosphere. Root water uptake leads to supersaturation of  $\text{CaCO}_3$  and precipitation of carbonates, e.g. as calcite along the root. After root death and decomposition of organic tissues the rhizolith remains in soil (top right). Bottom left: Calcified roots formed in soils on alluvial deposits (© Zamanian). Bottom right: The magnification of the rectangle on bottom left; note the preserved cell structure and dissolution/re-precipitation in cells.



**Fig. 4.** Carbonate hypocoatings. Left: Hypocoatings inside the soil matrix and around the soil pores or cracks (© Kuzyakov), Center: Hypocoating formation by water evaporation or sudden decrease of  $\text{CO}_2$  partial pressure in large pores, leading to  $\text{CaCO}_3$  precipitation inside the soil matrix and around large pores. Right: Cross section of PC hypocoating around a pore (XPL) (Courtesy O. Ehrmann). The thin-section of calcite hypocoating around a channel (right) is kindly provided by Dr. Otto Ehrmann (Bildarchiv Boden, <http://www.bildarchiv-boden.de>).

between the coating and the clast surface creates free space for precipitation of new carbonates (Brock and Buck, 2005). Coatings may also form at the top of clasts in regions with summer/fall precipitation. In wet summers, the stone surface will be warmer than the soil solution, leading to supersaturation of bicarbonate on the stone top and consequently  $\text{CaCO}_3$  precipitation (Amundson et al., 1997). The alteration in clast coating orientation (i.e. mostly at the bottom of clast), however, is an indicator of soil disturbance (Fig. 5 right).

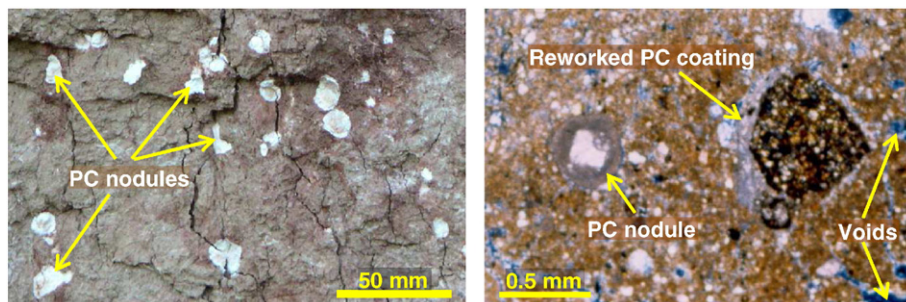
- F) Calcrete: The soil horizon impregnated and cemented with PC is termed calcrete (Goudie, 1972; Reeves, 1970) (Fig. 7). Calcrete reflects the recent or past existence of a shallow groundwater table. Fluctuating groundwater levels accompanied with intensive evapotranspiration accumulate carbonates in soil horizons (Khadkikar et al., 1998; Knuteson et al., 1989), leading to their cementation and the formation of calcrete (Fig. 8). Cementation by  $\text{CaCO}_3$  may occur also by 1) leaching of dissolved  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ions from upper horizons (Fig. 8) (Gile et al., 1966; Machette, 1985), or 2) dissolution of  $\text{Ca}^{2+}$  containing rock (i.e. limestone) and carbonate precipitation without translocation of dissolved ions (Rabenhorst and Wilding, 1986; West et al., 1988). Biological activities such as bio-mineralization of roots lead to the formation of laminar crusts known as rootcretes in soil (Verrecchia et al., 1993; Wright et al., 1996). Nonetheless, huge  $\text{CaCO}_3$  amounts accumulated as calcrete cannot be explained by the translocation of dissolved ions within the soil profile. They clearly reflect the  $\text{Ca}^{2+}$  relocation from higher landscape positions (Sauer et al., 2015). Considering the formation mechanisms, the properties of calcretes, however, will be different: for instance, the presence of high Mg-calcite is an indication of groundwater calcrete (Miller et al., 1985). The necessary time span for calcrete formation is millennia or longer. Soil erosion or deposition may change the depth of maximum PC accumulation (Alonso-Zarza, 2003; Gile, 1999) and

prolong or shorten the formation period of calcrete (See Section 2.4. Topography and soil position in the landscape and soil age). The thickness of calcrete, its location, micromorphology and formation stages are useful indicators of development and age of soils and landscapes (Adamson et al., 2015; Gile et al., 1966).

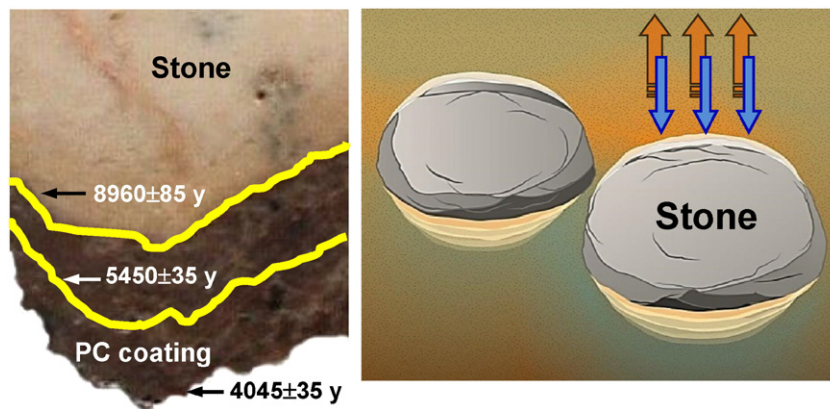
- G) Laminar caps are formed in the presence of several restrictions for vertical water percolation and the subsequent formation of a perched water table (Alonso-Zarza, 2003; Gile et al., 1966). Restricted water permeability leads to lateral water movement at the top of the low permeable zone. Such low permeable zones can for example be an existing calcrete or hard bedrock (Rabenhorst and Wilding, 1986). When the soil becomes dry, PC will precipitate in microlayers at the top of the low permeable zone and further decrease the permeability. A laminar cap forms a new horizon in the soil, which is nearly entirely occupied with PC and is impermeable to roots. Clay minerals and organic matter comprise non-calcareous materials in this horizon, and soil skeletal particles and coarse fragments such as pebbles and gravels are present in minor amounts and lower than 1% (Fig. 7) (Brock and Buck, 2009; Gile et al., 1966). The formation of a laminar cap may also be controlled by biological activity (e.g. Cyanobacteria, fungi or horizontal plant roots) (Verrecchia et al., 1995) in the same manner as calcrete formation.

#### 2.4. Factors affecting pedogenic carbonate accumulation in soil

A large complex of several external and internal as well as biotic and abiotic factors affects the formation processes, accumulation rates and total amounts of PC. The external factors such as climate, topography and organisms mainly affect PC localization and PC formation rates. These factors mainly affect the water balance and  $\text{CO}_2$  content in the



**Fig. 5.** Carbonate nodules. Left: PC nodules at lower depths (150 cm) of Voronic Chernosem, “Stone Steppe”, Russia (© Kuzyakov); Right: Cross section of PC nodule and clast coating in the topsoil (A horizon; 0–11 cm) in petric Calcisol (Zamanian, 2005). Photomicrograph is in XPL.



**Fig. 6.** Carbonate coatings on stones. Left: PC accumulation underneath stone particle (i.e. clast coating) and the chronological sequence of microlayers in PC coatings (Pustovoytov et al., 2007); Right: Coating formation by percolating water remaining underneath the coarse fragments (e.g. stones). The soluble ions (i.e.  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ ) will precipitate during soil dryness on the bottom side of the stone. In specific conditions, coatings may form on the upper side of stones (Amundson et al., 1997). The blue arrows show downward migration of water from the soil surface which may partly remain underneath stones. The orange arrows show water evaporation leading to soil dryness and supersaturation of the trapped solution and thus  $\text{CaCO}_3$  precipitation.

soil air. The internal soil factors such as parent material and physical and chemical properties are mainly responsible for the total amount of PC, its morphology and impurities.

#### 2.4.1. Climate

Climate, i.e. precipitation and temperature, is suggested as the main controlling factor for PC formation and localization (Borchardt and Lienkaemper, 1999; Eswaran et al., 2000). The amount and seasonal distribution of mean annual precipitation controls the depth of carbonate leaching and accumulation (Egli and Fitze, 2001) (see Section 1.2) (Fig. 9). Therefore, accumulation of PC near the soil surface is common for precipitation <500 mm (Landi et al., 2003; Retallack, 2005). Moreover, MAP controls the soil moisture regime and so, affects the morphology of PC features. For instance, drier conditions may lead to formation of euhedral or well-shaped  $\text{CaCO}_3$  crystals, whereas anhedral crystals with irregular and broken boundaries are formed at more humid periods (Kuznetsova and Khokhlova, 2012).

The effect of temperature on PC formation, accumulation and localization is complicated. PC can accumulate in soils in a wide range of temperatures from very hot conditions in hot deserts (Amit et al., 2011; Thomas, 2011) to cold climatic zones such as tundra (Courty et al., 1994; Pustovoytov, 1998). Increasing temperature decreases  $\text{CO}_2$  solubility (Krauskopf and Bird, 1994), which directly affects the supersaturation of soil solution with  $\text{CaCO}_3$  (Barker and Cox, 2011). Increasing temperature, however, boosts microbial respiration and thus increases the  $\text{CO}_2$  concentration in soil air (Lal and Kimble, 2000). This biotic effect of temperature overwhelms the abiotic effect of  $\text{CO}_2$  solubility (Gocke and Kuzyakov, 2011). Accordingly, higher temperatures increase the PC accumulation rates (Candy and Black, 2009; Gocke and Kuzyakov, 2011). Faster rates (due to warmer conditions) lead to more impurities such as rare earth elements (REE) in the PC structure (Gabitov et al., 2008; Violette et al., 2010). The presence of such co-precipitates affects the dissolution rate of PC after formation as well as its morphology and crystal size (Eisenlohr et al., 1999) (see Section 4.3.2).

The temperature controls PC morphology and the formation of  $\text{CaCO}_3$  polymorphs (Ma et al., 2010). Increase of temperature decreases the  $[\text{CO}_3^{2-}]/[\text{Ca}^{2+}]$  ratio and so, aragonite formation is favored instead of calcite or vaterite (Ma et al., 2010).

In conclusion, the balance between MAP (total amount and seasonality) and evapotranspiration (driven by temperature and wind speed) determines the rates and the amounts of PC as well as the depth of PC accumulation. Hence PC are formed during soil drying when

evapotranspiration exceeds precipitation (Birkeland, 1999; Gile et al., 1966; Hough et al., 2014; Rawlins et al., 2011).

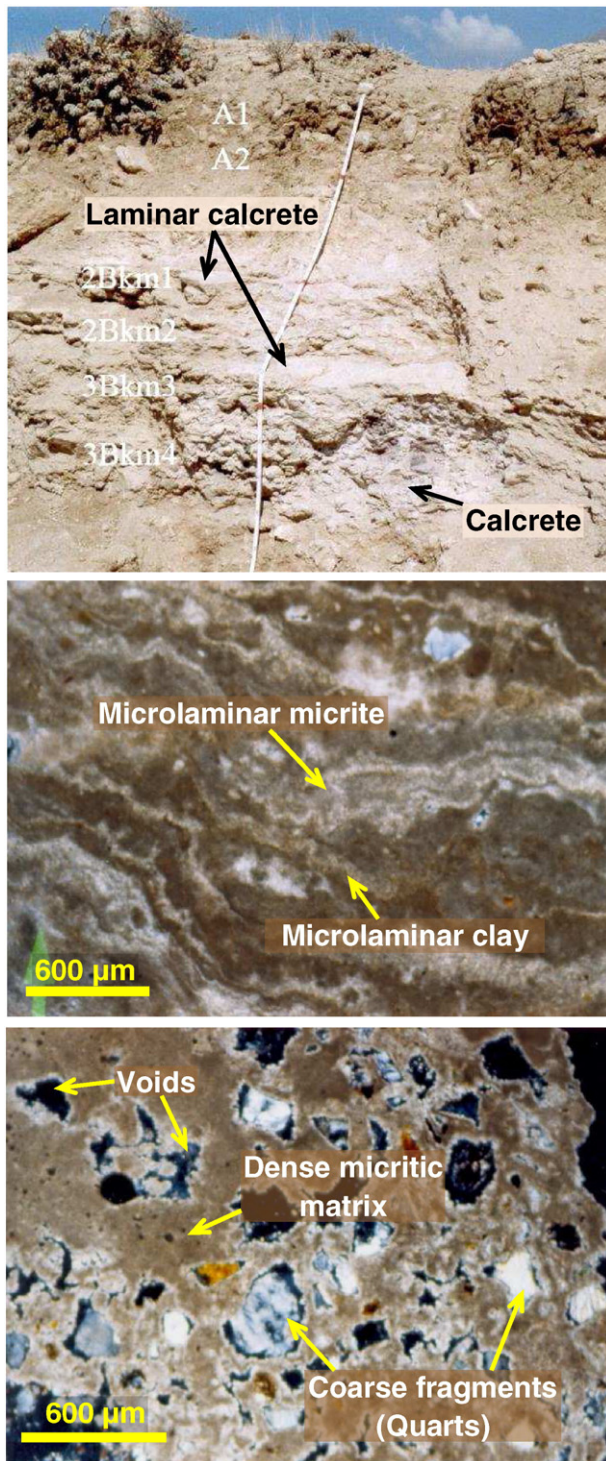
#### 2.4.2. Soil parent material

Soil parent material and the Ca source for  $\text{CaCO}_3$  precipitation affect the total amount, formation rates, mineralogical and isotopic composition of PC. There is more PC in soils formed on calcareous parent materials (Díaz-Hernández et al., 2003; Schlesinger et al., 1989). Moreover, thicker PC coatings form under limestone particles (i.e. particles larger than 1 cm) compared to sandstones (Pustovoytov, 2002; Treadwell-Steitz and McFadden, 2000). The source of Ca for PC formation can be examined by pursuing trace elements in the PC structure as well as examining the isotopic composition, e.g. Ca originated from atmospheric deposition is evident by similar  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in aerosols and accumulated PC (Chiquet et al., 1999).  $\delta^{13}\text{C}$  of PC on calcareous vs. non-calcareous parent materials usually shows a higher heterogeneity i.e. wider range of  $\delta^{13}\text{C}$ , because GC such as limestone particles remain inside the PC structure (Kraimer and Monger, 2009). In aeolian deposits, however, the finer particle size distribution of calcareous dust may lead to complete dissolution of GC and thus less  $\delta^{13}\text{C}$  heterogeneity in PC features (Kraimer and Monger, 2009). The weathering of non-calcareous parent materials contributes to the localization of cations such as rare earth elements, uranium, barium etc. as impurities in PC structure (Violette et al., 2010; Yang et al., 2014).

The weathering of non-calcareous parent materials such as igneous rocks in some old soils may provide nearly the total Ca available for PC formation (Landi et al., 2003; Naiman et al., 2000; Whipkey et al., 2000). However, it usually supplies <2% of Ca in precipitated PC (Capo and Chadwick, 1999). The presence of co-precipitated cations from parent material in the PC structure changes the crystallographic parameters of  $\text{CaCO}_3$  and controls the crystal morphology (Klein, 2002). For instance, impurities decrease the crystal size (Catoni et al., 2012). Elongated and needle-shaped crystals are formed in solution at higher concentrations (100 ppb) of  $(\text{REE}^{3+})/(\text{Ca}^{2+})$ , while rhombohedral and prismatic crystals are common at lower concentrations (10 ppb) (Barker and Cox, 2011). The impurities also inhibit PC dissolution because they remain on the crystal surface and decrease ion exchange (Eisenlohr et al., 1999).

Aluminosilicates as well as organic compounds such as fulvic and humic acids are additional impurities (Gabitov et al., 2008; Stumm and Morgan, 1996). The presence of aluminosilicates and organic compounds in PC structure affects crystal growth. For instance, binding of





**Fig. 7.** Calcrete morphology. Top: thick calcrete formed on alluvial deposits comprised two distinct horizons: the lower calcrete contains abundant coarse fragments impregnated and cemented with PC. The upper calcrete–laminar calcrete – comprises negligible coarse fragments but horizontal layers of PC accumulation (profile depth: ca. 150 cm). Middle: PC accumulation as microlayers in the upper calcrete. Bottom: Surrounded coarse fragments with micritic PC in the lower calcrete. Photomicrographs are in XPL (Zamanian, 2005).

carboxyl groups at or near crystal growth sites inhibits the growth rate of  $\text{CaCO}_3$  crystals (Reddy, 2012).

#### 2.4.3. Soil properties

Soil texture, structure, pH, ion strength and composition of soil solution can affect PC formation (Chadwick et al., 1989; Finneran and Morse,

2009; Ma et al., 2010; Reddy, 2012). Soil properties such as texture and structure control the accumulation depth of PC because they affect water holding capacity, water penetration and movement (Chadwick et al., 1989). The pH affects carbonate crystal size and morphology by controlling the supersaturation state of soil solution with  $\text{CaCO}_3$  (Ma et al., 2010). The ratio of bicarbonate/carbonate decreases as the soil pH becomes alkaline (e.g.  $\text{pH} > 8.5$ ). This favors higher nucleation rates and faster precipitation of smaller  $\text{CaCO}_3$  crystals (Ma et al., 2010). Ionic strength controls the mole fraction of free water during  $\text{CaCO}_3$  dissolution (Finneran and Morse, 2009). Therefore,  $\text{CaCO}_3$  dissolution in saline soils takes longer and precipitation occurs earlier compared to salt-free soils.

#### 2.4.4. Topography, soil position in the landscape and soil age

The topography and soil position in a landscape affect the total amounts, the accumulation rate and the accumulation depth of PC. The upper parts of a hillslope may contain no or few PC features, while thick calcretes may form at downslope positions because of groundwater presence or downslope flow of soil solution (Jacks and Sharma, 1995; Khadkikar et al., 1998). Stable land surfaces in a landscape usually show the greatest PC accumulation compared to the other positions. On unstable land surfaces the depth of PC accumulation and the total amount of PC in soil changes due to erosion and deposition.

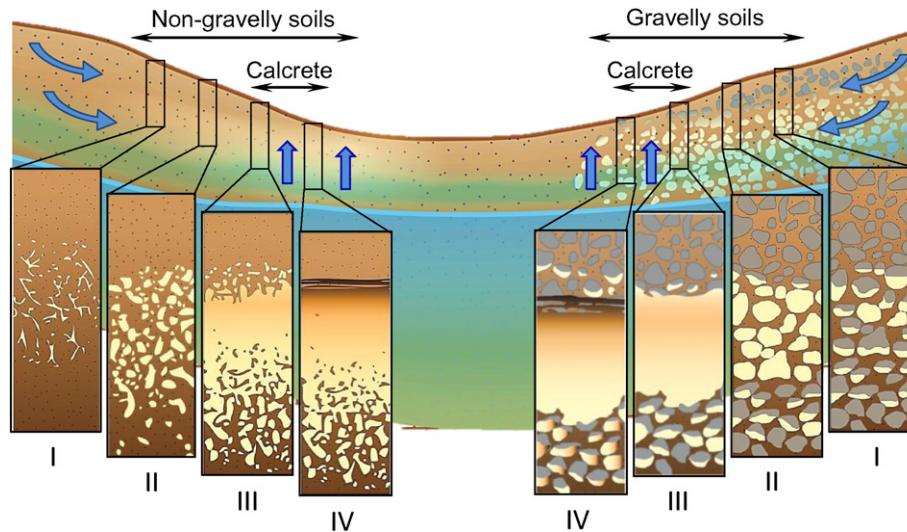
Erosion increases the PC exposure into the percolating water front, and rewetting cycles promotes carbonate dissolution. PC dissolution followed by the translocation of ions leads to less PC accumulation in the soil profile or their deeper localization. It can lead to complex profiles with overprinting over multiple formation phases that have been formed during various climate cycles.

Deposition also changes the depth of water percolation, reducing the PC accumulation in a particular depth of the soil profile (Alonso-Zarza, 2003; Candy and Black, 2009; Gile, 1999). On stable land surfaces, total PC is positively correlated with soil age. Increasing amounts over time also creates various PC morphologies (Adamson et al., 2015; Badía et al., 2009; Bockheim and Douglass, 2006; Díaz-Hernández et al., 2003). Disperse PC accumulations increase with soil age, will be connected to each other and finally plug soil pores, forming calcrete (Fig. 8). Therefore, various morphologies and stages for PC accumulation are used as an indicator of soil development (Fig. 8) (Amoroso, 2006; Gile et al., 1966; Machette, 1985; Pustovoytov, 2003).

#### 2.4.5. Local vegetation and soil organisms

In the presence of active roots, carbonate dissolution increases by 5 to 10 times. Carbonate solubility increases near roots because of (1) up to 100 times higher  $\text{CO}_2$  concentration in the rhizosphere versus atmosphere and (2) up to two units lower local pH because of  $\text{H}^+$  and carboxylic acid release by roots (Andrews and Schlesinger, 2001; Berthelin, 1988; Gocke et al., 2011b). The higher ions concentration leads to two-orders-of-magnitude-faster PC accumulation close to the roots compared to root-free soil (Gocke et al., 2011b; Kuzyakov et al., 2006), e.g. to rhizolith formation (Fig. 3). Note, however, differences in root distribution and thickness as well as variation in root respiration and exudation (Hamada and Tanaka, 2001; Kuzyakov and Domanski, 2002) change the PC formation rates under various plant species. For example, carbonate dissolution and re-precipitation under maize is higher than in soils covered by ryegrass because the root growing rates and exudation are higher under maize.

Soil microorganisms, i.e. bacteria and fungi, are also active in PC formation. If  $\text{Ca}^{2+}$  ions are available in solution, bacteria can produce a visible accumulation of carbonates within a few days (Monger et al., 1991). Extracellular polymers such as polysaccharides and amino acids may also control the morphology of  $\text{CaCO}_3$  (Braissant et al., 2003). For example the presence of aspartic acids favors the formation of needle shape crystals (Braissant et al., 2003). However, even components of bacterial cells such as cell walls may act as nuclei of carbonate precipitation (Perito et al., 2014).



**Fig. 8.** Calcrete formation: Accumulation of PC by  $\text{CaCO}_3$  redistribution within a landscape:  $\text{CaCO}_3$  will be mainly leached from upper parts of the landscape with groundwater (inclined blue arrows) and will be moved to a lower landscape positions. Upward movement of water by capillary rise (vertical blue arrow) will form calcrete at the middle parts of a landscape.  $\text{CaCO}_3$  relocated from higher landscape positions cements the carbonate deposition zone (calcic horizon) and finally form the calcrete (Knuteson et al., 1989). Considering the four steps of Gile et al.'s (1966) model, formation of coatings on clasts is the initial stages of PC accumulation in gravelly soils (right), while in non-gravelly soils (left) nodules would be formed. Connection of coatings as well as nodules by the gradual  $\text{CaCO}_3$  accumulation will plug the soil horizon (stage III) and forms calcrete. Water stagnation at the top of calcrete and subsequent gently drying soil will generate a laminar cap at the top of calcrete in the same way in gravelly and non-gravelly soils (stage IV).

### 3. Carbon and oxygen in pedogenic carbonates

#### 3.1. Sources of carbon, oxygen and calcium in pedogenic carbonates

Carbon in PC originates from dissolved  $\text{CO}_2$  in soil solution (Eqs. (1), (2)). Respiration of roots and microorganisms and the decomposition of

litter and SOM are the sole  $\text{CO}_2$  sources in the soil air during the growing season (Karberg et al., 2005). However, in frozen soils or soils with very low respiration rates (e.g. dry hot deserts), the  $\text{CO}_2$  concentration is partly controlled by the diffusion of atmospheric  $\text{CO}_2$  into the soil (Cerling, 1984).

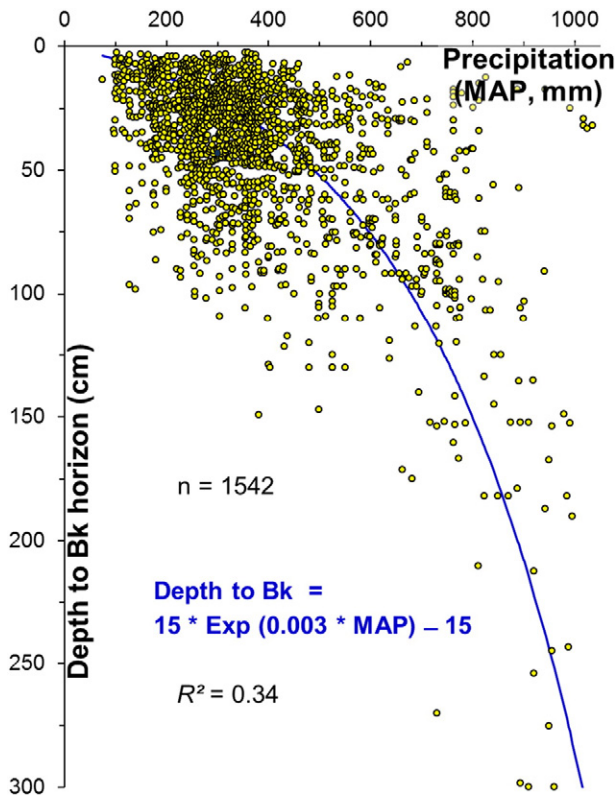
The source of oxygen in PC is related more to the soil water than to soil  $\text{CO}_2$ . This is confirmed by the close correlation between  $\delta^{18}\text{O}$  of PC and mean  $\delta^{18}\text{O}$  of local meteoric water (Cerling, 1984; Cerling and Quade, 1993).

Calcium in PC can originate from three sources: (1) dissolution of GC as limestone (and/or to a lesser extent dolostone) (Kelly et al., 1991; Rabenhorst and Wilding, 1986), (2) atmospheric deposition, which is the main source of Ca especially in non-calcareous soils (Naiman et al., 2000) and (3) weathering of Ca-bearing minerals other than carbonates (Landi et al., 2003; Naiman et al., 2000; Whipkey et al., 2000) such as augite, apatite, hornblende, gypsum, oligoclase and plagioclase.

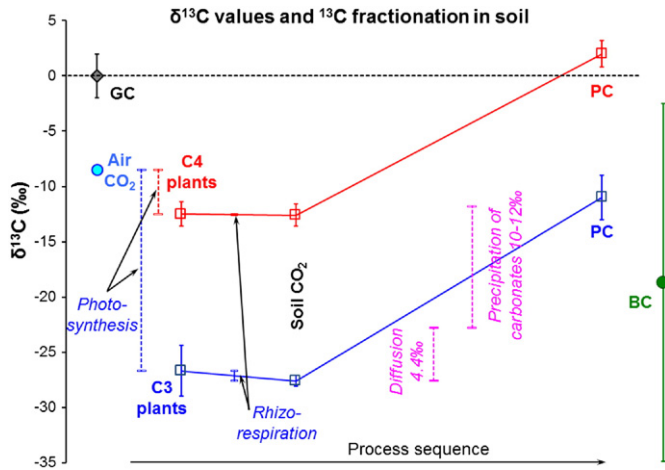
#### 3.2. Isotopic composition of carbon ( $\delta^{13}\text{C}$ , $\Delta^{14}\text{C}$ ) and oxygen ( $\delta^{18}\text{O}$ ) in pedogenic carbonates

The isotopic signature of PC –  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  – is controlled by the isotopic composition of soil  $\text{CO}_2$  and of water, respectively (Cerling, 1984). During the growing season, root and microorganism respiration is high and represents the only  $\text{CO}_2$  source in soil (Cerling, 1984); the relative abundance of  $\text{C}_3$  and  $\text{C}_4$  plants in the local vegetation controls the  $\delta^{13}\text{C}$  value of PC (Fig. 10). Due to isotopic discrimination by photosynthetic pathways, the  $\delta^{13}\text{C}$  of  $\text{CO}_2$  under  $\text{C}_3$  plant species ( $-27\%$  on average) differs from that under  $\text{C}_4$  species ( $-13\%$  on average) (Cerling et al., 1997). Further isotopic discrimination results from  $\text{CO}_2$  diffusion in soil (ca.  $+4.4\%$ ) and carbonate precipitation (ca.  $+11\%$ ). Consequently, PC are  $^{13}\text{C}$  enriched by about  $15\%$  compared to the respired  $\text{CO}_2$ . The values are ca.  $-12\%$  under pure  $\text{C}_3$  and  $+2\%$  under pure  $\text{C}_4$  vegetation (Fig. 10).

Since root and rhizomicrobial respiration are the dominant  $\text{CO}_2$  sources in soils (Kuz'yakov, 2006a), SOM decomposition has a minor effect on  $^{13}\text{C}$  of PC (Ueda et al., 2005). Diffusion of atmospheric  $\text{CO}_2$  (global average  $\delta^{13}\text{C} = -8.5\%$  in 2015) can further enrich  $^{13}\text{C}$  in PC. Nonetheless, the effect of diffused atmospheric  $\text{CO}_2$  is restricted maximally to the



**Fig. 9.** Correlation between the mean annual precipitation (MAP) and the upper depth of the pedogenic carbonate horizon (Bk) (data in Heidari et al., 2004; Khormali et al., 2012, 2006, 2003; Khresat, 2001; Kovda et al., 2014; Kuz'yakov, 2006b; Royer, 1999,  $n = 1542$ ).



**Fig. 10.** The  $\delta^{13}\text{C}$  values of carbonate forms in soil (changed after Nordt et al., 1996). The  $\delta^{13}\text{C}$  isotopic composition of soil  $\text{CO}_2$  and thus of pedogenic carbonates (PC) is controlled by local vegetation ( $\text{C}_3$  or  $\text{C}_4$  plants) (Cerling, 1984). The mean  $\delta^{13}\text{C}$  value and standard deviation for biogenic carbonates (BC) are calculated from: Dettman et al., 1999; Prendergast et al., 2015; Pustovoytov et al., 2010; Regev et al., 2011; Riera et al., 2013; Stern et al., 1994. Note the different  $^{13}\text{C}$  fractionation by rhizorespiration for  $\text{C}_3$  and  $\text{C}_4$  plants (Werth and Kuzyakov, 2010). The  $^{13}\text{C}$  fractionations are presented with dashed lines and mentioned in italics.

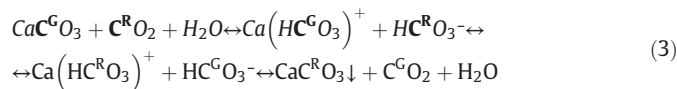
upper 50 cm of the soil (Cerling, 1984) and is negligible in the presence of vegetation.

The  $\Delta^{14}\text{C}$  of PC is determined by biological activities in soil. In contrast to  $\delta^{13}\text{C}$ , SOM decomposition affects  $\Delta^{14}\text{C}$  in PC. Therefore, the relative proportion of  $\text{CO}_2$  respired by the rhizosphere and the  $\text{CO}_2$  released from SOM decomposition determine the  $^{14}\text{C}$  abundance in PC. The contribution of SOM decomposition to  $^{14}\text{C}$  abundance in PC, however, is more important in deeper horizons. This is because the SOM age mostly increases with soil depth (i.e. the older the SOM, the more depleted the  $^{14}\text{C}$  abundance) (Amundson et al., 1994).

The  $\delta^{18}\text{O}$  of PC is controlled by the oxygen isotopic composition of meteoric water, from which carbonates originate (Cerling, 1984). Increasing evaporation leads to higher  $\delta^{18}\text{O}$  depletion in PC (Liu et al., 1996; Zhou and Chafetz, 2010). Since the temperature controls the amount of evaporation, changes in the isotopic composition of meteoric water corresponds to mean annual air temperature (MAAT) (Cerling, 1984; Hsieh et al., 1998a, 1998b).

#### 4. Implications of PC in paleoenvironmental and chronological studies

$\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  as well as  $\Delta^{14}\text{C}$  of PC are valuable proxies for paleoenvironmental and chronological investigations (Feakins et al., 2013; Levin et al., 2011; Monger et al., 2009; Pustovoytov et al., 2007a, 2007b; Wang et al., 1996). Dissolution of SIC and re-precipitation of dissolved ions (i.e.  $\text{Ca}^{2+}$  and DIC species) takes place under complete equilibrium with soil air  $\text{CO}_2$  (Eq. 3) (Cerling, 1984; Nordt et al., 1996).



where the index  $\text{G}$  reflects the origin of carbon from geogenic carbonate present in soil before dissolution and  $\text{R}$  reflects the carbon origin from  $\text{CO}_2$  respired by roots and microorganisms. Therefore, substituting  $\text{HC}^{\text{G}}\text{O}_3^-$  by  $\text{HC}^{\text{R}}\text{O}_3^-$  will conserve the  $\delta^{13}\text{C}$  fingerprints of dominant vegetation within accumulated PC (Fig. 10) (Amundson et al., 1989; Cerling et al., 1989).

The  $\Delta^{14}\text{C}$  of PC is applied to determine the absolute age of soils, sediments, cultural layers and late-Quaternary geomorphological units (Amundson et al., 1994; Chen and Polach, 1986; Gile, 1993;

Pustovoytov et al., 2007a, 2007b; Pustovoytov and Leisten, 2002; Wang et al., 1996). The radiocarbon ages help to distinguish between individual stages of PC formation and correlate them to past environmental changes (Fig. 6) (Candy and Black, 2009; Pustovoytov et al., 2007a, 2007b).

Along with radiocarbon dating (age limit up to 60,000 years), the Th/U-technique allows estimation of crystal growth within longer time intervals during soil formation (age determination up to over 500,000 y) (Ku et al., 1979; Sharp et al., 2003; Candy et al., 2005; Durand et al., 2007; Blisniuk et al., 2012). Uranium may be incorporated into the PC structure as impurities during crystal growth (see Section 3.3, parent material). The broader age range that can be determined is the major advantage of application of the Th/U-dating to Quaternary carbonate materials. Some sedimentological settings have been suggested to be favorable for diagenetic contamination of carbonate by environmental uranium, which may result in younger measured ages (McLaren and Rowe, 1996). However, the Th/U ages of different carbonate samples usually show a good match with independently estimated ages of their contexts. Such inter comparisons are based on archeological age estimations (Magnani et al., 2007), OSL and radiocarbon dating (Magee et al., 2009) or their combinations (Clark-Balzan et al., 2012). Although the sample quantities required for Th/U dating are larger compared to the  $^{14}\text{C}$  AMS procedure, substantial reduction in sample size can be achieved through the use of multi-collector inductively coupled plasma mass spectrometry (Seth et al., 2003) and laser ablation techniques (Spooner et al., 2016).

Since the  $\delta^{13}\text{C}$  of PC reflects that of soil  $\text{CO}_2$  and is related to the  $p\text{CO}_2$  in soil air and in the atmosphere, the  $\delta^{13}\text{C}$  of PC can be used as a  $\text{CO}_2$  paleobarometer to estimate the atmospheric  $\text{CO}_2$  concentration during the formation time of PC (Huang et al., 2012; Retallack, 2009). This  $\text{CO}_2$  paleobarometer shows a high potential for paleosols covered with pure  $\text{C}_3$  vegetation (presumably most pre-Miocene soils) or if the proportion of  $\text{C}_4$  biomass can be estimated (for example, if the humus horizons are preserved) (Ekart et al., 1999; Royer et al., 2001).

The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in the lattice of PC crystals enable estimating the temperature of PC formation (Ghosh et al., 2006a). The combination of  $^{13}\text{C}$  and  $^{18}\text{O}$  in  $\text{CaCO}_3$  crystals, known as  $\Delta_{47}$  or clumped isotopes, is the measuring  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  connected in one molecule simultaneously, for instance as  $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ . The  $\Delta_{47}$  value in a crystal lattice depends only on the environmental temperature: increasing the temperature will decrease the  $\Delta_{47}$  in that crystal (Eiler, 2007). Therefore, the  $\Delta_{47}$  value in PC can be used as a paleothermometer to estimate the temperature during PC formation (Ghosh et al., 2006a; Versteegh et al., 2013). The estimated PC formation temperature and the relation between environmental temperature and elevation enable drawing conclusions about the uplift range of geological surfaces (Ghosh et al., 2006b). Accordingly, the PC features now located at higher elevations with cooler temperature may have been formed in warmer environments (Peters et al., 2013).

#### 5. Recrystallization of soil carbonates

All the above-mentioned applications of  $\delta^{13}\text{C}$ ,  $\Delta^{14}\text{C}$ ,  $\delta^{18}\text{O}$  and clumped isotopes in PC are based on two assumptions:

- (1) The formed PC feature is completely free of GC admixtures.
- (2) The formed PC feature represents a geochemically closed system.

This means PC experiences no further cycle(s) of dissolution and re-precipitation (= recrystallization) after initial formation.

Deviations from these assumptions reveal uncertainties in chronological and re-constructional studies based on PC (Cerling, 1991; Pustovoytov and Leisten, 2002; Quast et al., 2006). Because recrystallization rates depend on various biotic and abiotic factors (Gocke et al., 2011b; Gocke and Kuzyakov, 2011), the resulting errors will differ, especially where recrystallization is relatively fast, e.g. in the presence of high root and microbial respiration (Gocke et al., 2011b; Kuzyakov et al., 2006).

The low solubility of carbonates ( $K_{\text{sp}} = 10^{-6} - 10^{-9}$ ) (Robbins, 1985) and consequently low recrystallization rates lead to difficulties

in measuring these rates over short periods. Recently, however, it has been shown that the sensitive  $^{14}\text{C}$  labeling approach (Gocke et al., 2011b; Gocke et al., 2010; Kuzyakov et al., 2006) can contribute to a better understanding of the recrystallization dynamics and their effects on the isotopic composition of C in PC. This technique labels soil air with  $^{14}\text{CO}_2$ . By tracing the  $^{14}\text{C}$  activity of a carbonate sample and knowing the amounts of added C as  $\text{CO}_2$ , the amounts of recrystallized carbonates can be calculated. This approach was used to show the dependence of  $\text{CaCO}_3$  recrystallization rates on (i)  $\text{CO}_2$  concentration in soil (Gocke et al., 2010), (ii) presence of plants with various root systems (Gocke et al., 2011b), (iii) temperature (Gocke and Kuzyakov, 2011), and (iv) migration of recrystallized  $\text{CaCO}_3$  along soil profile (Gocke et al., 2012). The very slow rates assessed by the  $^{14}\text{C}$  labeling approach (about  $0.00003 \text{ day}^{-1}$ ) demonstrated that at least centuries or probably even several millennia are necessary for full recrystallization and thus for complete formation of PC (Kuzyakov et al., 2006). This means that the first assumption may not be achieved even after a long time, at least in PC features formed in loess deposits. Furthermore, the exponential nature of recrystallization (Kuzyakov et al., 2006) – partial redissolution and recrystallization of formed PC – may also make the second assumption questionable.

### 5.1. Uncertainties of paleoenvironmental reconstructions based on pedogenic carbonates

The recrystallization of PC under conditions different from the environment during PC formation (e.g. changes in local vegetation or environmental temperature) will strongly complicate the application of the isotopic signature of PC for paleo-reconstruction studies. The new isotopic signals of a PC feature will reflect the altered and not the original environmental conditions (Pendall et al., 1994). Considering the first assumption, mixing of old PC as well as “dead” (i.e. not applicable for radiocarbon dating) limestone particles with newly formed PC overestimates the absolute ages of soils, landscape or geomorphological surfaces (Pendall et al., 1994; Pustovoytov and Terhorst, 2004). For instance, if only 1% dead limestone particles remain in the structure of a given PC specimen (i.e. not full recrystallization of GC), the age of PC will be overestimated by more than two times. If the amount of remaining GC is 5%, the age overestimation will increase to about 10 times (Kuzyakov et al., 2006). Moreover, the difference of  $\delta^{13}\text{C}$  values of the remaining GC to that of PC (Fig. 10) leads to a less negative  $\delta^{13}\text{C}$  of PC (Pendall et al., 1994; Quast et al., 2006) and consequently to doubtful paleoecological interpretations.

Recrystallization will also affect the stable isotopic signature and interpretations for paleoenvironmental studies and PC-based radiocarbon dating. If only 1% of modern  $^{14}\text{C}$  is mixed with a dead limestone specimen, the age estimation will be 36,500 years. Increasing the contamination with modern  $^{14}\text{C}$  to 10% alters the age of that limestone to about 18,500 years (Williams and Polach, 1969).

PC recrystallization also affects  $\delta^{18}\text{O}$  (Cerling, 1991) and may thus overestimate PC formation temperature by up to  $20^\circ\text{C}$  (Ghosh et al., 2006b). Therefore, interpretation of the  $\delta^{13}\text{C}$ ,  $\Delta^{14}\text{C}$ ,  $\delta^{18}\text{O}$  and  $\Delta_{47}$  signatures in PC for paleoenvironmental reconstructions and dating should consider possible deviations from the above-mentioned assumptions.

Formation of PC following BC dissolution will also affect the chronological and paleoecological interpretations based on BC. In archeological sites, various BC types preserved in soils are frequently used to interpret their isotopic signatures. This includes:

- Shells (i.e. mollusk shells) (Xu et al., 2010; Yanes et al., 2013)
- Bone pieces (Berna et al., 2004; Krueger, 1991; Zazzo et al., 2009)
- Eggshell particles (Janz et al., 2009; Kandel and Conard, 2005; Long et al., 1983; Vogel et al., 2001)
- Tooth enamel and dentin (Feakins et al., 2013; Hedges et al., 1995; Hoppe et al., 2004)

- Old wood ashes (Regev et al., 2011) and calcified fossil seeds (Pustovoytov et al., 2004; Regev et al., 2011).

BC features are used to recognize the settlements or habitats, diet regimes and extinction periods of ancient humans, animals and plants (Hoppe et al., 2004; Janz et al., 2009; Kandel and Conard, 2005) as well as to reconstruct the environmental conditions during their lifetimes (Villagran and Poch, 2014; Xu et al., 2010; Yanes et al., 2013). PC formation and mixing with fossil BC will complicate the results of such paleo-reconstruction studies, e.g. the age of a 45,000 y-old bone will be estimated 20,000 y if only 5% contamination with modern C took place (Zazzo and Saliège, 2011). Paleoenvironmental reconstructions and dating based on PC as well as BC should consider possible recrystallization and isotopic exchange.

### 5.2. Evidence of pedogenic carbonate recrystallization after formation

The recrystallization of PC features after formation can be recognized in isotopic composition as well as morphology. The following evidence confirms the recrystallization of PC features in different environmental conditions as the dominant process during their formation.

- (a) Relatively young radiocarbon ages of PC features compared to geological periods are usually explained by admixtures of modern  $^{14}\text{C}$  during recrystallization (Pustovoytov and Terhorst, 2004). A correspondence between measured  $\Delta^{14}\text{C}$  ages of PC with other chronological data is therefore used to evaluate the PC contamination and the reliability of achieved dates. The other chronological data include stratigraphy of the sampling context or the ages of accompanying datable compounds such as organic C and artefacts (Pustovoytov and Terhorst, 2004; Vogel et al., 2001).
- (b) Large  $\delta^{13}\text{C}$  variation in PC from paleosols with similar ages (and probable similar vegetation and  $p\text{CO}_2$  in the respective geological period) is referred to recrystallization. In contrast, fewer  $\delta^{13}\text{C}$  differences in PC from contrasting geological time spans are also introduced as recrystallization evidence (Quast et al., 2006).
- (c) The size of PC features is positively correlated to the  $\delta^{13}\text{C}$  signature of recently recrystallized carbonates (Kraimer and Monger, 2009). The smaller the PC size, the more  $\delta^{13}\text{C}$  changes due to recrystallization is expected.
- (d) The microscopic indications of PC dissolution under a polarized microscope can be recognized as follows (Durand et al., 2010):

1. PC grains with well-rounded shapes.
2. Presence of crystals with pronounced serration.
3. Formation of mouldic voids (e.g. preferential dissolution of shell fragments leaves empty spaces previously occupied by carbonates).
4. Clay-coating networks without carbonate crystals (formed after partial dissolution of carbonate grains and further clay illuviation with pore filling).
5. Depletion of hypocatings (i.e. soil carbonate-free matrix around voids such as channels).

- (e) The dissolved ions may recrystallize on the former PC feature. The microscopic evidence of such recrystallization is (Durand et al., 2010):

1. Irregular distribution of crystal size and mottled crystal mosaics of different sizes (i.e. replacement of finer crystals with coarser ones).
2. Star-like masses of elongated and radially arranged sparite crystals around a central zone of microsparite crystals.

3. Curved contacts between neighboring sparitic (>20  $\mu\text{m}$ ) carbonate crystals.

## 6. Conclusions and outlook

### 6.1. Conclusions

Various formation mechanisms and environmental factors result in distinct morphological features of PC such as nodules and coatings, which form in various time spans – from a few weeks (e.g. hypocoatings) and decades (e.g. rhizoliths) to hundreds of thousands or even millions of years (e.g. calcrete). PC forms therefore reflect soil genesis processes and record the effects of soil-forming factors.  $\delta^{13}\text{C}$ ,  $\Delta^{14}\text{C}$  and  $\delta^{18}\text{O}$  as well as  $\Delta_{47}$  in PC are valuable tools for paleoenvironmental reconstructions and soil age estimation. PC features, however, have variable physical and chemical properties including various  $\text{CaCO}_3$  contents and impurities. This reflects the response of PC features to environmental conditions such as changes in local vegetation or climatic properties. Furthermore, depending on the duration of PC formation period, the isotopic inventory of individual PC features will reveal different resolutions in paleo-reconstruction and chronological studies.

PC can undergo recrystallization after formation. This complicates the interpretations of paleoenvironment records and chronological studies based on PC isotopic composition. Every recrystallization cycle may occur under new environmental conditions – i.e. climate or local vegetation – differing from the previous one. Full or even partial re-equilibration to the new environment will insert new signals into the isotopic inventory of PC. Recrystallization therefore resets the radiometric clock by adding modern  $^{14}\text{C}$  to the isotopic inventory of PC. It can therefore lead to a strongly biased assessment of air  $p\text{CO}_2$  or temperature (as well as vegetation or precipitation) for the period of PC formation. The result is misleading paleoenvironmental reconstructions. Nonetheless, incorporating the variety of PC features (with corresponding formation mechanisms and time, as well as physical and chemical properties and microscopic indications) enables considering how recrystallization may have altered the isotopic composition of PC features.

### 6.2. Future research directions

Based on the overview of the mechanisms and rates of PC formation and of their applications for reconstructing soil genesis and paleoenvironment, as well as considering the huge SIC stocks in soil, the following research directions can be grouped into three issues:

#### (1) Mechanisms and rates of PC formation.

- The effects of biotic processes such as respiration ( $\text{CO}_2$  concentration), carboxylic acid excretion (pH changes) or water uptake (Ca concentration in rhizosphere) by plants and microorganisms on PC formation were shown in a few studies (Kuz'yakov et al., 2006; Monger et al., 1991). However, the biotic activities are frequently disregarded with respect to PC formation. This calls for demonstrating the importance of biota for PC formation under a broad range of environmental conditions. It remains unclear whether PC can be formed in the absence of biological activity at all.
- Both roots and microorganisms may have similar functions in PC formation: respiration, acid release, etc. We are not aware of any study comparing the importance of roots or microorganisms for PC formation. This should be done for individual PC forms.
- Various plant species such as shrubs, grasses and herbs have different root systems, rooting depth and resistance to higher pH due to  $\text{CaCO}_3$  accumulation. How various plant species affect PC formation rates as well as the depth of PC accumulation should be clarified.
- Formation mechanisms of various PC features and the budget of the elements (e.g. Ca) remain unclear. More studies such

as comparisons of the Ca content in parent material as well as in soil layers with PC are needed to identify the Ca source(s) in PC.

#### (2) Implications for paleoenvironment reconstructions and soil genesis.

- The reliability of PC features as proxies for paleoenvironment reconstructions and dating purposes is still questionable because of recrystallization. This calls for quantifying how the environmental factors such as soil moisture, temperature, initial GC content, and the depth of PC formation affect PC recrystallization. In this respect,  $^{14}\text{C}$  labeling of soil  $\text{CO}_2$  showed high potential for understanding the dynamics of carbonate recrystallization in soils (Kuz'yakov et al., 2006). The radiometric ages of PC features should be compared with independently estimated ages of their contexts, such as archeological sites or geomorphic landscape elements. Furthermore, long-term experimental observation of  $\text{CaCO}_3$  alteration with time in native soils can serve as a good complimentary approach.
- Individual PC features, considering variations in their physical and chemical properties, should respond differently to changes in environmental conditions, i.e. will have different recrystallization rates. Therefore, the recrystallization rates of various PC features should be compared under identical environmental conditions.
- A part of  $^{13}\text{C}$  enrichment in PC comparing to the respired  $\text{CO}_2$  is because of soil  $\text{CO}_2$  diffusion (Cerling, 1984). The  $\text{CO}_2$  diffusion in soil (and thus changes in  $\delta^{13}\text{C}$  of PC) is, however, related to soil properties such as soil water content, temperature and clay content as well as the diffusion distance within the soil profile. The above-mentioned 4.4‰  $^{13}\text{C}$  enrichment in soil  $\text{CO}_2$  by diffusion should therefore be analyzed for various soils with contrasting physical and chemical properties.

#### (3) Natural and anthropogenic effects on PC and consequences for the concentration of atmospheric $\text{CO}_2$ .

- The contribution of  $\text{CaCO}_3$  to  $\text{CO}_2$  fluxes from soil to the atmosphere because of fertilization and management is completely unknown. Soil acidification due to urea or ammonium fertilization as well as legume cultivation strongly affects  $\text{CaCO}_3$  dissolution and  $\text{CO}_2$  release to the atmosphere. This calls for investigating the effects of various soil cultivation systems such as fertilizer forms and levels, as well as management practices – till, no-till, liming, irrigation frequency and other managements – on  $\text{CaCO}_3$  dissolution and  $\text{CO}_2$  efflux. These anthropogenic effects on  $\text{CaCO}_3$  dissolution should be compared to the rates of natural acidification processes related to litter decomposition and rhizosphere fluxes of  $\text{H}^+$  ions and organic acids.
- Development of a mechanism-based model predicting the upper and maximal depths of PC accumulation in soil profiles is important for understanding soil genesis as well as fertilization and irrigation management. This requires incorporating the relations between the depth of PC accumulation and various environmental parameters – not only mean annual precipitation as in Fig. 9 but also soil water balance, its seasonal dynamics, the initial carbonate content in parent material and soil physical properties.

Concluding, despite the importance of SIC and PC for terrestrial C stocks and the global C cycle, the number of studies on SIC is very limited, especially compared to those dealing with SOC. Most of these studies were descriptive, focused on the presentation of properties, contents, forms and depths of PC. Only few studies attempted to develop the concepts and models of PC formation mechanisms and relate them to environmental factors. Such a mechanism-based understanding and models will strongly contribute to predicting terrestrial C stocks and changes in

the global C cycle. This will help closely link long-term geological with short-term biological C cycles.

## Acknowledgements

We would like to acknowledge the German Research Foundation (DFG) for their support (KU 1184/34-1). Special thanks to Dr. Otto Ehrmann (<http://www.bildarchiv-boden.de>) for providing us photos of earthworm biospherolith (Fig. 2, right) and calcite hypocoating (Fig. 4, right). Special thanks to Miss. Yue Sun for drawing graphics in Figs. 3, 4, 6 and 8. We would like to thank the Soil Science Department, University of Tehran (Karaj, Iran), for their help in preparing soil thin sections and the University of Tarbiat Modares (Tehran, Iran) for SEM images of calcified root cells (Fig. 3).

## References

- Adams, J.M., Post, W.M., 1999. A preliminary estimate of changing calcrete carbon storage on land since the last glacial maximum. *Glob. Planet. Chang.* 20, 243–256. [http://dx.doi.org/10.1016/S0921-8181\(99\)00015-6](http://dx.doi.org/10.1016/S0921-8181(99)00015-6).
- Adamson, K., Candy, I., Whitfield, L., 2015. Coupled micromorphological and stable isotope analysis of Quaternary calcrete development. *Quat. Res.* xxx. <http://dx.doi.org/10.1016/j.yqres.2015.05.002> (xxx–xxx).
- Alonso-Zarza, A.M., 1999. Initial stages of laminar calcrete formation by roots: examples from the Neogene of central Spain. *Sediment. Geol.* 126, 177–191. [http://dx.doi.org/10.1016/S0037-0738\(99\)00039-1](http://dx.doi.org/10.1016/S0037-0738(99)00039-1).
- Alonso-Zarza, A.M., 2003. Palaeoenvironmental significance of palustrine carbonates and calcretes in the geological record. *Earth-Sci. Rev.* 60, 261–298. [http://dx.doi.org/10.1016/S0012-8252\(02\)00106-X](http://dx.doi.org/10.1016/S0012-8252(02)00106-X).
- Amit, R., Simhai, O., Ayalon, A., Enzel, Y., Matmon, A., Crouvi, O., Porat, N., McDonald, E., 2011. Transition from arid to hyper-arid environment in the southern Levant deserts as recorded by early Pleistocene cummulic Aridisols. *Quat. Sci. Rev.* 30, 312–323. <http://dx.doi.org/10.1016/j.quascirev.2010.11.007>.
- Amoroso, L., 2006. Age calibration of carbonate rind thickness in late Pleistocene soils for surficial deposit age estimation, Southwest USA. *Quat. Res.* 65, 172–178. <http://dx.doi.org/10.1016/j.yqres.2005.06.003>.
- Amundson, R.G., Doner, H.E., Chadwick, O.A., Sowers, J.M., 1989. The stable isotope chemistry of pedogenic carbonates at Kyle Canyon, Nevada. *Soil Sci. Soc. Am. J.* 53, 201. <http://dx.doi.org/10.2136/sssaj1989.03615995005300010037x>.
- Amundson, R., Wang, Y., Chadwick, O., Trombore, S., McFadden, L., McDonald, E., Wells, S., DeNiro, M., 1994. Factors and processes governing the 14C content of carbonate in desert soils. *Earth Planet. Sci. Lett.* 125, 385–405. [http://dx.doi.org/10.1016/0012-821X\(94\)90228-3](http://dx.doi.org/10.1016/0012-821X(94)90228-3).
- Amundson, R., Graham, R.C., Franco-Vizcaino, E., 1997. Orientation of carbonate laminations in gravelly soils along a winter/Summer Precipitation Gradient in Baja California, Mexico. *Soil Sci. Soc. Am. J.* 61, 940–952. <http://dx.doi.org/10.1097/00010694-199712000-00009>.
- Andrews, J.A., Schlesinger, W.H., 2001. Soil CO<sub>2</sub> dynamics, acidification, and chemical weathering in a temperate forest with experimental CO<sub>2</sub> enrichment. *Glob. Biogeochem. Cycles* 15, 149–162. <http://dx.doi.org/10.1029/2000GB001278>.
- Aylward, G.H., 2007. *SI Chemical Data*, Auflage: 6. Auflage. ed. John Wiley & Sons, Milton, Qld.
- Badía, D., Martí, C., Palacio, E., Sancho, C., Poch, R.M., 2009. Soil evolution over the Quaternary period in a semiarid climate (Segre river terraces, northeast Spain). *Catena* 77, 165–174. <http://dx.doi.org/10.1016/j.catena.2008.12.012>.
- Barker, S.L., Cox, S.F., 2011. Oscillatory zoning and trace element incorporation in hydrothermal minerals: insights from calcite growth experiments. *Geofluids* 11, 48–56. <http://dx.doi.org/10.1111/j.1468-8123.2010.00305.x>.
- Barta, G., 2011. Secondary carbonates in loess-paleosol sequences: a general review. *Cent. Eur. J. Geosci.* 3, 129–146. <http://dx.doi.org/10.2478/s13533-011-0013-7>.
- Batjes, N.H., 1996. Total carbon and nitrogen in the soils of the world. *Eur. J. Soil Sci.* 47, 151–163. <http://dx.doi.org/10.1111/j.1365-2389.1996.tb01386.x>.
- Baumhardt, R.L., Lascano, R.J., 1993. Physical and hydraulic properties of a calcic horizon. *Soil Sci. Soc. Am. J.* 57, 368–375. <http://dx.doi.org/10.1097/00010694-199306000-00002>.
- Becze-Deák, J., Langohr, R., Verrecchia, E.P., 1997. Small scale secondary CaCO<sub>3</sub> accumulations in selected sections of the European loess belt. Morphological forms and potential for paleoenvironmental reconstruction. *Geoderma* 76, 221–252. [http://dx.doi.org/10.1016/S0016-7061\(96\)00106-1](http://dx.doi.org/10.1016/S0016-7061(96)00106-1).
- Berna, F., Matthews, A., Weiner, S., 2004. Solubilities of bone mineral from archaeological sites: the recrystallization window. *J. Archaeol. Sci.* 31, 867–882. <http://dx.doi.org/10.1016/j.jas.2003.12.003>.
- Berthelin, J., 1988. Microbial weathering processes in natural environments. In: Lerman, A., Meybeck, M. (Eds.), *Physical and Chemical Weathering in Geochemical Cycles*. NATO ASI Series, Springer Netherlands, pp. 33–59.
- Birkeland, 1999. *Soils and Geomorphology*. Oxford University Press.
- Blisniuk, K., Oskin, M., Fletcher, K., Rockwell, T., Sharp, W., 2012. Assessing the reliability of U-series and 10Be dating techniques on alluvial fans in the Anza Borrego Desert, California. *Quat. Geochronol.* 13, 26–41. <http://dx.doi.org/10.1016/j.quageo.2012.08.004>.
- Bockheim, J.G., Douglass, D.C., 2006. Origin and significance of calcium carbonate in soils of southwestern Patagonia. *Geoderma* 136, 751–762. <http://dx.doi.org/10.1016/j.geoderma.2006.05.013>.
- Boettinger, J.L., Southard, R.J., 1991. Silica and carbonate sources for aridisols on a granitic pediment, Western Mojave Desert. *Soil Sci. Soc. Am. J.* 55, 1057. <http://dx.doi.org/10.2136/sssaj1991.03615995005500040028x>.
- Borchardt, G., Lienkaemper, J.J., 1999. Pedogenic calcite as evidence for an early Holocene dry period in the San Francisco Bay area, California. *Geol. Soc. Am. Bull.* 111, 906–918.
- Braissant, O., Cailleau, G., Dupraz, C., Verrecchia, E.P., 2003. Bacterially induced mineralization of calcium carbonate in terrestrial environments: The role of exopolysaccharides and amino acids. *J. Sediment. Res.* 73, 485–490. <http://dx.doi.org/10.1306/111302730485>.
- Brock, A.L., Buck, B.J., 2005. A new formation process for calcic pendants from Pahranaagat Valley, Nevada, USA, and implication for dating quaternary landforms. *Quat. Res.* 63, 359–367. <http://dx.doi.org/10.1016/j.yqres.2005.01.007>.
- Brock, A.L., Buck, B.J., 2009. Polygenetic development of the Mormon Mesa, NV petrocalcic horizons: geomorphic and paleoenvironmental interpretations. *Catena* 77, 65–75. <http://dx.doi.org/10.1016/j.catena.2008.12.008>.
- Bughio, M.A., Wang, P., Meng, F., Qing, C., Kuzuyakov, Y., Wang, X., Junejo, S.A., 2016. Neof ormation of pedogenic carbonates by irrigation and fertilization and their contribution to carbon sequestration in soil. *Geoderma* 262, 12–19. <http://dx.doi.org/10.1016/j.geoderma.2015.08.003>.
- Callot, G., Chamayou, H., Maertens, C., Salsac, L., 1982. *Mieux Comprendre les Interactions Sol-Racine. Incidence sur la nutrition minerale*. INRA.
- Candy, I., Black, S., 2009. The timing of Quaternary calcrete development in semi-arid southeast Spain: investigating the role of climate on calcrete genesis. *Sediment. Geol.* 218, 6–15. <http://dx.doi.org/10.1016/j.sedgeo.2009.03.005>.
- Candy, I., Black, S., Sellwood, B.W., 2005. U-series isochron dating of immature and mature calcretes as a basis for constructing Quaternary landform chronologies for the Sorbas basin, southeast Spain. *Quat. Res.* 64, 100–111. <http://dx.doi.org/10.1016/j.yqres.2005.05.002>.
- Capo, R.C., Chadwick, O.A., 1999. Sources of strontium and calcium in desert soil and calcrete. *Earth Planet. Sci. Lett.* 170, 61–72.
- Catoni, M., Falsone, G., Bonifacio, E., 2012. Assessing the origin of carbonates in a complex soil with a suite of analytical methods. *Geoderma* 175–176, 47–57. <http://dx.doi.org/10.1016/j.geoderma.2012.01.022>.
- Cerling, T.E., 1984. The stable isotopic composition of modern soil carbonate and its relationship to climate. *Earth Planet. Sci. Lett.* 71, 229–240. [http://dx.doi.org/10.1016/0012-821X\(84\)90089-X](http://dx.doi.org/10.1016/0012-821X(84)90089-X).
- Cerling, T.E., 1991. Carbon dioxide in the atmosphere: evidence from Cenozoic and Mesozoic paleosols. *Am. J. Sci.* 291, 377–400. <http://dx.doi.org/10.2475/ajs.291.4.377>.
- Cerling, T.E., Quade, J., 1993. Stable Carbon and Oxygen Isotopes in Soil Carbonates. In: Lohmann, K.C., McKenzie, J., Savin, S. (Eds.), *Swart, P.K. American Geophysical Union, Climate Change in Continental Isotopic Records*, pp. 217–231.
- Cerling, T.E., Quade, J., Wnag, Y., Bowman, J.R., 1989. Carbon isotopes in soils and paleosols as ecology and paleoecology indicators. *Nature* 341, 139–139. <http://dx.doi.org/10.1038/341138a0>.
- Cerling, T.E., Harris, J.M., MacFadden, B.J., Leakey, M.G., Quade, J., Eisenmann, V., Ehleringer, J.R., 1997. Global vegetation change through the Miocene/Pliocene boundary. *Nature* 389, 153–158. <http://dx.doi.org/10.1038/389153a0>.
- Chadwick, O.A., Sowers, J.M., Amundson, R.G., 1989. Morphology of calcite crystals in clast coatings from four soils in the Mojave desert region. *Soil Sci. Soc. Am. J.* 53, 211–219.
- Chen, Y., Polach, H., 1986. Validity of 14C ages of carbonate in sediments. *Radiocarbon* 28, 464–472. [http://dx.doi.org/10.2458/azu\\_js\\_rc.28.957](http://dx.doi.org/10.2458/azu_js_rc.28.957).
- Chiquet, A., Michard, A., Nahon, D., Hamelin, B., 1999. Atmospheric input vs in situ weathering in the genesis of calcretes: an Sr isotope study at Galvez (Central Spain). *Geochim. Cosmochim. Acta* 63, 311–323.
- Clark-Balzan, L.A., Candy, I., Schwenninger, J.-L., Bouzouggar, A., Blockley, S., Nathan, R., Barton, N.E., 2012. Coupled U-series and OSL dating of a Late Pleistocene cave sediment sequence, Morocco, North Africa: Significance for constructing Palaeolithic chronologies. *Quat. Geochronol.* 12, 53–64.
- Courty, M.-A., Marlin, C., Dever, L., Tremblay, P., Vachier, P., 1994. The properties, genesis and environmental significance of calcitic pendants from the high Arctic (Spitsbergen). *Geoderma* 61, 71–102. [http://dx.doi.org/10.1016/0016-7061\(94\)90012-4](http://dx.doi.org/10.1016/0016-7061(94)90012-4).
- Dettman, D.L., Reische, A.K., Lohmann, K.C., 1999. Controls on the stable isotope composition of seasonal growth bands in aragonitic fresh-water bivalves (unionidae). *Geochim. Cosmochim. Acta* 63, 1049–1057. [http://dx.doi.org/10.1016/S0016-7037\(99\)00020-4](http://dx.doi.org/10.1016/S0016-7037(99)00020-4).
- Díaz-Hernández, J.L., Fernández, E.B., González, J.L., 2003. Organic and inorganic carbon in soils of semiarid regions: a case study from the Guadix-Baza basin (Southeast Spain). *Geoderma* 114, 65–80. [http://dx.doi.org/10.1016/S0016-7061\(02\)00342-7](http://dx.doi.org/10.1016/S0016-7061(02)00342-7).
- Drees, L.R., Wilding, L.P., Nordt, L.C., 2001. Reconstruction of soil inorganic and organic carbon sequestration across broad geoclimatic regions. *Soil Carbon Sequestration and the Greenhouse Effect*, SSSA Special Publication Number 57. Soil Science Society of America (Madison, WI, USA).
- Durand, N., Gunnell, Y., Curmi, P., Ahmad, S.M., 2007. Pedogenic carbonates on Precambrian silicate rocks in South India : origin and paleoclimatic significance. *Quat. Int.* 162–163, 35–49.
- Durand, N., Monger, H.C., Canti, M.G., 2010. Calcium Carbonate Features, in: *Interpretation of Micromorphological Features of Soils and Regoliths*. Elsevier, pp. 149–194.
- Egli, M., Fitze, P., 2001. Quantitative aspects of carbonate leaching of soils with differing ages and climates. *Catena* 46, 35–62. [http://dx.doi.org/10.1016/S0341-8162\(01\)00154-0](http://dx.doi.org/10.1016/S0341-8162(01)00154-0).
- Eiler, J.M., 2007. Clumped-isotope geochemistry—the study of naturally-occurring, multiply-substituted isotopologues. *Earth Planet. Sci. Lett.* 309–327. <http://dx.doi.org/10.1016/j.epsl.2007.08.020>.
- Eisenlohr, L., Meteva, K., Gabrovšek, F., Dreybrodt, W., 1999. The inhibiting action of intrinsic impurities in natural calcium carbonate minerals to their dissolution kinetics in aqueous H<sub>2</sub>O–CO<sub>2</sub> solutions. *Geochim. Cosmochim. Acta* 63, 989–1001. [http://dx.doi.org/10.1016/S0016-7037\(98\)00301-9](http://dx.doi.org/10.1016/S0016-7037(98)00301-9).

- Ekart, D.D., Cerling, T.E., Montanez, I.P., Tabor, N.J., 1999. A 400 million year carbon isotope record of pedogenic carbonate: implications for paleoatmospheric carbon dioxide. *Am. J. Sci.* 299, 805–827.
- Elis, F., 2002. Contribution of termites to the formation of hardpans in soils of arid and semiarid region of South Africa. Presented at the 17th WCSS, Thailand.
- Emmerich, W.E., 2003. Carbon dioxide fluxes in a semiarid environment with high carbonate soils. *Agric. For. Meteorol.* 116, 91–102.
- Eswaran, H., Reich, P.F., Kimble, J.M., Beinroth, F.H., Padmanabhan, E., Moncharoen, P., 2000. Global carbon stocks. In: Lal, R., Kimble, J.M., Eswaran, H., Stewart, B.A. (Eds.), *Global Climate Change and Pedogenic Carbonates*. CRC Press, Boca Raton, Fla, pp. 15–25.
- FAO, 1996. *Global climate change and agricultural production. Direct and Indirect Effects of Changing Hydrological, Pedological and Plant Physiological Processes*. John Wiley & Sons Ltd., West Sussex, England.
- Feakins, S.J., Levin, N.E., Liddy, H.M., Sieracki, A., Eglinton, T.I., Bonnefille, R., 2013. North-east African vegetation change over 12 m.y. *Geology* 41, 295–298. <http://dx.doi.org/10.1130/G33845.1>.
- Finneran, D.W., Morse, J.W., 2009. Calcite dissolution kinetics in saline waters. *Chem. Geol.* 268, 137–146. <http://dx.doi.org/10.1016/j.chemgeo.2009.08.006>.
- Gabitov, R.I., Gaetani, G.A., Watson, E.B., Cohen, A.L., Ehrlich, H.L., 2008. Experimental determination of growth rate effect on U6+ and Mg2+ partitioning between aragonite and fluid at elevated U6+ concentration. *Geochim. Cosmochim. Acta* 72, 4058–4068. <http://dx.doi.org/10.1016/j.gca.2008.05.047>.
- Georgen, P.C., Davis-Carter, J., Taylor, H.M., 1991. Root growth and water extraction patterns from a calcic horizon. *Soil Sci. Soc. Am. J.* 55, 210. <http://dx.doi.org/10.2136/sssaj1991.03615995005500010036x>.
- Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W., Schauble, E.A., Schrag, D., Eiler, J.M., 2006a.  $^{13}\text{C}$ – $^{18}\text{O}$  bonds in carbonate minerals: a new kind of paleothermometer. *Geochim. Cosmochim. Acta* 70, 1439–1456. <http://dx.doi.org/10.1016/j.gca.2005.11.014>.
- Ghosh, P., Garzione, C.N., Eiler, J.M., 2006b. Rapid uplift of the altiplano revealed through  $^{13}\text{C}$ – $^{18}\text{O}$  bonds in paleosol carbonates. *Science* 311, 511–515. <http://dx.doi.org/10.1126/science.1119365>.
- Gile, L.H., 1961. A classification of ca horizons in soils of a desert region, Dona Ana County, New Mexico. *Soil Sci. Soc. Am. J.* 25, 52. <http://dx.doi.org/10.2136/sssaj1961.03615995002500010024x>.
- Gile, L.H., 1993. Carbonate stages in sandy soils of the Leasburg surface, southern New Mexico. *Soil Sci.* 156, 101–110. <http://dx.doi.org/10.1097/00010694-199308000-00006>.
- Gile, L.H., 1999. Eolian and associated pedogenic features of the Jornada Basin floor, Southern New Mexico. *Soil Sci. Soc. Am. J.* 63, 151. <http://dx.doi.org/10.2136/sssaj1999.03615995006300010022x>.
- Gile, L.H., Peterson, F.F., Grossman, R.B., 1966. Morphological and genetic sequences of carbonate accumulation in desert soils. *Soil Sci.* 101. <http://dx.doi.org/10.1097/00010694-196605000-00001>.
- Gocke, M., Kuzyakov, Y., 2011. Effect of temperature and rhizosphere processes on pedogenic carbonate recrystallization: relevance for paleoenvironmental applications. *Geoderma* 166, 57–65. <http://dx.doi.org/10.1016/j.geoderma.2011.07.011>.
- Gocke, M., Pustovoytov, K., Kuzyakov, Y., 2010. Effect of  $\text{CO}_2$  concentration on the initial recrystallization rate of pedogenic carbonate – revealed by  $^{14}\text{C}$  and  $^{13}\text{C}$  labeling. *Geoderma* 155, 351–358. <http://dx.doi.org/10.1016/j.geoderma.2009.12.018>.
- Gocke, M., Pustovoytov, K., Kühn, P., Wiesenberg, G.L.B., Löscher, M., Kuzyakov, Y., 2011a. Carbonate rhizoliths in loess and their implications for paleoenvironmental reconstruction revealed by isotopic composition:  $\delta^{13}\text{C}$ ,  $^{14}\text{C}$ . *Chem. Geol.* 283, 251–260. <http://dx.doi.org/10.1016/j.chemgeo.2011.01.022>.
- Gocke, M., Pustovoytov, K., Kuzyakov, Y., 2011b. Carbonate recrystallization in root-free soil and rhizosphere of *Triticum aestivum* and *Lolium perenne* estimated by  $^{14}\text{C}$  labeling. *Biogeochemistry* 103, 209–222. <http://dx.doi.org/10.1007/s10533-010-9456-z>.
- Gocke, M., Pustovoytov, K., Kuzyakov, Y., 2012. Pedogenic carbonate formation: recrystallization versus migration—process rates and periods assessed by  $^{14}\text{C}$  labeling. *Glob. Biogeochem. Cycles* 26, GB1018. <http://dx.doi.org/10.1029/2010GB003871>.
- Goudie, A., 1972. *The chemistry of world calcrete deposits*. *J. Geol.* 80, 449–463.
- Hamada, Y., Tanaka, T., 2001. Dynamics of carbon dioxide in soil profiles based on long-term field observation. *Hydrol. Process.* 15, 1829–1845. <http://dx.doi.org/10.1002/hyp.242>.
- Hedges, R.M., Lee-Thorp, J.A., Tuross, N.C., 1995. Is tooth enamel carbonate a suitable material for radiocarbon dating? *Radiocarbon* 37, 285–290. [http://dx.doi.org/10.2458/azu\\_js\\_rc.37.1675](http://dx.doi.org/10.2458/azu_js_rc.37.1675).
- Heidari, A., Mahmoodi, S., Stoops, G., Mees, F., 2004. Micromorphological characteristics of vertisols of Iran Including Nonsmectitic Soils. *Arid Land Res. Manag.* 19, 29–46. <http://dx.doi.org/10.1080/15324980509887164>.
- Hinsinger, P., 1998. How Do Plant roots acquire mineral nutrients? Chemical Processes Involved in the rhizosphere. *Adv. Agron.* 64, 225–265. [http://dx.doi.org/10.1016/S0065-2113\(08\)60506-4](http://dx.doi.org/10.1016/S0065-2113(08)60506-4).
- Hoppe, K.A., Stover, S.M., Pascoe, J.R., Amundson, R., 2004. Tooth enamel biomineralization in extant horses: implications for isotopic microsampling. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 206, 355–365. <http://dx.doi.org/10.1016/j.palaeo.2004.01.012>.
- Hough, B.G., Fan, M., Passey, B.H., 2014. Calibration of the clumped isotope geothermometer in soil carbonate in Wyoming and Nebraska USA: implications for paleoelevation and paleoclimate reconstruction. *Earth Planet. Sci. Lett.* 391, 110–120. <http://dx.doi.org/10.1016/j.epsl.2014.01.008>.
- Hsieh, Y.-P., 1993. Radiocarbon signatures of turnover rates in active soil organic carbon pools. *Soil Sci. Soc. Am. J.* 57, 1020. <http://dx.doi.org/10.2136/sssaj1993.03615995005700040023x>.
- Hsieh, J.C.C., Chadwick, O.A., Kelly, E.F., Savin, S.M., 1998a. Oxygen isotopic composition of soil water: quantifying evaporation and transpiration. *Geoderma* 82, 269–293. [http://dx.doi.org/10.1016/S0016-7061\(97\)00105-5](http://dx.doi.org/10.1016/S0016-7061(97)00105-5).
- Hsieh, J.C.C., Savin, Samuel M., Kelly, E.F., Chadwick, O.A., 1998b. Measurement of soil-water  $\delta^{18}\text{O}$  values by direct equilibration with  $\text{CO}_2$ . *Geoderma* 82, 255–268. [http://dx.doi.org/10.1016/S0016-7061\(97\)00104-3](http://dx.doi.org/10.1016/S0016-7061(97)00104-3).
- Huang, C.M., Retallack, G.J., Wang, C.S., 2012. Early cretaceous atmospheric  $\text{pCO}_2$  levels recorded from pedogenic carbonates in China. *Cretac. Res.* 33, 42–49. <http://dx.doi.org/10.1016/j.cretres.2011.08.001>.
- IPCC, 2007. *Climate Change 2007: Synthesis Report*.
- IPCC, 1990. Report prepared for Intergovernmental Panel on Climate Change by Working Group I. In: Houghton, J.T., Jenkins, G.J., Ephraums, J.J. (Eds.), Cambridge University Press, Cambridge, Great Britain, 410 pp.
- Jacks, G., Sharma, V.P., 1995. Geochemistry of calcic horizons in relation to hillslope processes, southern India. *Geoderma* 67, 203–214. [http://dx.doi.org/10.1016/0016-7061\(95\)00002-6](http://dx.doi.org/10.1016/0016-7061(95)00002-6).
- Jaillard, B., 1987. *Les Structures Rhizomorphes Calcaires: Modele de Reorganisation Des Mineraux Du Sol Par les Racines Montpellier*.
- Janz, L., Elston, R.G., Burr, G.S., 2009. Dating North Asian surface assemblages with ostrich eggshell: implications for palaeoecology and extirpation. *J. Archaeol. Sci.* 36, 1982–1989. <http://dx.doi.org/10.1016/j.jas.2009.05.012>.
- Kandel, A.W., Conard, N.J., 2005. Production sequences of ostrich eggshell beads and settlement dynamics in the Geelbek Dunes of the Western Cape, South Africa. *J. Archaeol. Sci.* 32, 1711–1721. <http://dx.doi.org/10.1016/j.jas.2005.05.010>.
- Karberg, N.J., Pregitzer, K.S., King, J.S., Friend, A.L., Wood, J.R., 2005. Soil carbon dioxide partial pressure and dissolved inorganic carbonate chemistry under elevated carbon dioxide and ozone. *Oecologia* 142, 296–306. <http://dx.doi.org/10.1007/s00442-004-1665-5>.
- Kelly, E.F., Amundson, R.G., Marino, B.D., DeNiro, M.J., 1991. Stable carbon isotopic composition of carbonate in Holocene grassland soils. *Soil Sci. Soc. Am. J.* 55, 1651. <http://dx.doi.org/10.2136/sssaj1991.03615995005500060025x>.
- Khadkikar, A.S., Merh, S.S., Malik, J.N., Chamyal, L.S., 1998. Calcretes in semi-arid alluvial systems: formative pathways and sinks. *Sediment. Geol.* 116, 251–260. [http://dx.doi.org/10.1016/S0037-0738\(97\)00103-6](http://dx.doi.org/10.1016/S0037-0738(97)00103-6).
- Khormali, F., Abtahi, A., Mahmoodi, S., Stoops, G., 2003. Argillic horizon development in calcareous soils of arid and semiarid regions of southern Iran. *catena* 53, 273–301. [http://dx.doi.org/10.1016/S0341-8162\(03\)00040-7](http://dx.doi.org/10.1016/S0341-8162(03)00040-7).
- Khormali, F., Abtahi, A., Stoops, G., 2006. Micromorphology of calcitic features in highly calcareous soils of Fars Province, Southern Iran. *Geoderma* 132, 31–46. <http://dx.doi.org/10.1016/j.geoderma.2005.04.024>.
- Khormali, F., Ghergherechi, S., Kehl, M., Ayoubi, S., 2012. Soil formation in loess-derived soils along a subhumid to humid climate gradient, Northeastern Iran. *Geoderma* 179–180, 113–122. <http://dx.doi.org/10.1016/j.geoderma.2012.02.002>.
- Khresat, S.A., 2001. Calcic horizon distribution and soil classification in selected soils of north-western Jordan. *J. Arid Environ.* 47, 145–152. <http://dx.doi.org/10.1006/jare.2000.0712>.
- Klappa, C.F., 1980. Rhizoliths in terrestrial carbonates: classification, recognition, genesis and significance. *Sedimentology* 27, 613–629.
- Klein, C., 2002. *Manual of Mineral Science*. John Wiley & Sons Australia, Limited.
- Knuteson, J.A., Richardson, J.L., Patterson, D.D., Prunty, L., 1989. Pedogenic carbonates in a calcaquoll associated with a recharge wetland. *Soil Sci. Soc. Am. J.* 53, 495. <http://dx.doi.org/10.2136/sssaj1989.03615995005300020032x>.
- Kovda, I.V., Wilding, L.P., Drees, L.R., 2003. Micromorphology, submicroscopy and microprobe study of carbonate pedofeatures in a Vertisol gilgai soil complex, South Russia. *CATENA, Achievements in Micromorphology* 54, pp. 457–476. [http://dx.doi.org/10.1016/S0341-8162\(03\)00121-8](http://dx.doi.org/10.1016/S0341-8162(03)00121-8).
- Kovda, I., Morgun, E., Gongalsky, K., 2014. Stable isotopic composition of carbonate pedofeatures in soils along a transect in the southern part of European Russia. *CATENA, Landscapes and Soils through Time* 112, pp. 56–64. <http://dx.doi.org/10.1016/j.catena.2013.01.005>.
- Kraimer, R.A., Monger, H.C., 2009. Carbon isotopic subsets of soil carbonate—a particle size comparison of limestone and igneous parent materials. *Geoderma* 150, 1–9. <http://dx.doi.org/10.1016/j.geoderma.2008.11.042>.
- Krauskopf, K.B., Bird, D.K., 1994. *Introduction To Geochemistry*, 3rd. edition. ed. McGraw-Hill Science/Engineering/Math, New York.
- Krueger, H.W., 1991. Exchange of carbon with biological apatite. *J. Archaeol. Sci.* 18, 355–361. [http://dx.doi.org/10.1016/0305-4403\(91\)90071-V](http://dx.doi.org/10.1016/0305-4403(91)90071-V).
- Ku, T.-L., Bull, W.B., Freeman, S.T., Knauss, K.G., 1979. Th230–U234 dating of pedogenic carbonates in gravelly desert soils of Vidal Valley, southeastern California. *Geol. Soc. Am. Bull.* 90, 1063. [http://dx.doi.org/10.1130/0016-7606\(1979\)90<1063:TDOPCI>2.0.CO;2](http://dx.doi.org/10.1130/0016-7606(1979)90<1063:TDOPCI>2.0.CO;2).
- Kuznetsova, A.M., Khokhlova, O.S., 2012. Submicromorphology of pedogenic carbonate accumulations as a proxy of modern and paleoenvironmental conditions. *Bol. Soc. Mex.* 64, 199–205.
- Kuzyakov, Y., 2006a. Sources of  $\text{CO}_2$  efflux from soil and review of partitioning methods. *Soil Biol. Biochem.* 38, 425–448. <http://dx.doi.org/10.1016/j.soilbio.2005.08.020>.
- Kuzyakov, Y., 2006b. *Bodengeographische Und Agrarökologische Exkursion: Moskau – Volgograd Selbstverlag*. (56 pp.).
- Kuzyakov, Y., Domanski, G., 2002. Model for rhizodeposition and  $\text{CO}_2$  efflux from planted soil and its validation by  $^{14}\text{C}$  pulse labelling of ryegrass. *Plant Soil* 239, 87–102. <http://dx.doi.org/10.1023/A:1014939120651>.
- Kuzyakov, Y., Shevtzova, E., Pustovoytov, K., 2006. Carbonate re-crystallization in soil revealed by  $^{14}\text{C}$  labeling: experiment, model and significance for paleo-environmental reconstructions. *Geoderma* 131, 45–58. <http://dx.doi.org/10.1016/j.geoderma.2005.03.002>.
- Lal, R., 2012. *World soils and the carbon cycle in relation to climate change and food security*. Carbon Management and Sequestration Center, the Ohio State University, USA, Columbus.

- Lal, R., Kimble, J.M., 2000. Pedogenic carbonates and the global carbon cycle. In: Lal, R., Kimble, J.M., Eswaran, H., Stewart, B.A. (Eds.), *Global Climate Change and Pedogenic Carbonates*. CRC Press, Boca Raton, Fla, pp. 1–14.
- Lambers, H., Mougél, C., Jaillard, B., Hinsinger, P., 2005. Plant-microbe-soil interactions in the rhizosphere: an evolutionary perspective. *Plant Soil* 321, 83–115. <http://dx.doi.org/10.1007/s11104-009-0042-x>.
- Lambkin, D.C., Gwilliam, K.H., Layton, C., Canti, M.G., Pearce, T.G., Hodson, M.E., 2011. Production and dissolution rates of earthworm-secreted calcium carbonate. *Pedobiologia*. 9th International Symposium on Earthworm Ecology, Xalapa, Veracruz, Mexico, 5th–10th September 2010 54, Supplement, pp. S119–S129. <http://dx.doi.org/10.1016/j.pedobi.2011.09.003>.
- Landi, A., Mermut, A.R., Anderson, D.W., 2003. Origin and rate of pedogenic carbonate accumulation in Saskatchewan soils, Canada. *Geoderma* 117, 143–156. [http://dx.doi.org/10.1016/S0016-7061\(03\)00161-7](http://dx.doi.org/10.1016/S0016-7061(03)00161-7).
- Levin, N.E., Brown, F.H., Behrensmeier, A.K., Bobe, R., Cerling, T.E., 2011. Paleosol carbonates from the Omo Group: Isotopic records of local and regional environmental change in East Africa. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 307, 75–89. <http://dx.doi.org/10.1016/j.palaeo.2011.04.026>.
- Liu, B., Phillips, F.M., Campbell, A.R., 1996. Stable carbon and oxygen isotopes of pedogenic carbonates, Ajo Mountains, southern Arizona: implications for paleoenvironmental change. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 124, 233–246. [http://dx.doi.org/10.1016/0031-0182\(95\)00093-3](http://dx.doi.org/10.1016/0031-0182(95)00093-3).
- Liu, Z., Dreybrodt, W., Wang, H., 2010. A new direction in effective accounting for the atmospheric CO<sub>2</sub> budget: considering the combined action of carbonate dissolution, the global water cycle and photosynthetic uptake of DIC by aquatic organisms. *Earth-Sci. Rev.* 99, 162–172. <http://dx.doi.org/10.1016/j.earscirev.2010.03.001>.
- Long, A., Hendershott, R., Martin, P.S., 1983. Radiocarbon dating of fossil eggshell. *Radiocarbon* 25, 533–539. [http://dx.doi.org/10.2458/azu\\_js\\_rc.25.811](http://dx.doi.org/10.2458/azu_js_rc.25.811).
- Ma, Y.F., Gao, Y.H., Feng, Q.L., 2010. Effects of pH and temperature on CaCO<sub>3</sub> crystallization in aqueous solution with water soluble matrix of pearls. *J. Cryst. Growth* 312, 3165–3170. <http://dx.doi.org/10.1016/j.jcrysgro.2010.07.053>.
- Machette, M.N., 1985. Calcic soils of the southwestern United States. *Geol. Soc. Am. Spec. Pap.* 203, 1–22. <http://dx.doi.org/10.1130/SPE203-p1>.
- Magee, J.W., Miller, G.H., Spooner, N.A., Questiaux, D.G., McCulloch, M.T., Clark, P.A., 2009. Evaluating Quaternary dating methods: radiocarbon, U-series, luminescence, and amino acid racemization dates of a late Pleistocene emu egg. *Quat. Geochronol.* 4, 84–92.
- Magnani, G., Bartolomei, P., Cavulli, F., Esposito, M., Marino, E.C., Neri, M., Rizzo, A., Scaruffi, S., Tosi, M., 2007. U-series and radiocarbon dates on mollusc shells from the uppermost layer of the archaeological site of KHB-1, Rás al Khabbah, Oman. *J. Archaeol. Sci.* 34, 749–755.
- McLaren, S.J., Rowe, P.J., 1996. The reliability of uranium-series mollusc dates from the western Mediterranean basin. *Quat. Sci. Rev.* 15, 709–717.
- Miller, J.J., Acton, D.F., St. Arnaud, R.J., 1985. The effect of groundwater on soil formation in a morainal landscape in saskatchewan. *Can. J. Soil Sci.* 65, 293–307. <http://dx.doi.org/10.4141/cjss85-033>.
- Miller, J.J., Dudas, M.J., Longstaffe, F.J., 1987. Identification of pedogenic carbonate minerals using stable carbon and oxygen isotopes, x-ray diffraction and sem analyses. *Can. J. Soil Sci.* 67, 953–958. <http://dx.doi.org/10.4141/cjss87-090>.
- Monger, C., 2002. Pedogenic carbonate links between biotic and abiotic CaCO<sub>3</sub>. Presented at the 17th WCSS, Thailand.
- Monger, H.C., Adams, H.P., 1996. Micromorphology of calcite-silica deposits, Yucca Mountain, Nevada. *Soil Sci. Soc. Am. J.* 60, 519. <http://dx.doi.org/10.2136/sssaj1996.03615995006000020026x>.
- Monger, H.C., Gallegos, R.A., 2000. Biotic and abiotic processes and rates of pedogenic carbonate accumulation in the Southwestern United States: relationship to atmospheric CO<sub>2</sub> sequestration. In: Lal, R., Kimble, J.M., Eswaran, H., Stewart, B.A. (Eds.), *Global Climate Change and Pedogenic Carbonates*. CRC Press, Boca Raton, Fla.
- Monger, H.C., Daugherty, L.A., Lindemann, W.C., Liddell, C.M., 1991. Microbial precipitation of pedogenic calcite. *Geology* 19, 997–1000. [http://dx.doi.org/10.1130/0091-7613\(1991\)019<0997:MPOPC>2.3.CO;2](http://dx.doi.org/10.1130/0091-7613(1991)019<0997:MPOPC>2.3.CO;2).
- Monger, H.C., Cole, D.R., Buck, B.J., Gallegos, R.A., 2009. Scale and the isotopic record of C4 plants in pedogenic carbonate: From the biome to the rhizosphere. *Ecology* 90, 1498–1511.
- Monger, H.C., Kraimer, R.A., Khresat, S., Cole, D.R., Wang, X., Wang, J., 2015. Sequestration of inorganic carbon in soil and groundwater. *Geology* 43, 375–378. <http://dx.doi.org/10.1130/G36449.1>.
- Naiman, Z., Quade, J., Patchett, P.J., 2000. Isotopic evidence for eolian recycling of pedogenic carbonate and variations in carbonate dust sources throughout the southwest United States. *Geochim. Cosmochim. Acta* 64, 3099–3109. [http://dx.doi.org/10.1016/S0016-7037\(00\)00410-5](http://dx.doi.org/10.1016/S0016-7037(00)00410-5).
- Nieder, R., Benbi, D.K., 2008. *Carbon and Nitrogen in the Terrestrial Environment*. Springer.
- Nordt, L., Wilding, L., Hallmark, C., Jacob, J., 1996. Stable carbon isotope composition of pedogenic carbonates and their use in studying pedogenesis. In: Boutton, T.W., Yamasaki, S. (Eds.), *Mass Spectrometry of Soils*. Marcel Dekker, New York, pp. 133–154.
- Nordt, L.C., Hallmark, C.T., Wilding, L.P., Boutton, T.W., 1998. Quantifying pedogenic carbonate accumulations using stable carbon isotopes. *Geoderma* 82, 115–136. [http://dx.doi.org/10.1016/S0016-7061\(97\)00099-2](http://dx.doi.org/10.1016/S0016-7061(97)00099-2).
- Pendall, E.G., Harden, J.W., Trumbore, S.E., Chadwick, O.A., 1994. Isotopic approach to Soil carbonate dynamics and implications for paleoclimatic interpretations. *Quat. Res.* 42, 60–71. <http://dx.doi.org/10.1006/qres.1994.1054>.
- Perito, B., Marvasi, M., Barabesi, C., Mastromei, G., Bracci, S., Vendrell, M., Tiano, P., 2014. A bacillus subtilis cell fraction (BCF) inducing calcium carbonate precipitation: biotechnological perspectives for monumental stone reinforcement. *J. Cult. Herit.* 15, 345–351. <http://dx.doi.org/10.1016/j.culher.2013.10.001>.
- Peters, N.A., Huntington, K.W., Hoke, G.D., 2013. Hot or not? Impact of seasonally variable soil carbonate formation on paleotemperature and O-isotope records from clumped isotope thermometry. *Earth Planet. Sci. Lett.* 361, 208–218. <http://dx.doi.org/10.1016/j.epsl.2012.12.024>.
- Prendergast, A.L., Stevens, R.E., Hill, E.A., Barker, G.W., Hunt, C., O'Connell, T.C., 2015. Carbon isotope signatures from land snail shells: Implications for palaeovegetation reconstruction in the eastern Mediterranean. *Quat. Int.* <http://dx.doi.org/10.1016/j.quaint.2014.12.053>.
- Pustovoytov, K., 1998. Pedogenic carbonate cutans as a record of the Holocene history of relic tundra-steppes of the Upper Kolyma Valley (North-Eastern Asia). *Catena* 34, 185–195. [http://dx.doi.org/10.1016/S0341-8162\(98\)00088-5](http://dx.doi.org/10.1016/S0341-8162(98)00088-5).
- Pustovoytov, K., 2002. <sup>14</sup>C dating of pedogenic carbonate coatings on wall stones at Göbekli Tepe (Southeastern Turkey). *Neolithics* 2, 3–4.
- Pustovoytov, K., 2003. Growth rates of pedogenic carbonate coatings on coarse clasts. *Quat. Int. Paleopedology* 106–107, 131–140. [http://dx.doi.org/10.1016/S1040-6182\(02\)00168-4](http://dx.doi.org/10.1016/S1040-6182(02)00168-4).
- Pustovoytov, K., Leisten, T., 2002. Diagenetic alteration of artificial lime mortar in a Mediterranean soil: <sup>14</sup>C and stable carbon isotopic data. Presented at the 17th WCSS, Thailand.
- Pustovoytov, K., Terhorst, B., 2004. An isotopic study of a late Quaternary loess-paleosol sequence in SW Germany. *Rev. Mex. Cienc. Geol.* 21, 88–93.
- Pustovoytov, K.E., Riehl, S., Mittmann, S., 2004. Radiocarbon age of carbonate in fruits of lithospermum from the early Bronze Age settlement of Hirbet ez-Zeraqon (Jordan). *Veg. Hist. Archaeobot.* 13, 207–212. <http://dx.doi.org/10.1007/s00334-004-0044-9>.
- Pustovoytov, K., Schmidt, K., Parzinger, H., 2007a. Radiocarbon dating of thin pedogenic carbonate laminae from Holocene archaeological sites. *The Holocene* 17, 835–843. <http://dx.doi.org/10.1177/0959683607080524>.
- Pustovoytov, K., Schmidt, K., Taubald, H., 2007b. Evidence for Holocene environmental changes in the northern fertile crescent provided by pedogenic carbonate coatings. *Quat. Res.* Reconstructing past environments from remnants of human occupation and sedimentary archives in western Eurasia 67, pp. 315–327. <http://dx.doi.org/10.1016/j.yqres.2007.01.002>.
- Pustovoytov, K., Riehl, S., Hilger, H.H., Schumacher, E., 2010. Oxygen isotopic composition of fruit carbonate in lithospermeae and its potential for paleoclimate research in the Mediterranean. *Glob. Planet. Change, Oxygen isotopes as tracers of Mediterranean variability: linking past, present and future* 71, pp. 258–268. <http://dx.doi.org/10.1016/j.gloplacha.2009.11.015>.
- Qualls, R.G., Bridgman, S.D., 2005. Mineralization rate of <sup>14</sup>C-labelled dissolved organic matter from leaf litter in soils of a weathering chronosequence. *Soil Biol. Biochem.* 37, 905–916. <http://dx.doi.org/10.1016/j.soilbio.2004.08.029>.
- Quast, A., Hoefs, J., Paul, J., 2006. Pedogenic carbonates as a proxy for palaeo-CO<sub>2</sub> in the palaeozoic atmosphere. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 242, 110–125. <http://dx.doi.org/10.1016/j.palaeo.2006.05.017>.
- Rabenhorst, M.C., Wilding, L.P., 1986. Pedogenesis on the Edwards Plateau, Texas: III. New model for the formation of petrocalcic horizons I. *Soil Sci. Soc. Am. J.* 50, 693. <http://dx.doi.org/10.2136/sssaj1986.03615995005000030029x>.
- Rawlins, B.G., Henrys, P., Breward, N., Robinson, D.A., Keith, A.M., Garcia-Bajo, M., 2011. The importance of inorganic carbon in soil carbon databases and stock estimates: a case study from England. *Soil Use Manag.* 27, 312–320. <http://dx.doi.org/10.1111/j.1475-2743.2011.00348.x>.
- Reddy, M.M., 2012. Calcite growth-rate inhibition by fulvic acid and magnesium ion—possible influence on biogenic calcite formation. *J. Cryst. Growth* 352, 151–154. <http://dx.doi.org/10.1016/j.jcrysgro.2011.12.069>.
- Reeves, J.C.C., 1970. Origin, classification, and geologic history of caliche on the Southern High Plains, Texas and Eastern New Mexico. *J. Geol.* 78, 352–362.
- Regev, L., Eckmeier, E., Mintz, E., Weiner, S., Boaretto, E., 2011. Radiocarbon concentrations of wood ash calcite: potential for dating. *Radiocarbon* 53, 117–127. [http://dx.doi.org/10.2458/azu\\_js\\_rc.53.3446](http://dx.doi.org/10.2458/azu_js_rc.53.3446).
- Retallack, G.J., 2005. Pedogenic carbonate proxies for amount and seasonality of precipitation in paleosols. *Geology* 33, 333–336. <http://dx.doi.org/10.1130/G21263.1>.
- Retallack, G.J., 2009. Refining a pedogenic-carbonate CO<sub>2</sub> paleobarometer to quantify a middle Miocene greenhouse spike. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 281, 57–65. <http://dx.doi.org/10.1016/j.palaeo.2009.07.011>.
- Riera, V., Anadón, P., Oms, O., Estrada, R., Maestro, E., 2013. Dinosaur eggshell isotope geochemistry as tools of palaeoenvironmental reconstruction for the upper cretaceous from the tremp formation (Southern Pyrenees). *Sediment. Geol.* 294, 356–370. <http://dx.doi.org/10.1016/j.sedgeo.2013.06.001>.
- Robbins, C.W., 1985. The CaCO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system in soils. *J. Agron. Educ.* 14.
- Royer, D.L., 1999. Depth to pedogenic carbonate horizon as a paleoprecipitation indicator? *Geology* 27, 1123–1126. [http://dx.doi.org/10.1130/0091-7613\(1999\)027<1123:DTPCHA>2.3.CO;2](http://dx.doi.org/10.1130/0091-7613(1999)027<1123:DTPCHA>2.3.CO;2).
- Royer, D.L., Berner, R.A., Beerling, D.J., 2001. Phanerozoic atmospheric CO<sub>2</sub> change: evaluating geochemical and paleobiological approaches. *Earth-Sci. Rev.* 54, 349–392. [http://dx.doi.org/10.1016/S0012-8252\(00\)00042-8](http://dx.doi.org/10.1016/S0012-8252(00)00042-8).
- Salomons, W., Mook, W.G., 1976. Isotope geochemistry of carbonate dissolution and reprecipitation in soils. *Soil Sci.* 122. <http://dx.doi.org/10.1097/00010694-197607000-00003>.
- Sauer, D., Stein, C., Glatzel, S., Kühn, J., Zarei, M., Stahr, K., 2015. Duricrusts in soils of the Alentejo (southern Portugal)—types, distribution, genesis and time of their formation. *J. Soils Sediments* 15, 1437–1453. <http://dx.doi.org/10.1007/s11368-015-1066-x>.
- Schlesinger, W.H., 1985. The formation of caliche in soils of the Mojave Desert, California. *Geochim. Cosmochim. Acta* 49, 57–66. [http://dx.doi.org/10.1016/0016-7037\(85\)90191-7](http://dx.doi.org/10.1016/0016-7037(85)90191-7).
- Schlesinger, W.H., Marion, G.M., Fonteyn, P.J., 1989. Stable isotope ratios and the dynamics of caliche in desert soils. In: Rundel, P.W., Ehleringer, J.R., Nagy, K.A. (Eds.), *Stable Isotopes in Ecological Research*. Ecological Studies, Springer New York, pp. 309–317.



- Seth, B., Thirlwall, M.F., Houghton, S.L., Craig, C.-A., 2003. Accurate measurements of Th–U isotope ratios for carbonate geochronology using MC-ICP-MS. *J. Anal. At. Spectrom.* 18, 1323–1330.
- Sharp, W.D., Ludwig, K.R., Chadwick, O.A., Amundson, R., Glaser, L.L., 2003. Dating fluvial terraces by  $^{230}\text{Th}/\text{U}$  on pedogenic carbonate, Wind River basin, Wyoming. *Quat. Res.* 59, 139–150. [http://dx.doi.org/10.1016/S0033-5894\(03\)00003-6](http://dx.doi.org/10.1016/S0033-5894(03)00003-6).
- Shi, Y., Baumann, F., Ma, Y., Song, C., Kühn, P., Scholten, T., He, J.-S., 2012. Organic and inorganic carbon in the topsoil of the Mongolian and Tibetan grasslands: pattern, control and implications. *Biogeosciences* 9, 2287–2299. <http://dx.doi.org/10.5194/bg-9-2287-2012>.
- Siegenthaler, U., Sarmiento, J.L., 1993. Atmospheric carbon dioxide and the ocean. *Nature* 365, 119–125. <http://dx.doi.org/10.1038/365119a0>.
- Soil Survey Staff, 2010. *Keys to Soil Taxonomy*, 2010, 11. edition. ed. Natural Resources Conservation Service, Washington.
- Spooner, P.T., Chen, T., Robinson, L.F., Coath, C.D., 2016. Rapid uranium-series age screening of carbonates by laser ablation mass spectrometry. *Quat. Geochronol.* 31, 28–39.
- Stern, L.A., Johnson, G.D., Chamberlain, C.P., 1994. Carbon isotope signature of environmental change found in fossil ratite eggshells from a South Asian Neogene sequence. *Geology* 22, 419–422. [http://dx.doi.org/10.1130/0091-7613\(1994\)022<0419:CISOEC>2.3.CO;2](http://dx.doi.org/10.1130/0091-7613(1994)022<0419:CISOEC>2.3.CO;2).
- Stumm, W., Morgan, J.J., 1996. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd. edition. ed. Wiley-Interscience, New York.
- Suchý, V., 2002. The “white beds” – a fossil caliche of the barrandian area: Its origin and paleoenvironmental significance. *J. Czech Geol. Soc.* 47, 45–54.
- Thomas, D.S.G., 2011. *Arid Zone Geomorphology: Process*. John Wiley & Sons, Form and Change in Drylands.
- Treadwell-Steitz, C., McFadden, L.D., 2000. Influence of parent material and grain size on carbonate coatings in gravelly soils, Palo Duro Wash, New Mexico. *Geoderma* 94, 1–22. [http://dx.doi.org/10.1016/S0016-7061\(99\)00075-0](http://dx.doi.org/10.1016/S0016-7061(99)00075-0).
- Ueda, S., Go, C.-S.U., Ishizuka, S., Tsuruta, H., Iswandi, A., Muriyasar, D., 2005. Isotopic Assessment of  $\text{CO}_2$  Production through Soil Organic Matter Decomposition in the Tropics 71 pp. 109–116. <http://dx.doi.org/10.1007/s10705-004-1197-8>.
- USDA-NRCS, 2000. *Soil Inorganic Carbon Map*.
- Verrecchia, E.P., 2011. Pedogenic Carbonates, in: *Encyclopedia of Earth Sciences Series* (Springer Science+Business Media B.V.).
- Verrecchia, E.P., Verrecchia, K.E., 1994. Needle-fiber calcite: a critical review and a proposed classification. *J. Sediment. Res.* 64.
- Verrecchia, E.P., Dumont, J.-L., Verrecchia, K.E., 1993. Role of calcium oxalate biomineralization by fungi in the formation of calcretes; a case study from Nazareth, Israel. *J. Sediment. Res.* 63, 1000–1006. <http://dx.doi.org/10.1306/D4267C6C-2B26-11D7-8648000102C1865D>.
- Verrecchia, E.P., Freyret, P., Verrecchia, K.E., Dumont, J.-L., 1995. Spherulites in calcrete laminar crusts: biogenic  $\text{CaCO}_3$  precipitation as a major contributor to crust formation. *J. Sediment. Res.* 65.
- Versteegh, E.A.A., Black, S., Canti, M.G., Hodson, M.E., 2013. Earthworm-produced calcite granules: a new terrestrial palaeothermometer? *Geochim. Cosmochim. Acta* 123, 351–357. <http://dx.doi.org/10.1016/j.gca.2013.06.020>.
- Villagran, X.S., Poch, R.M., 2014. A new form of needle-fiber calcite produced by physical weathering of shells. *Geoderma* 213, 173–177. <http://dx.doi.org/10.1016/j.geoderma.2013.08.015>.
- Violette, A., Riotte, J., Braun, J.-J., Oliva, P., Marechal, J.-C., Sekhar, M., Jeandel, C., Subramanian, S., Prunier, J., Barbiero, L., Dupre, B., 2010. Formation and preservation of pedogenic carbonates in South India, links with paleo-monsoon and pedological conditions: clues from Sr isotopes, U–Th series and REEs. *Geochim. Cosmochim. Acta* 74, 7059–7085. <http://dx.doi.org/10.1016/j.gca.2010.09.006>.
- Vogel, J.C., Visser, E., Fuls, A., 2001. *Suitability of Ostrich Eggshell for Radiocarbon Dating*.
- Wang, Y., McDonald, E., Amundson, R., McFadden, L., Chadwick, O., 1996. An isotopic study of soils in chronological sequences of alluvial deposits, Providence Mountains, California. *Geol. Soc. Am. Bull.* 108, 379–391. [http://dx.doi.org/10.1130/0016-7606\(1996\)108<0379:AISOSI>2.3.CO;2](http://dx.doi.org/10.1130/0016-7606(1996)108<0379:AISOSI>2.3.CO;2).
- Wang, Y., Li, Y., Ye, X., Chu, Y., Wang, X., 2010. Profile storage of organic/inorganic carbon in soil: from forest to desert. *Sci. Total Environ.* 408, 1925–1931. <http://dx.doi.org/10.1016/j.scitotenv.2010.01.015>.
- Wang, X., Wang, J., Xu, M., Zhang, W., Fan, T., Zhang, J., 2015. Carbon accumulation in arid croplands of northwest China: pedogenic carbonate exceeding organic carbon. *Sci. Rep.* 5. <http://dx.doi.org/10.1038/srep11439>.
- Werth, M., Kuzyakov, Y., 2010.  $^{13}\text{C}$  fractionation at the root–microorganisms–soil interface: a review and outlook for partitioning studies. *Soil Biol. Biochem.* 42, 1372–1384. <http://dx.doi.org/10.1016/j.soilbio.2010.04.009>.
- West, L.T., Wilding, L.P., Hallmark, C.T., 1988. Calciustolls in Central Texas: II. Genesis of Calcic and Petrocalcic Horizons. *Soil Sci. Soc. Am. J.* 52, 1731. <http://dx.doi.org/10.2136/sssaj1988.03615995005200060040x>.
- Whipkey, C.E., Capo, R.C., Chadwick, O.A., Stewart, B.W., 2000. The importance of sea spray to the cation budget of a coastal Hawaiian soil: a strontium isotope approach. *Chem. Geol.* 168, 37–48.
- Wieder, M., Yaalon, D.H., 1982. Micromorphological fabrics and developmental stages of carbonate nodular forms related to soil characteristics. *Geoderma* 28, 203–220. [http://dx.doi.org/10.1016/0016-7061\(82\)90003-9](http://dx.doi.org/10.1016/0016-7061(82)90003-9).
- Williams, G.E., Polach, H.A., 1969. The evaluation of  $^{14}\text{C}$  ages for soil carbonate from the arid zone. *Earth Planet. Sci. Lett.* 7, 240–242. [http://dx.doi.org/10.1016/0012-821X\(69\)90059-4](http://dx.doi.org/10.1016/0012-821X(69)90059-4).
- World reference base for soil resources, 2014. *FAO*.
- Wright, V.P., Beck, V.H., Sanz-Montero, M.E., Verrecchia, E.P., Freyret, P., Verrecchia, K.E., Dumont, J.-L., 1996. Spherulites in calcrete laminar crusts; biogenic  $\text{CaCO}_3$  precipitation as a major contributor to crust formation; discussion and reply. *J. Sediment. Res.* 66, 1040–1044. <http://dx.doi.org/10.2110/jsr.66.1040>.
- Xie, J., Li, Y., Zhai, C., Li, C., Lan, Z., 2008.  $\text{CO}_2$  absorption by alkaline soils and its implication to the global carbon cycle. *Environ. Geol.* 56, 953–961. <http://dx.doi.org/10.1007/s00254-008-1197-0>.
- Xu, B., Gu, Z., Han, J., Liu, Z., Pei, Y., Lu, Y., Wu, N., Chen, Y., 2010. Radiocarbon and stable carbon isotope analyses of land snails from the Chinese loess plateau: environmental and chronological implications. *Radiocarbon* 52, 149–156. [http://dx.doi.org/10.2458/azu\\_js\\_rc.52.3243](http://dx.doi.org/10.2458/azu_js_rc.52.3243).
- Yanes, Y., Gómez-Puche, M., Esquembre-Bebia, M.A., Fernández-López-De-Pablo, J., 2013. Younger Dryas–Early Holocene transition in the south-eastern Iberian Peninsula: insights from land snail shell middens. *J. Quat. Sci.* 28, 777–788. <http://dx.doi.org/10.1002/jqs.2673>.
- Yang, S., Ding, Z., Gu, Z., 2014. Acetic acid-leachable elements in pedogenic carbonate nodules and links to the East-Asian summer monsoon. *catena*, Loess and dust dynamics, environments, landforms, and pedogenesis: a tribute to Edward Derbyshire 117, pp. 73–80. <http://dx.doi.org/10.1016/j.catena.2013.06.030>.
- Zamanian, K., 2005. *Study of Fashand-Hashtgerd Soils and Investigation of the Mechanisms of Petrocalcic Horizon Formation in these Soils* (Master Thesis) Tehran, Iran.
- Zazzo, A., Saliège, J.-F., 2011. Radiocarbon dating of biological apatites: a review. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 310, 52–61. <http://dx.doi.org/10.1016/j.palaeo.2010.12.004>.
- Zazzo, A., Saliège, J.-F., Person, A., Boucher, H., 2009. Radiocarbon dating of calcined bones: where does the carbon come from? *Radiocarbon* 51, 601–611. [http://dx.doi.org/10.2458/azu\\_js\\_rc.51.3519](http://dx.doi.org/10.2458/azu_js_rc.51.3519).
- Zhou, J., Chafetz, H.S., 2010. Pedogenic carbonates in Texas: stable-isotope distributions and their implications for reconstructing region-wide paleoenvironments. *J. Sediment. Res.* 80, 137–150. <http://dx.doi.org/10.2110/jsr.2010.018>.