Invited review

Pedogenic carbonates: Forms and formation processes

Kazem Zamanian a,⁎, Konstantin Pustovoytov b, Yakov Kuzyakov a,c

a Department of Soil Science of Temperate Ecosystems, Georg August University of Goettingen, Buesgenweg 2, 37077 Goettingen, Germany
b Institute of Soil Science and Land Evaluation (310), University of Hohenheim, Schloss Hohenheim 1, 70599 Stuttgart, Germany
c Department of Agricultural Soil Science, University of Goettingen, Buesgenweg 2, 37077 Goettingen, Germany

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A B S T R A C T

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 CO2. 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, calcrites and laminar caps.

The second part of the review focuses on the isotopic composition of PC: δ13C, Δ14C and δ18O, as well as clumped 13C and 18O isotopes known as Δ47. The isotopic signature of PC enables reconstructing the formation environment: the dominating vegetation (δ13C), temperature (δ18O and Δ47), and the age of PC formation (Δ14C). The uncertainties in reconstructional 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.

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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, 1999) 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 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 CO2 (Bughio 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 water cycles due to irrigation could release great amounts of SIC and increase CO2 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 CO2 (Landi et al., 2003; Xie et al., 2008) if calcium (Ca2+) 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 Ca2+ 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 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 ha−1 may accumulate at MAP exceeding 1000 mm for example in Amazonian forests and monsoon 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): carbonates which have remained or are inherited from soil parent materials such as limestone particles or alloacted onto the soil from other locations by calcareous dust or landslide etc.

2. Biogenic carbonates (BC): 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.

1 Here we do not review the forms and formation of geogenic and biogenic carbonates in soil.
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; Georgen et al., 1991).

Fine PC crystals (i.e. micrite < 4 μm) 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-Deàk 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, 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 CaCO₃ – considering the solubility product (K_{sp} ≈ 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 CO₂. The dissolution rate of CO₂ and concentration of dissolved inorganic carbon (DIC) species (i.e. HCO₃⁻, CO₃²⁻, H₂CO₃° and CO₂), however, is controlled by the partial pressure of CO₂ (pCO₂) in the soil atmosphere (Andrews and Schlesinger, 2001; Karberg et al., 2005). CaCO₃ solubility in pure H₂O at 25 °C is 0.013 g L⁻¹, whereas in weak acids such as carbonic acid, the solubility increases up to five times (Aylward, 2007). The acidity produced by CO₂ dissolution removes OH⁻ ions and shifts the Eq. (1) to the right, leading to further dissolution of CaCO₃. The

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2 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 pCO₂ in the soil air increases the solubility of CaCO₃, otherwise the pH will drop.

\[
\text{CaCO}_3 + 2\text{H}_2\text{O} \rightarrow \text{Ca}^{2+}_{(aq)} + 2\text{OH}^{-}_{(aq)} + \text{H}_2\text{CO}_3^{-}_{(aq)}
\]

(1)

\[
\text{CO}_2(g) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3^{-}_{(aq)} \left( \text{HCO}_3^{-} + \text{CO}_2_{(aq)} + \text{H}_2\text{CO}_3^{-}_{(aq)} \right) + 2\text{H}^+
\]

(2)

(2) Movement of dissolved ions: the dissolved Ca²⁺ 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 Ca²⁺ ions and DIC species is strongly restricted. Because pCO₂ in the soil air strongly decreases close to the surface, CaCO₃ solubility declines, the solution becomes supersaturated and CaCO₃ precipitates. The rare cases of upward CaCO₃ migration are possible only from continuously evaporating groundwater (e.g. in calcretes, see Section 2.3.), or in the case of a higher CO₂ 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 CaCO₃, the solutes precipitate. Supersaturation of soil solution in respect to CaCO₃ may take place for two reasons: 1) decreasing soil water content mainly connected with evapotranspiration and 2) decreasing pCO₂ (Robbins, 1985; Salomon 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; Roeyer, 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 CO₂ concentration) accumulates PC near or even at the soil surface (Khadikkar et al., 1998; Knutson 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 CaCO₃ 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 Ca²⁺ 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 ¹⁴C 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 Ca²⁺ towards the root and precipitation of CaCO₃ along the root (Fig. 3 top). Because Ca²⁺ uptake is much lower than the water uptake, the remaining Ca²⁺ ions precipitate with CO₃ from rhizomicrobial respiration as CaCO₃, thus forming the rhizoliths (Callot et al., 1982; Hinsinger, 1998; Lambers et al., 2009). The other rare possibility is the release of HCO₃⁻ instead of H⁺ by roots to compensate for the uptake of anions such as NO₃⁻. Increasing soil pH by released HCO₃⁻ induces CaCO₃ 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. CaCO₃ 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 Ca²⁺ toxicity by CaCO₃ 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 pseudomyceyls are formed by penetration of percolating water through the soil matrix and rapid precipitation of CaCO₃ around large and medium soil pores (Fig. 4). Rapid precipitation is common because of the strong pCO₂ 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 CaCO₃ is young, potentially forming within weeks to months.

D) Nodules (Fig. 5) are formed in situ by impregnation of soil matrix with CaCO₃ at specific locations (Durand et al., 2010). This
Table 1: Characteristics of the most common pedogenic carbonate features in soils.

<table>
<thead>
<tr>
<th>PC features mostly related to biotic controls</th>
<th>Shape</th>
<th>Size</th>
<th>Density&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Porosity&lt;sup&gt;3&lt;/sup&gt;</th>
<th>Impurities&lt;sup&gt;4&lt;/sup&gt;</th>
<th>Formation&lt;sup&gt;5&lt;/sup&gt; category</th>
<th>Formation time scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Earthworm biospheroliths&lt;sup&gt;A&lt;/sup&gt;</td>
<td>Spheroidal</td>
<td>Few mm</td>
<td>High</td>
<td>Moderate</td>
<td>Moderate</td>
<td>4</td>
<td>Days</td>
</tr>
<tr>
<td>Calcified root cells&lt;sup&gt;A&lt;/sup&gt;</td>
<td>Branch shape structures</td>
<td>Less than mm in diameter and up to few cm length</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>4</td>
<td>Weeks to months</td>
</tr>
<tr>
<td>Rhiololiths&lt;sup&gt;B&lt;/sup&gt;</td>
<td>Cylindrical structures</td>
<td>Up to several cm in diameter and up to several meters length</td>
<td>High</td>
<td>Moderate</td>
<td>Low to high outward root center</td>
<td>4</td>
<td>Months to years</td>
</tr>
<tr>
<td>Needle fiber calcite</td>
<td>Microscopic needle shape crystals</td>
<td>Some μm</td>
<td>Very high</td>
<td>Very low</td>
<td>Very low to pure calcite</td>
<td>4 or could be even not pedogenic</td>
<td>Days</td>
</tr>
<tr>
<td>Pseudomorph calcite after gypsum</td>
<td>Microscopic lenticular crystals</td>
<td>Some μm</td>
<td>Very high</td>
<td>Very low</td>
<td>Very low to pure calcite</td>
<td>Not clear, probably 4</td>
<td>Not clear</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PC features mostly related to abiotic controls</th>
<th>Shape</th>
<th>Size</th>
<th>Density&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Porosity&lt;sup&gt;3&lt;/sup&gt;</th>
<th>Impurities&lt;sup&gt;4&lt;/sup&gt;</th>
<th>Formation&lt;sup&gt;5&lt;/sup&gt; category</th>
<th>Formation time scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft masses</td>
<td>Diffuse powder</td>
<td>Visible powder</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>probably 3</td>
<td>Weeks</td>
</tr>
<tr>
<td>Hypocoatings&lt;sup&gt;C&lt;/sup&gt;</td>
<td>Laminated carbonate inside soil matrix and along soil pores</td>
<td>Few mm thickness with diffuse boundary into soil matrix</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>2</td>
<td>Weeks to months</td>
</tr>
<tr>
<td>Nodules&lt;sup&gt;D&lt;/sup&gt;</td>
<td>Spheroidal</td>
<td>Few mm to few cm in diameter</td>
<td>Low to very high</td>
<td>Low to very high</td>
<td>High</td>
<td>3</td>
<td>Decades</td>
</tr>
<tr>
<td>Clast Coatings&lt;sup&gt;E&lt;/sup&gt;</td>
<td>Laminated carbonate beneath (or at the top of) clasts</td>
<td>Few mm to few cm thickness, the same length as related clast</td>
<td>Low</td>
<td>Low to very high</td>
<td>Moderate</td>
<td>1, (2)&lt;sup&gt;6&lt;/sup&gt;</td>
<td>Centuries to millennia</td>
</tr>
<tr>
<td>Calcretes&lt;sup&gt;F&lt;/sup&gt;</td>
<td>Cemented horizon&lt;sup&gt;7&lt;/sup&gt;</td>
<td>At least 10 cm</td>
<td>Very high</td>
<td>Very low</td>
<td>High</td>
<td>2, (1, 3, 4)</td>
<td>Millennia</td>
</tr>
<tr>
<td>Laminar caps&lt;sup&gt;G&lt;/sup&gt;</td>
<td>Laminated horizon&lt;sup&gt;7&lt;/sup&gt;</td>
<td>Few mm to even meter</td>
<td>Very high</td>
<td>Very low</td>
<td>Very low</td>
<td>1, (4)</td>
<td>Millennia</td>
</tr>
</tbody>
</table>

<sup>1</sup> The information for pedogenic carbonate features were inferred considering data in: Alonso-Zarza, 1999; Anundson et al., 1997; Barta, 2011; Becze-Deák 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: < 10; low: 10–30; moderate: 30–50; high: >50% (minerals or particles other than calcite).

<sup>4</sup> See Section 2.2. (Formation mechanisms of pedogenic carbonate).

<sup>5</sup> In parentheses: probable mechanism(s) other than the main one.

<sup>6</sup> Calcretes and laminar caps are new soil horizons which are formed by cementation.
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 CaCO₃ 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 CaCO₃. CaCO₃ 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 CaCO₃ (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 (δ¹³C and δ¹⁸O) 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. 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 ~0.8 mg CaCO₃ earthworm⁻¹ 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).

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 Ca²⁺ accumulation and CaCO₃ precipitation in the rhizosphere. Root water uptake leads to supersaturation of CaCO₃ 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.
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 CaCO₃ 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 (Khadbikar et al., 1998; Knuteson et al., 1989), leading to their cementation and the formation of calcrete (Fig. 8). Cementation by CaCO₃ may occur also by 1) leaching of dissolved Ca²⁺ and HCO₃⁻ ions from upper horizons (Fig. 8) (Gile et al., 1966; Machette, 1985), or 2) dissolution of Ca²⁺ containing rock (i.e. limestone) and carbonate precipitation without translocation of dissolved ions (Rabenhorst and Wilding, 1986). 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 CaCO₃ amounts accumulated as calcrete cannot be explained by the translocation of dissolved ions within the soil profile. They clearly reflect the Ca²⁺ relocation from higher landscape positions (Sauer et al., 2015). Considering the formation mechanisms, the properties of calcrites, however, will be different: for instance, the presence of high Mg-calcrete 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). 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 CO₂ content in the

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 CO₂ partial pressure in large pores, leading to CaCO₃ 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).

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.
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 Fitz, 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 CaCO₃ 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 (Ammit et al., 2011; Thomas, 2011) to cold climatic zones such as tundra (Courty et al., 1999; Pustovoytov, 1998). Increasing temperature decreases CO₂ solubility (Krauskopf and Bird, 1994), which directly affects the supersaturation of soil solution with CaCO₃ (Barker and Cox, 2011). Increasing temperature, however, boosts microbial respiration and thus increases the CO₂ concentration in soil air (Lal and Kimble, 2000). This biotic effect of temperature overwhelms the abiotic effect of CO₂ 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., 2011). Faster rates (due to warmer conditions) lead to more impurities such as rare earth elements (REE) in the PC structure (Gabitov et al., 2011). The presence of co-precipitated cations from parent material (GC) and thus less δ¹³C of PC on calcareous vs. non-calcareous parent materials usually shows a higher heterogeneity i.e. wider range of δ¹³C, 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 δ¹³C 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; Whippley 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 CaCO₃ and controls the crystal morphology (Klein, 2002). For instance, impurities decrease the crystal size (Catoní et al., 2012). Elongated and needle-shaped crystals are formed in solution at higher concentrations (100 ppb) of (REE⁺³⁺)/(Ca²⁺), 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 precipitated PC (Pustovoytov et al., 2007); Right: Coating formation by percolating water remaining underneath the coarse fragments (e.g. stones). The soluble ions (i.e. Ca²⁺ and HCO₃⁻) will precipitate during soil dryness on the bottom side of the stone. In specific conditions, coatings may form on the upper side of stones (Amandson 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 CaCO₃ precipitation.

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. Ca²⁺ and HCO₃⁻) will precipitate during soil dryness on the bottom side of the stone. In specific conditions, coatings may form on the upper side of stones (Amandson 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 CaCO₃ precipitation.
carboxyl groups at or near crystal growth sites inhibits the growth rate of CaCO₃ 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 CaCO₃ (Ma et al., 2010). The ratio of bicarbonate/carbonate decreases as the soil pH becomes alkaline (e.g. pH > 8.5). This favors higher nucleation rates and faster precipitation of smaller CaCO₃ crystals (Ma et al., 2010). Ionic strength controls the mole fraction of free water during CaCO₃ dissolution (Finneran and Morse, 2009). Therefore, CaCO₃ 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 calcrites 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 calcrite (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 CO₂ concentration in the rhizosphere versus atmosphere and (2) up to two units lower local pH because of 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 Ca²⁺ 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 CaCO₃ (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. 7. Calcrite morphology. Top: thick calcrite formed on alluvial deposits comprised two distinct horizons: the lower calcrite contains abundant coarse fragments impregnated and cemented with PC. The upper calcrite–laminar calcrite – comprises negligible coarse fragments but horizontal layers of PC accumulation (profile depth: ca. 150 cm). Middle: PC accumulation as microlayers in the upper calcrite. Bottom: Surrounded coarse fragments but horizontal layers of PC accumulation (pro

[45x167]—

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 calcrite (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).

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3. Carbon and oxygen in pedogenic carbonates

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

Carbon in PC originates from dissolved CO2 in soil solution (Eqs. (1), (2)). Respiration of roots and microorganisms and the decomposition of litter and SOM are the sole CO2 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 CO2 concentration is partly controlled by the diffusion of atmospheric CO2 into the soil (Cerling, 1984).

The source of oxygen in PC is related more to the soil water than to soil CO2. This is confirmed by the close correlation between δ18O of PC and mean δ18O 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 (δ13C, Δ14C) and oxygen (δ18O) in pedogenic carbonates

The isotopic signature of PC – δ13C and δ18O – is controlled by the isotopic composition of soil CO2 and of water, respectively (Cerling, 1984). During the growing season, root and microorganism respiration is high and represents the only CO2 source in soil (Cerling, 1984); the relative abundance of C3 and C4 plants in the local vegetation controls the δ13C value of PC (Fig. 10). Due to isotopic discrimination by photosynthetic pathways, the δ13C of CO2 under C3 plant species (−27% on average) differs from that under C4 species (−13% on average) (Cerling et al., 1997). Further isotopic discrimination results from CO2 diffusion in soil (ca. +4.4‰) and carbonate precipitation (ca. +11‰). Consequently, PC are 13C enriched by about 15‰ compared to the respired CO2. The values are ca. −12‰ under pure C3 and +2‰ under pure C4 vegetation (Fig. 10).

Since root and rhizomicrobial respiration are the dominant CO2 sources in soils (Kuzyakov, 2006a), SOM decomposition has a minor effect on 13C of PC (Ueda et al., 2005). Diffusion of atmospheric CO2 (global average δ13C = −8.5‰ in 2015) can further enrich 13C in PC. Nonetheless, the effect of diffused atmospheric CO2 is restricted maximally to the
upper 50 cm of the soil (Cerling, 1984) and is negligible in the presence of vegetation.

The $\Delta^{14}C$ of PC is determined by biological activities in soil. In contrast to $\delta^{13}C$, SOM decomposition affects $\Delta^{14}C$ in PC. Therefore, the relative proportion of CO$_2$ respired by the rhizosphere and the CO$_2$ released from SOM decomposition determine the $\Delta^{14}C$ abundance in PC. The contribution of SOM decomposition to $\Delta^{14}C$ 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 $\Delta^{14}C$ abundance) (Amundson et al., 1994).

The $\delta^{18}O$ of PC is controlled by the oxygen isotopic composition of meteoric water, from which carbonates originate (Cerling, 1984). Increasing evaporation leads to higher $\delta^{18}O$ 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

$\delta^{13}C$ and $\delta^{18}O$ as well as $\Delta^{14}C$ 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 and Wetzel, 1996). Dissolution of SIC and DIC species takes place under complete equilibrium with soil air CO$_2$ (Eq. 3) (Cerling, 1984; Nordt et al., 1996).

\[
\text{CaCO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^2+ + \text{HCO}_3^- \to \text{CaCO}_3 + \text{H}_2\text{O} + \text{Ca}^2+ + \text{HCO}_3^-
\]

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

The $\Delta^{14}C$ 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; Blising 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 $\delta^{13}C$ 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 (Sponer et al., 2016).

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

The $\delta^{13}C$ and $\delta^{18}O$ in the lattice of PC crystals enable estimating the temperature of PC formation (Ghosh et al., 2006a). The combination of $\delta^{13}C$ and $\delta^{18}O$ in CaCO$_3$ crystals, known as $\Delta_{AT}$ or clumped isotopes, is the measuring $\delta^{18}O$ and $\delta^{13}C$ connected in one molecule simultaneously, for instance as $\text{Ca}^{13}C\text{O}^{18}O\text{Si}^{16}O$. The $\Delta_{AT}$ value in a crystal lattice depends only on the environmental temperature: increasing the temperature will decrease the $\Delta_{AT}$ in that crystal (Eiler, 2007). Therefore, the $\Delta_{AT}$ 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 $\delta^{13}C$, $\Delta^{14}C$, $\delta^{18}O$ 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 ($K_{sp} = 10^{-6} - 10^{-9}$) (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 $^{14}$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 $^{14}$CO$_2$. By tracing the $^{14}$C activity of a carbonate sample and knowing the amounts of added C as CO$_2$, the amounts of recrystallized carbonates can be calculated. This approach was used to show the dependence of CaCO$_3$ recrystallization rates on (i) 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 CaCO$_3$ along soil profile (Gocke et al., 2012). The very slow rates assessed by the $^{14}$C labeling approach (about 0.00003 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 recrystallization 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 $\delta^{13}$C values of the remaining GC to that of PC (Fig. 10) leads to a less negative $\delta^{13}$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 $^{14}$C is mixed with a dead limestone specimen, the age estimation will be 36,500 years. Increasing the contamination with modern $^{14}$C to 10% alters the age of that limestone to about 18,500 years (Williams and Polach, 1969).

PC recrystallization also affects $\delta^{18}$O (Cerling, 1991) and may thus overestimate PC formation temperature by up to 20 °C (Ghosh et al., 2006b). Therefore, interpretation of the $\delta^{13}$C, $\Delta^{14}$C, $\delta^{18}$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 archaeological 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 $^{14}$C during recrystallization (Pustovoytov and Terhorst, 2004). A correspondence between measured $\Delta^{14}$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 $\delta^{13}$C variation in PC from paleosols with similar ages (and probable similar vegetation and pCO$_2$ in the respective geological period) is referred to recrystallization. In contrast, fewer $\delta^{13}$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 $\delta^{13}$C signature of recently recrystallized carbonates (Kraimer and Monger, 2009). The smaller the PC size, the more $\delta^{13}$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 hypocoatings (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 µm) 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. calcrite). PC forms therefore reflect soil genesis processes and record the effects of soil-forming factors. δ13C, Δ14C and δ18O as well as Δδ2H in PC are valuable tools for paleoenvironmental reconstructions and soil age estimation. PC features, however, have variable physical and chemical properties including various CaCO3 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 14C to the isotopic inventory of PC. It can therefore lead to a strongly biased assessment of air pCO2 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 (CO2 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 Naykov 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 CaCO3 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, 14C labeling of soil CO2 showed high potential for understanding the dynamics of carbonate recrystallization in soils (Kuz Naykov 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 CaCO3 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 13C enrichment in PC comparing to the respired CO2 is because of soil CO2 diffusion (Cerling, 1984). The CO2 diffusion in soil (and thus changes in δ13C 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‰ 13C enrichment in soil CO2 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 CO2.
- The contribution of CaCO3 to CO2 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 CaCO3 dissolution and CO2 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 management — on CaCO3 dissolution and CO2 efflux. These anthropogenic effects on CaCO3 dissolution should be compared to the rates of natural acidification processes related to litter decomposition and rhizosphere fluxes of 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.

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