

Factors Affecting Pedogenic Carbonate Formation and Recrystallization

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As a principal part of the atmosphere–lithosphere interface, soil plays a key role in regulating the atmospheric CO₂ concentration and global climate. Comprising two major pools (carbonate in soils and bicarbonate in groundwater), soil inorganic carbon (SIC) is deemed as the primary carbon (C) sink and source in areas with low mean annual rainfall. SIC may originate from soil parent material or from the formation of secondary carbonate when divalent cations from an extraneous source are supplied. The latter may result in pedogenic carbonate (PC) formation, increasing soil C content and sequestering atmospheric carbon. Since the sequestration of atmospheric CO₂ through formation of pedogenic carbonate is gaining popularity as a method to support climate change mitigation efforts and to claim carbon credits, the mechanisms influencing the formation and migration of pedogenic carbonate need to be well understood.

pedogenic carbonate

enhanced rock weathering

CO₂ mineralization

1. Introduction

Containing more than 2500 PgC over the first meter of the vertical profile, soils are regarded as the largest terrestrial and the third-largest C reservoir on Earth, after fossil fuel reserves and the oceans ^{[1][2]}. As carbon storage in soil impacts diverse aspects of life on Earth, it has been subjected to scientific interest from actors working in various disciplines, such as earth scientists, agronomists, and even policymakers ^[3]. The dynamics of soil carbon are a function of several parameters that influence C flux exchange between the air and soil system, and thus contribute to moderating atmospheric CO₂ levels ^{[4][5][6]}.

Soil C comprises two discrete segments, soil organic carbon (SOC) and soil inorganic carbon (SIC), with the latter typically considered a more stable sink ^{[2][5][7]}. Decomposition of plant and animal residues, synthetic reactions and microbial activities are the main origins of the SOC pool ^{[8][9]}. On the contrary, SIC refers to mineral-based carbon, generated through the weathering of bedrock materials ^{[8][10]}. Turnover of SIC is believed to be 70–400 times longer compared to that of SOC ^[11]. While the SOC is estimated to be the major C pool in shallow (<1 m) soil globally ^[1], the SIC contribution has been found significant in arid and semi-arid areas, where the SIC/SOC ratio is in the range of 2–17 ^{[12][13]}. SIC is usually found in the form of calcite (CaCO₃) ^[14], although a significant contribution of dolomite (CaMg(CO₃)₂) has been reported in a few studies ^{[5][15][16]}. Recently, there has been greater research interest in evaluating the SIC pool and its impact on the global C budget ^{[10][17][18]}, and this trend overcomes the prior neglect of the SIC pool, in the context of climate change mitigation, as it had been traditionally viewed as being less dynamic compared to its organic counterpart ^{[7][19]}.

The precipitation–dissolution–re-precipitation regime ($\text{CaCO}_3(\text{s}) + \text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$) is a primary factor in the distribution of the SIC pool over the vertical soil profile [20]. Monger et al. [17] described the SIC pool in humid and arid soil profiles using the terms ‘flushing’ and ‘non-flushing’, respectively. Flushing refers to a wet climatic condition favoring the downward migration of dissolved carbonate ($\text{Ca}^{2+} + 2\text{HCO}_3^-$, at near-neutral pH) to the groundwater system, whereas solid carbonate is more likely to accumulate in the non-flushing regime [17]. The global rate of sequestered C influx (as HCO_3^-) to groundwater is approximately 0.2–0.36 Pg annually, with a residence time in the order of 100’s to 1000’s of years [10][14].

The SIC pool is categorized into two components, lithogenic carbonate (LC) and pedogenic carbonate (PC), with the former originating from the parent material of soil (e.g., limestone or carbonate-rich unconsolidated sediment) [10][18]. The dissolution–reprecipitation of LC, as well as the mechanism of solvation of $\text{CO}_2(\text{g})$ in soil moisture (as $\text{CO}_3^{2-}/\text{HCO}_3^-$) followed by its precipitation with Ca- and Mg-ions, lead to the formation of PC [17]. The formation of PC may modify soil characteristics, such as soil porosity, soil water content, and gaseous diffusion (e.g., of $\text{O}_2(\text{g})$) [4].

The carbon exchange between soil and air is influenced by PC dynamics and hence is connected with the global climate [21]. Photosynthesis and root respiration are the major pathways for moving CO_2 from the atmosphere into the terrestrial ecosystem [10][12]. The main contributors to PC formation and accumulation include windblown dust [10][22], fertilizers [6], irrigation water [10][23], wet deposition [24][25], and bedrock weathering [10][22].

To accrue net SIC augmentation in the form of PC, the alkaline earth metal must be provided from an extraneous non-carbonate source; otherwise, the sequestered C equals the amount released to the atmosphere (e.g., during limestone calcination to produce quick lime) [17][26]. Hence, a narrower classification is needed to distinguish PC formation induced from an extraneous source and that resulting from recrystallization of pre-existing PC/LC; these PC sources are referred to as pedo-atmogenic and pedo-lithogenic carbonate, respectively [6][10][14]. A detailed description of the formation modes of both types can be found in Monger et al. [10].

2. Pedogenic Carbonate Formation Mechanisms

Formation of PC involves a series of reactions: (1) dissolution of CO_2 and an alkaline earth metal-bearing mineral in the soil–water system; (2) migration of dissolved ions with soil water flow; and (3) precipitation of carbonate under favorable geochemical conditions (i.e., one that results in carbonate saturation and that depends on chemical properties of the aqueous medium) [4]. Depending on the soil water movement direction, this process may occur through several mechanisms, namely perdescendum (downward movement of solution) [27], perascendum (upward movement of the solution) [28][29], in-situ (absence of significant movement), and biologically induced mechanisms [4][30]. These processes have been explained in detail in published studies, including Zamanian et al. [4] and Li et al. [31].

Li et al. [31] argued that mechanisms, such as perdescendum or perascendum, may not fully explain the formation of carbonate nodules in loess sedimentary deposits. Instead, these authors attributed the pedogenesis of this

carbonate to an “evapotransporative” mechanism, comprising evaporation at the surface and transpiration in the subsurface, with the former as the dominant process [31]. Díaz-Hernández et al. [15] identified various physiochemical mechanisms for the formation of surficial calcite (dominant over 0–180 cm) and deep dolomite (dominant deeper than 180 cm) owing to the weathering of basaltic rocks in a volcanic deposit site. Accordingly, it was proposed that calcite forms in an evaporative medium, whereas dolomite evolves in equilibrium with the groundwater system [15]. Laudicina et al. [32] described two pathways of PC formation involving biological factors: (i) biogenic pathways, where there is organic carbon enriched with a supplement of extraneous Ca^{2+} through rainfall; and (ii) dissolution and recrystallization of LC with a lower biogenic contribution.

PC occurs in several morphological forms, reflecting the dominance of certain abiotic/biotic processes [4][30]. Different morphological forms of carbonate may also be indicative of various sources (e.g., dissolution-recrystallization and atmospheric deposition), various PC formation mechanisms, as well as its emergence under certain humidity or vegetation regimes [16][29][30]. For instance, the dominance of biological activities may induce the formation of needle-fiber calcite crystals [33]. The distinctive morphological and physical characteristics of carbonate have been found useful for distinguishing several erosion-deposition sequences and soil type [34][35]. The formation of distinct types of PC may happen over different time scales, ranging between days and millennia [4].

3. Factors Affecting Pedogenic Carbonate Formation and Recrystallization

The formation of PC is a complex process, incorporating a wide variety of abiotic (e.g., climate, soil properties and characteristics, landscape) and biotic agents, as discussed and classified by Zamanian et al. [4] and illustrated in **Figure 1**. Each factor may affect morphology, leachability, and accumulation rate of PC as well as CO_2 solubility and Ca^{2+} availability in soil; all are influential aspects of PC dynamics in soil. Ferdush and Paul [10] reviewed how different biotic and abiotic factors may modify the SIC pool under elevated atmospheric CO_2 level conditions.

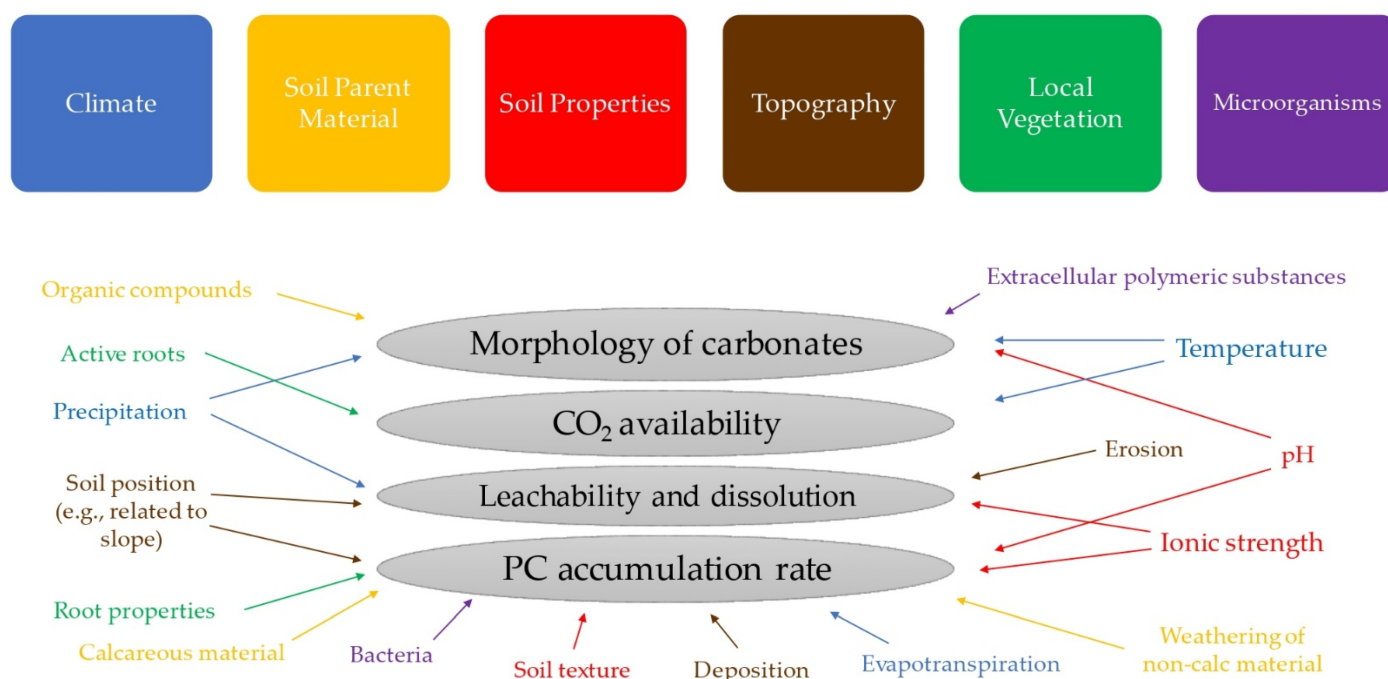


Figure 1. Illustration of environmental factors affecting PC migration and accumulation in soil discussed in Zamanian et al. [4].

Optimized moisture content, suitable pH range (i.e., greater acidity is conducive to silicate mineral weathering, and near-neutral conditions are required for stability of solid carbonate), CO_2 supply, and availability of divalent cations (particularly Ca^{2+}) are four essential conditions for PC formation [17][36]. The recrystallization rate of PC increases with CO_2 concentration elevation [37][38][39]. Zhao et al. [39] found that crystallization rate is a function of specific soil properties; the rate proportionally increases/decreases with salinity/pH, respectively. The latter effect is related to a negative correlation between CaCO_3 solubility with pH, wherein lower pH eases the dissolution, and thus recrystallization, of CaCO_3 [39]. They attributed the positive correlation between salinity and PC formation to a higher accumulation of exchangeable cations (e.g., Ca^{2+}) in saline soil [39]. These authors also demonstrated that the increase of CO_2 partial pressure from 0.04 vol% (atmospheric) to 4 vol% results in a 100-fold increase in the carbonate recrystallization rate. Although the same trend was observed in the experiment conducted by Gocke et al. [37], several controls (e.g., fluctuation of CO_2 concentration in soil, temperature, root density, native crop regime, and soil texture) were also important as regulators of the rate of re-precipitation in natural soil systems. These factors, investigated in several studies as key aspects, are discussed next.

Hasinger et al. [36] demonstrated that the presence of a macroporous layer in soil facilitates CO_2 gas diffusion over the vertical and lateral profile of soil, acting as feedstock for PC formation. Investigating inter-seasonal variability of PC formation and seasonality of rainfall, Gallagher et al. [40] determined hydrological parameters (rainfall, evaporation, and soil water content) as the primary factors, rather than the mean annual temperature that was believed to previously be the main control. However, the vital role of temperature in PC dynamics in forest-steppe soils (alongside the mentioned hydrological parameters and biological activities in the growing season) has also been documented [41].

Select studies have highlighted the role of fine particles (nominally, clay) in the formation and accumulation of secondary carbonate [15][42]. According to Díaz-Hernández et al. [42], clay particles take up water that has migrated to the subsoil and therefore are conducive to the precipitation of carbonate. In contrast, the presence of gravel and sand particles can influence the hydrological regime and PC dynamics by facilitating the transport of water to subsoil layers [42]. Li et al. [13] also observed the same trend of SIC accumulation (with a PC isotopic signature) in a clay layer in the Yellow River Delta.

Microbial and root respiration, including the mineralization of organic carbon in the rhizosphere, are the main factors in supplying CO₂ in a subsoil medium [12][37]. Recent laboratory [43] and field-scale [44] studies showed that biotic processes (microbial activity) in deserts could induce biogenic PC formation through biomineralization with rates higher than abiotic pathways. Accordingly, the presence of bacteria may enhance the adsorption of Ca²⁺, by its attachment to the bacterial membrane, cell wall, and extracellular polymeric substances (EPS) layer, as highlighted by Liu et al. [43]. Furthermore, an increase in pH through metabolic activities (e.g., ureolysis, denitrification, ammonification, and sulfate reduction) can facilitate the precipitation of CaCO₃ [44]. A genus of termites, macrotermes can contribute to secondary carbonate formation through supplying Ca²⁺ that originates from plant tissues and biomineralization [45][46]. On the other hand, in the absence of biotic agents, Fa et al. [47] showed that in semi-arid deserts carbon remains in the dissolved inorganic carbon (DIC) phase, and migration of CO₂-originating carbon to groundwater is observed. Microorganisms have also been shown by Zhao et al. [38] to retard the recrystallization of PC due to partial surficial growth of microorganisms on CaCO₃ crystals, stabilizing the formed PC.

The impact of various land-use changes on pedogenic carbon pool modification, the potential of stabilizing atmospheric CO₂ through PC formation, the challenges and techniques of tracking the formation of PC through engineered pathways in soils, and isotopic signature as a technique for distinguishing neo-formed carbonate in soil, are further explored, discussed and scrutinized by Khalidy et al. [1].

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