



Review

Soil Inorganic Carbon Formation and the Sequestration of Secondary Carbonates in Global Carbon Pools: A Review

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Abstract: Soil inorganic carbon (SIC), a potential carbon sink especially in arid and semi-arid environments, contributes to soil development, landscape stability, carbon (C) sequestration, and global C dynamics but due to the lack of SIC scientific reporting in most C sequestration research, its importance is unclear. A detailed overview of primary and secondary carbonate occurrence, formation, and importance is much needed to understand the role of pedogenic (PC)/secondary carbonate (a common biogeochemically derived soil mineral over time) in the SIC. The mechanisms involved in the formation of PC including carbon dioxide (CO₂) from microbial respiration and precipitation, silicate mineral weathering, dissolution, and reprecipitation are highlighted. The isotopic composition of carbonates related to biological C₃ or C₄ carbon fixation pathways and other paleoecologic and/or climatic factors responsible for new soil carbonate formation are discussed in detail. To address the lack of knowledge associated with SIC, this review attempts to highlight the currently known aspects of the literature, and briefly describe the formation and methodologies that can aid in addressing the research gaps surrounding SIC sequestration. The authors also suggest that greater focus needs to be provided on the actual measurement of SIC to develop a more comprehensive SIC inventory to provide sound data for future research direction, and modeling efforts and to predict C terrestrial storage and change efficiently.

Keywords: dissolution; silicate mineral weathering; reprecipitation; paleoecology; isotopes



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1. Introduction

Soil, a natural dynamic body, is considered to be the largest terrestrial carbon (C) pool of both inorganic and organic forms [1,2], containing approximately 2500 Pg C worldwide [3], and is the third largest global reservoir/pool of C after marine C and fossil fuel reservoirs [4,5]. The soil C pool contains both organic (OC) and inorganic (IC) C [3], both playing crucial roles in contributing to the global C pool. Soil organic carbon (SOC) comprises plant litter, microbial biomass, and microbial byproducts [4]. According to the Intergovernmental Panel on Climate Change (IPCC) [6], the SOC pool contains 697 Pg of carbon in the surface (0–30 cm) layer of the soil and 1500 Pg of carbon in the 0–100 cm depth [6]. Lal et al. [7] stated that >50% of soil C is present between a 0.3 and 1 m depth of the soil profile [3,8,9]. Soil inorganic carbon (SIC) is mainly composed of carbonates (CO₃²⁻) and bicarbonates (HCO₃⁻) of Ca²⁺, Mg²⁺, potassium (K⁺), and sodium (Na⁺) [1,10,11]. Primary or lithogenic (inherited from soil parent material) carbonates are also known as carbonated rocks (e.g., limestone). Secondary or pedogenic carbonates formed as a result of soil processes that accumulate in the soil as weathered materials [12], including calcium carbonate (CaCO₃), contribute an estimated 950 Pg C towards the global C pool [8,13].

Soil has a vital role as a global C sink, and therefore it is crucial to count both SOC and SIC as C stocks when evaluating different land-use management and climatic conditions [14]. Much work has been performed regarding SOC related to its accumulation and storage in soil, but inorganic C is often ignored, resulting in the sparse availability

of data [15]. Concerns about global climate change have led many scientists to study the cultivation impacts and different land management practices on SOC stocks and, thus, developing strategies on SOC can be managed effectively to mitigate the results of a changing climate. Because of this, SIC is often ignored, because most work on C sequestration is focused on C changes in the upper soil profile (0.3 m depth) [7,14,16], with deeper depths (0.3 to 1 m), where SIC is most likely to be found, being less frequently studied. Although SIC commonly exists in the carbonate form and makes up at least one-third of the total carbon in the soil (Table 1), there has been a lack of definitive research about SIC pools in different soil orders due to various land-use practices [1,14,17]. Most previous research on SIC has been conducted in semiarid or arid ecosystems [7,13,18,19]. Figure 1 shows the regions of the globe where both SIC and soil total C exhibit the greatest variation and probabilities of influencing the total soil C pool.

Table 1. Worldwide estimated soil organic C (SOC) and inorganic C (SIC) in the soil carbon pool by depth. (Adopted from [3,6,8,20]).

Pool	Soil Depth (cm)		
	0–30	0–100	0–200
SOC	725 Pg	1500 Pg	2450 Pg
SIC	250 Pg	750 Pg	-- ¹

¹ Information for deeper depths is commonly not found in worldwide data.

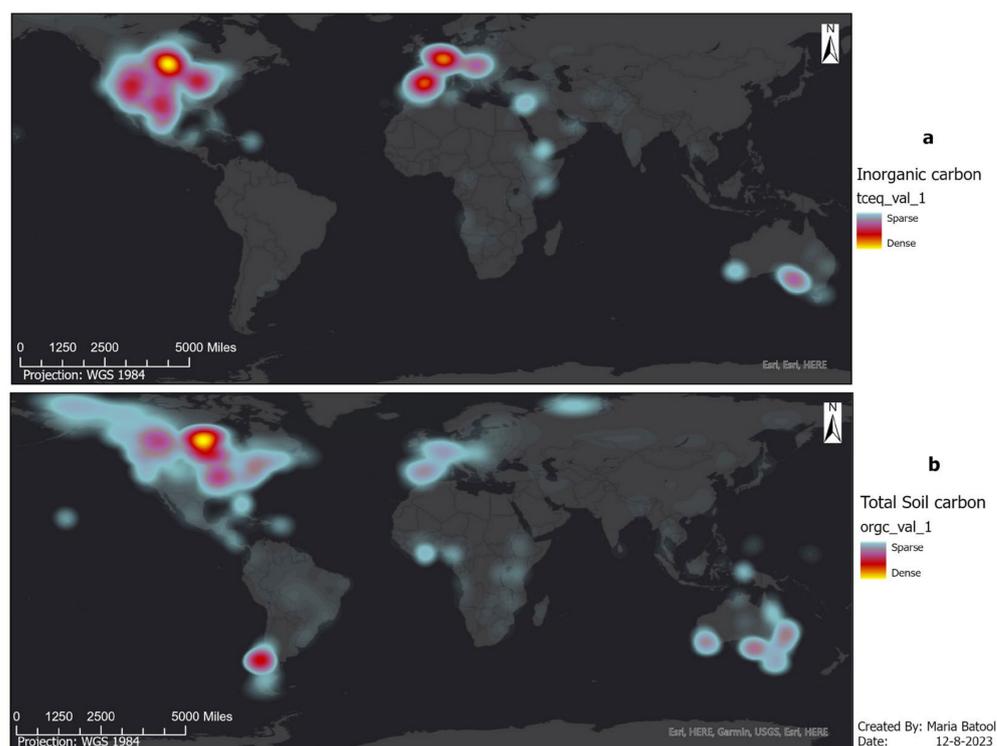


Figure 1. Global variation of STC and SIC at a depth of 1 m. (a) Soil total C distribution; (b) Soil inorganic C distribution (data are sourced from the World Soil Information Purpose and Strategy ISRIC World Soil Information, 2023, and modified from [21]).

This review attempts to highlight soil C pool dynamics, SIC's role in C sequestration, land management practices and their influence on C stocks, and the interaction of SIC with other atmospheric, biological, and anthropogenic factors. In addition, the occurrence of primary and secondary carbonates, their formation, and their role in soil C pool dynamics are also discussed in his review paper. The objectives of this review are to (1) define the role of inorganic C stocks in C sequestration; (2) describe the SIC formation processes;

(3) illustrate the atmospheric calcium (Ca^{2+}) and magnesium (Mg^{2+}) contributions to SIC formation; (4) describe the role of biogenic SIC formation in global drylands; (5) describe the role of stable isotopes in assessing SIC formation; (6) clarify the role of land management in SIC accumulation and storage in global C pools.

2. SIC and Its Importance

About 41% percent of the world is dominated by arid and semiarid land [3,20,22]. Soil inorganic carbon (SIC) is the most common carbon sink in those arid, semiarid, and subhumid climates [11,13], contributing 1.4 times more accumulating carbon than SOC, making it unquestionably a significant component of global C sequestration [13,20]. SIC is largely comprised of carbonates [1,4,11,13], which are considered a natural, consistently forming mineral component of soil, and is most commonly in the form of calcite (CaCO_3), dolomite ($\text{MgCa}(\text{CO}_3)_2$), aragonite (CaCO_3), and, less commonly, siderite (FeCO_3) [11,13]. Carbonates are considered to be mainly formed from calcareous parent materials or dust-borne materials [23] in the form of (a) primary or lithogenic or (b) secondary or pedogenic carbonates [1,17,24]. Lithogenic carbonates [12] resulting from carbonated parent material [11,13] do not appear to present a noticeable impact on the net global C pool [11]. Lithogenic carbonates are further categorized as in situ (residual) and ex situ (transported from foreign locations and designated as alluvial, colluvial, eolian, or glacial) [25]. However, secondary, authigenic (carbonate originated in sediments at or after the time of deposition), or pedogenic carbonates are carbonates that are developed from different authigenic sources due to soil micromorphology, geology, and pedology [12,25]. Whether pedogenic carbonates can be a crucial pathway for atmospheric CO_2 sequestration or not is still a controversial question [11,13,25]. Figure 2 illustrates the differing pathways of lithogenic or pedogenic carbonate formation.

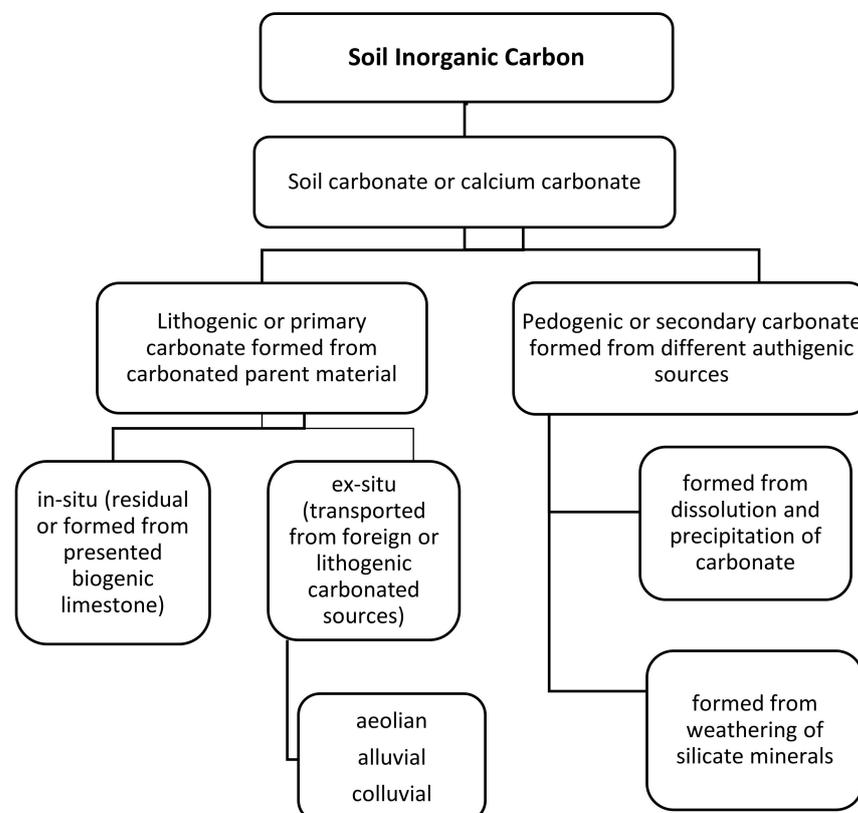
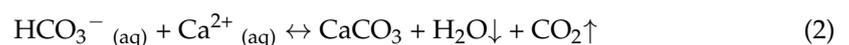


Figure 2. A flowchart depicting SIC and carbonate formation stages, including lithogenic and pedogenic pathways; modified from [25,26].

The formation of secondary carbonates depends upon factors including the soil micro-morphology, determined by the source from which secondary carbonates are being formed either as calcitic (carbonate dissolution) or silicatic (reprecipitation) forms [25]. Secondary carbonates (Bk or Calcic horizons) found at different soil depths depend upon the depth of leaching caused by rainfall and evapotranspiration [23]. Calcic soil horizons are formed through the dissolution of carbonates from the upper part of the solum (A horizon). These then accumulate in lower soil depths as water moves through the soil profile [23]. Early hypotheses of carbonate formation which was largely developed in the southwest [27] and its formation considered to be a result of capillary rise and groundwater evaporation, lakes with shallow depths, or algal reefs [27,28]. In contrast to the above hypothesis, evidence collected more recently has created arguments where carbonate formation processes for primary and secondary carbonates are more generally considered to be: (1) the weathering of Ca-silicate minerals; (2) the dissolution of carbonates and precipitation; (3) the pedogenic formation of carbonates.

2.1. Carbonate Dissolution and Precipitation

The amount and fluctuation of CO₂ in the soil is highly dependent upon atmospheric CO₂ and CO₂ produced through soil microbial and root respiration [29–31]. Under aerobic conditions, microbial respiration (O₂ consumption and CO₂ production) gives rise to calcite dissolution and precipitation [31,32]. In low-pH soils, atmospheric CO₂ and HCO₃[−] levels are low and not sufficient for the required high CO₂ concentrations to form carbonates. On the other hand, in high-pH soils, the conditions are reversed, leading to the precipitation of carbonate minerals [20,33]. Here, the consumption of one mole of atmospheric CO₂ by dissolution in soil water results in the formation of bicarbonates (HCO₃[−]), which, in the presence of Ca²⁺, precipitates an equal amount of CaCO₃ [20,25,34]. The leaching of carbonates can occur in the soil system, eventually transporting the precipitated CO₂ deeper into the soil profile. The leaching depth is dependent upon the water infiltration rate, soil pH, and carbonate concentration [13]. In two-way reactions of dissolution and reprecipitation, no net CO₂ production or consumption occurs, since half of the C is from the calcite source and half is from carbonic acid H₂CO₃ [35]. The following equations explain the continuous changes occurring in the SIC pool [34–38]



Elevated atmospheric CO₂ concentrations can create CO₂ saturation, leading to the release of CO₂ back to the atmosphere. This dissolution–precipitation can result in an SIC sink if carbonates continue leaching downward and are deposited at deeper soil depths [20,39]. A study by Gallagher and Breecker [30] proposed that highly precise measurements for monitoring dissolution and precipitation drivers can improve the estimation of soil CO₂ changes induced by microbial respiration. They demonstrated that carbonate dissolution can influence the complexity of interpreting biological respiration effects impacting isotopic carbon composition, and further suggest that carbonate dissolution and precipitation both may also have a positive shift in the δ¹³C values in soil CO₂. These effects are more noticeable in Aridisols due to carbonate accumulation at shallow depths, though it may also be expected in soils where carbonates have leached down into deeper soil horizons.

2.2. Weathering and Metamorphism of Ca-Silicate Minerals

Pedogenic carbonates can also form from the weathering of Ca- and Mg-rich igneous parent materials reacting with biologically respired soil CO₂. The C sequestration

by pedogenic CaCO_3 is dependent upon the source of Ca [35,40], and is shown in the following reactions:



Urey's [41] work is classic evidence of atmospheric CO_2 level changes over a geological era, controlled and affected by natural processes, such as Ca-silicate mineral weathering (SMW), which is aided by carbonic acid (CO_2 dissolved in soil H_2O) [32,38]. This acts as a moderator of atmospheric CO_2 concentrations on a millennial time scale as compared to carbonates, which act as moderators on a centennial time scale [13]. SMW transformation into carbonate and retransformation to silicate is a process called metamorphosis [32,38]. The forward (weathering) and backward (metamorphosis) reactions of calcite are presented above as unidirectional by Berner [38], in which calcium-bearing silicates convert into carbonates (Equation (3)) [13]. The downward arrow indicates the movement of CO_2 either as a gas or sequestered as carbonates. The Ca^{2+} comes from outside the system through the weathering of the bedrock, silicate minerals, or possibly from fertilizers or atmospheric dust [25,34]. In addition, Chamberlin [42] reported that a typical amount of CO_2 , set free by limestone dissolution, distributes throughout the ocean and atmosphere by the law of diffusion and results in the abundant accumulation of carbonic acid in the ocean. The formation of calcite (CaCO_3) or dolomite ($\text{MgCa}(\text{CO}_3)_2$) from SMW continues without the interruption of metamorphosis (the change of carbonates to silicate minerals) [32,38,42]. The CO_2 also takes part in the calcitic or dolomitic limestone weathering and precipitation in the oceans. The reaction above (Equation (4)) is a depiction of the weathering and precipitation of carbonate to bicarbonates by Berner [38], which also depicts the imbalance that might be created between the ocean and atmospheric chemistry due to this process. Yet, it is still adding to the silicate mineral weathering and retransformation (metamorphosis) in the C geochemical cycle.

Expediting this process, if possible, could increase a net carbon sink on a long-term time-scale of a thousand years, but, unfortunately, silicate weathering in soils is typically slow, consuming only $0.001\text{--}0.01 \text{ t C-CO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ [28,42]. Thus, increasing agricultural practices (irrigation and fertilizers) even three times the current rate to increase the rate of SMW would still not be enough to offset the increase in carbon emissions in the future [32].

2.3. SIC Formation Models

According to Monger [27], other than shallow lakes and deep groundwater geologic factors, the formation of pedogenic carbonates can be divided into four models, which are described in Figure 3.

Other models have been created based on these four models. These compartmentalized models utilize information obtained from certain chemical and physical properties of soil (i.e., the soil texture, bulk density, cation-exchange capacity, moisture, water-holding capacity, temperature, mineralogy, etc.) [27,43]. The biogenic model is related to plants and their microbial associations rely on calcite formation in soil. Rivadeneyra et al. [44] studied carbonate formation by a bacterium (*Deleya halophila* strain CCM3662) which is known for its ability to precipitate carbonates. This *D. halophila* biomineralization procedure investigated the carbonate precipitation potential by using scanning electron microscopy (SEM) and X-ray diffraction analysis. The study showed that precipitation occurred mainly as aragonite (CaCO_3). Little Mg^{2+} was noted in the presence of the charged surfaces of the cell walls of *D. halophila* in an open medium without the interruption of certain cells after 25 days of incubation. Apart from these four models, carbonates formed from alluvial parent material and calcareous deposits in soil profiles are considered to be lithogenic or primary carbonates. These are not included in the above models and are considered to be geogenic in origin.

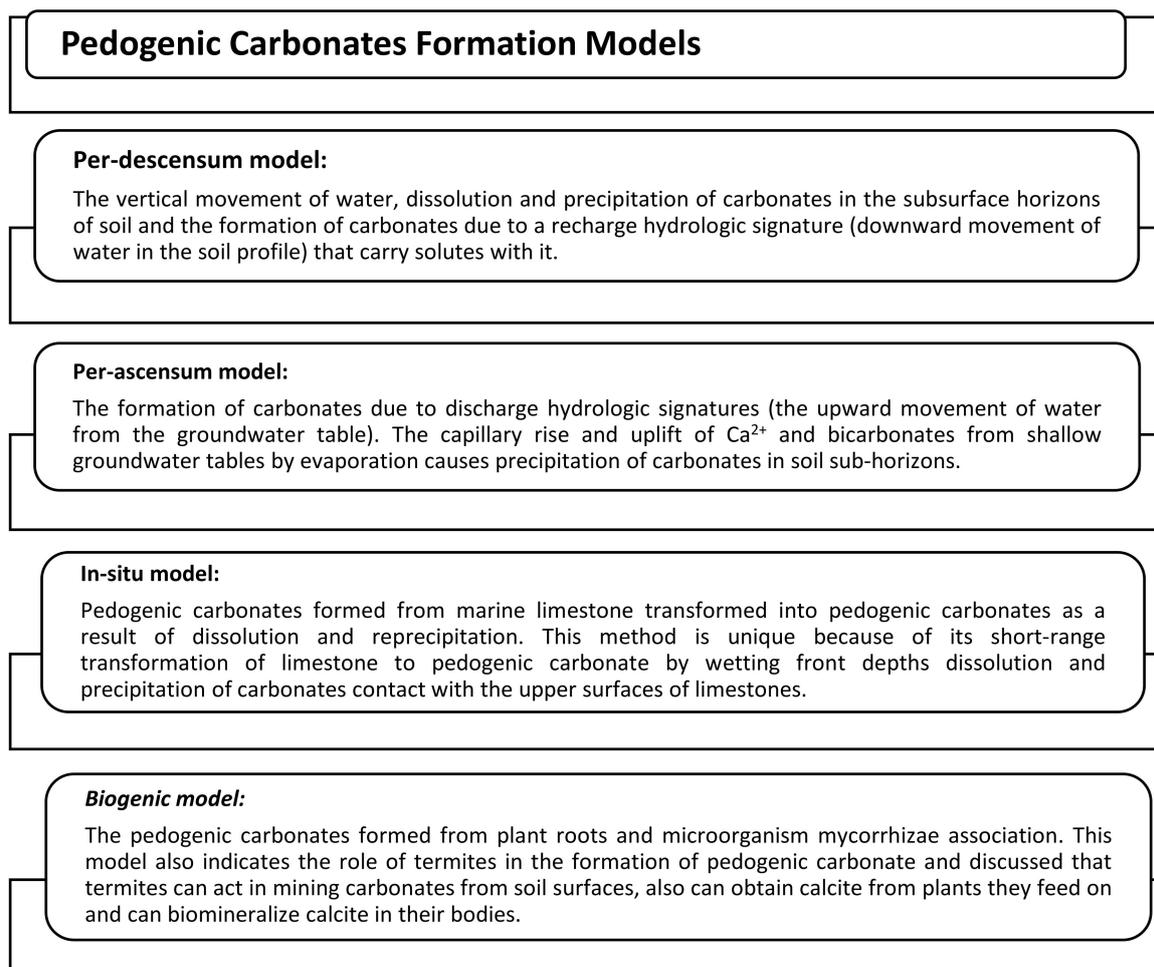


Figure 3. Pedogenic carbonate formation models from other than aquatic sources; modified from [27].

2.4. Formation of Pedogenic or Secondary Carbonates

Soil horizons influenced by secondary carbonate formation are often known as caliche; especially if the accumulated carbonates harden or become cemented. The caliche depth depends upon the leaching intensity, controlled by factors such as temperature and rain-fall [23]. Their formation is due to a balanced equilibrium of carbonic acid from CO_2 dissolution, and carbonate and bicarbonate precipitation with carbonic acid combined with Ca^{2+} forming calcite (CaCO_3).

When carbonate dissolution occurs, the resulting CO_2 increases in the soil air, which is added to by increases in root respiration and microbially mediated OM decomposition in a specific subsurface soil zone. SIC sequestration equilibria are possible when Ca^{2+} and Mg^{2+} cations come from outside the soil ecosystem (i.e., rock and soil material weathering, fertilizer addition, and biosolid use), or from rainwater infiltration and percolation. Thus, the formation of pedogenic carbonates is dependent on the availability of reactive cations, the hyperactivity of soil microorganisms, and leaching [13,23,45]. Pedogenic carbonates are found as concretions, nodules, masses, or coatings on peds [46], mainly in the lower solum (B horizon), and may occur near mycorrhizae and plant roots. The location of pedogenic carbonates depicts the similarity between them and SOC as an increase in one quantity affecting the rate of the accumulation of the other [13,45,47].

Schaetzl et al. [46] examined pedogenic carbonates in three pedons from two counties in Michigan. They found that secondary carbonates accumulated as coatings, threads, and filaments mainly in the lower B and upper C horizons at depths ranging from 33 cm to 236 cm. Pedogenic carbonates were more dominant in a prairie soil profile fulfilling the

taxonomic diagnostic requirement for a Calcic horizon by having 15% or more CaCO_3 present. In another study, Landi et al. [48] examined the quantities of pedogenic carbonates accumulated at different landscape elevation points of dark-brown and black chernozems in Saskatchewan, Canada. They found that the average amount of pedogenic carbonate that accumulated in a 1 m soil depth was 15 kg C m^{-2} at all points examined. They also noted that, when compared to lithogenic carbonates, pedogenic carbonates accumulated more in higher landscape elevations than in more level, stable surfaces when using a 1 m soil depth sampling criteria. Usually, a foot slope position has more moisture than the shoulder and summit positions, resulting in carbonate movement to greater depths, so deeper sampling is appropriate in these positions. Gile [49] found that pedogenic carbonates in multiple pedons in a Typic Haplargrid on a ridge side and drainage way of southern New Mexico (United States) occurred in the range of 22 kg m^{-2} (ridge side) to 108 kg m^{-2} (drainage way). This difference was mainly due to the shallow soil depth on the ridge side as compared to deeper soil depths in the drainage way, which enabled greater leaching.

Landi et al. [48] reported that the pedogenic carbonate accumulation rate is 1.4 times greater than the C sequestered by organic C in soils of different climatic and land management zones (prairies and forests) in Saskatchewan, Canada. They concluded that the mean turnover time for C depends highly on the soil age, with SOC having less turnover time (a few hundred years), while pedogenic SIC turnover continues across a time frame of hundreds to thousands of years. These findings also indicate that the pedogenic carbonate accumulation rate, storage, and soil depth are directly proportional to the increase in annual precipitation (rainfall). Infiltrating rainfall moves Ca^{2+} from lithogenic sources or eolian dust deeper into the soil profile. Later, when water evaporates, CaCO_3 precipitates and is left behind [48,49]. Pedogenic carbonate formation, accumulation, and storage depend on several factors, including climatic and land management variations. Soil types certainly help our understanding that pedogenic carbonates are a significant part of global carbon dynamics. Schlesinger [50] reported the average rate of pedogenic carbonate formation in the Mojave Desert of California to be 1.0 to $3.5 \text{ g CaCO}_3/\text{m}^2/\text{year}$ over 20,000 years, depending upon the source of carbonate formation (calcareous or noncalcareous loess) in arid and semiarid soils.

2.5. Factors Influencing SIC (Natural and Anthropogenic)

SIC storage and distribution can be influenced by several mutually performing biotic and abiotic factors triggered by multiple biogeochemical processes occurring in the soil ecosystem [51,52]. Natural factors, including climate, landscape, moisture, and microbial respiration, greatly influence the formation and accumulation of pedogenic carbonate, especially in arid and semiarid areas [52]. High temperature and summer precipitation increased microbial respiration and SOM mineralization. The combined moisture and CO_2 form carbonic acid in the soil system, which gives rise to bicarbonates which are precipitated in the form of carbonates when drier conditions persist [51].

Among soil properties, the texture, water-holding capacity, permeability, evapotranspiration, and leaching are the drivers controlling the accumulation of carbonates with the depth in the soil. The higher the clay content in the soil, the more micropores, the greater the water-holding capacity, and the higher the cation-exchange capacity (CEC), allowing an increased precipitation of dissolved carbonates with lower CO_2 concentrations. In contrast, sandy soils have more macropores, a lower surface area, and a lower water-holding capacity, which is not favorable for cation exchange [20,51,52]. A hillslope topography can greatly impact the carbonate accumulation in the different positions of a hillslope soil catena due to water relations in the landscape. Depending on the landscape history, the depth of carbonate accumulation may be lower in the summit and shoulder positions, and higher in the back and toe slope, because of groundwater and capillary rise or the downward movement of surface water. Surface runoff can be a consideration for more pedogenic carbonate accumulation in the upper horizons of the lower backslope [52]. Erosion and loess deposition can greatly reduce the amount of SIC in the soil profile depths

with time, and are capable of changing the topography and carbon dynamics of a particular land parcel.

2.5.1. Soil pH

Soil carbon dynamics are impacted by changes in the soil pH, which result from complex chemical and biological activities occurring in the soil [20,53,54]. Ref. [53] suggested from evidence that a decrease in the soil pH (acidity) will decrease the SIC but increase the SOC. The reduction in the SIC in acidic soils is due to CaCO_3 reacting with H^+ ions and the consumption of CaCO_3 , thereby buffering the soil pH in the direction of pH neutrality ($\text{pH} = 7$), and releasing CO_2 and Ca^{2+} ions to displace H^+ ions on soil exchange sites [55]. Soils with a higher pH (>7) have a greater saturation with basic cations (Ca^{2+} and Mg^{2+}), which can react with dissolved bicarbonates and carbonates, resulting in the precipitation of SIC once critical concentrations of ions are reached. In areas of higher rainfall, Ca^{2+} and Mg^{2+} can leach deeper into the soil profile, resulting in SIC precipitation in the deeper profile. If calcite dissolution is accelerated and CO_2 in the soil water is elevated due to high plant root and microbial respiration, the potential net CO_2 sink can be $0.03\text{--}0.12 \text{ tC ha}^{-1} \text{ yr}^{-1}$ [32,56].

2.5.2. Wet Deposition of Ca^{2+} and Mg^{2+}

Carbon dioxide levels in the soil atmosphere can be at least an order of magnitude higher than the CO_2 in the atmosphere above the soil surface [57]. The atmospheric wet deposition of Ca^{2+} and Mg^{2+} in rainfall needs to be considered in pedogenic carbonate formation (carbonate precipitation by increasing Mg^{2+} and Ca^{2+} concentrations) [24,31]. Pedogenic carbonate accumulation in soil is triggered by lithogenic carbonate dissolution and increased CO_2 from biological respiration in the soil system. This is controlled by the soil water content. According to Gile et al. [58] Ca^{2+} -based carbonate starts precipitating as small filaments or thin nodules, which convert to calcite masses with continuous precipitation until pore spaces are filled [31]. If free Mg^{2+} is present in the soil system, it also precipitates with Ca^{2+} , forming dolomite ($\text{MgCa}(\text{CO}_3)_2$). Dolomite, magnesite, aragonite, and siderite are formed along with calcite in this manner [2]. Dolomite is readily identified because of its wide occurrence in soil and occurs as a metastable form of soil carbonate [31]. Ca^{2+} and Mg^{2+} deposition through rainfall events aids this process.

Mikhailova et al. [24] reported on the potential contribution of Mg^{2+} and Ca^{2+} wet deposition (WD) leading to SIC sequestration, and noted that the new metastable carbonate formation (i.e., dolomite) needed external Ca^{2+} and Mg^{2+} WD from atmospheric sources. Among the twelve soil orders, Mollisols and Alfisols have a high potential to sequester C by Ca^{2+} and Mg^{2+} WD through carbonate precipitation. A similar study conducted by Goddard et al. [2] reported similar trends among Ca^{2+} and Mg^{2+} WD in different soil orders within the continental US from 1994 to 2003. They found Mollisols, followed by Alfisols and Ultisols, accumulated $3.7 \times 10^7 \text{ kg}$, $3.6 \times 10^7 \text{ kg}$, and $2.8 \times 10^8 \text{ kg}$ SIC, respectively, in Oregon, Washington, northern California, and the east-coast portion of the US because of a high Mg^{2+} deposition from sea-salt aerosols.

Different soil orders can also receive varying quantities of Mg^{2+} as WD depending upon the presence and quantity of irrigation, as well as applied fertilizers, resulting in differing potential rates to accumulate SIC. The wet deposition of Ca^{2+} and Mg^{2+} may contribute to other mineral formations (dolomite, aragonite, and siderite) along with calcite as pedogenic carbonates [24,31]. Aridisols and Entisols found in the midwestern US region could be considered to be significant SIC pools because of their calcium-rich loess deposits and a lower rainfall environment (mean annual precipitation $< 120 \text{ cm/year}$). Here, the formation of carbonates in the top 1 m of soil is more likely as compared to Mollisols and Entisols, which receive higher rainfall amounts and accumulate pedogenic carbonates much deeper in the profile [44].

3. Biogenetic Stages of Pedogenic Carbonate Accumulation in Drylands

3.1. Morphological Patterns

Dust-borne calcareous material, which occurs in areas encompassed by deserts, has been proposed as a soil carbonate source [58,59]. The Desert Project Guidebook, originating from research on the deserts of New Mexico [60,61], presents a hypothesis that there is sufficient geological evidence supporting carbonate accumulations originating from sources other than water tables or lakes. Gile et al. [44] support the concept of pedogenic carbonate formation and note that (1) more carbonate will accumulate as soils age and develop with time, and (2) carbonate horizons form parallel to the soil horizons. This hypothesis presents the concept of pedogenic carbonate accumulation comprising varying stages within two morphological patterns of soil textures: (1) low or no gravel (<20% gravel) and (2) fine-texture and high-gravel soil materials (50% gravel) [60,61].

The low and high gravel formation concept represents different morphologies. Initial carbonate accumulation in soil pores accompanied by other factors, such as an increase in the bulk density, infiltration rate, and leaching, results in the Calcic horizon having barrier characteristics, which later develops a laminar zone on top of the Calcic horizon. The laminar zone is a new soil layer and may be of greater thickness due to fluvial and lacustrine material deposition [59]. Downward water movement with calcium deposition in the laminar zone, followed by water evaporation from soil pores, leads to carbonate coatings on soil structural units. Coatings with a prismatic or crystalline structure show evidence of several wetting and drying sequences in soil. Carbonate deposition on the upper laminar zone from lakes or ponds is considered as new, soft, or young carbonates as compared to the mature (hard and older) ones under the laminar zone, and are designated as the Bk or K horizon [44–60,62]. The Bk or K horizon is the major accumulator of CaCO_3 due to its morphological aspect of carbonate deposition [59]. The K horizon contains carbonates in concretions, masses, or filaments in the subsurface soil. The diagnostic requirement for a horizon to be called the Bk or K horizon is the presence of 15 to 40% authigenic carbonate [59].

3.2. Environmental Patterns

Pertinent questions that arise in pedogenic depositional environments are: (1) what are the sources of Ca^{2+} in new carbonates? and (2) what external environmental processes are the leading drivers of CaCO_3 formation in different soil horizons? It is clear that soils developed in semiarid and arid environments contain proportionately more C as carbonates, and explaining their sources is essential to understanding the pedogenic process.

According to the Desert Project [60,62], the main sources of Ca^{2+} are dust and rainwater. Reheis and Kihl [63] reported that dust deposition due to annual dust flux changes in southern Nevada and California is a result of an increase in the annual mean precipitation rather than the mean annual temperature. Most of the dust from beach areas is rich in carbonates and soluble salts. However, if CaCO_3 dust is counted as a pedogenetic source of carbonate, then no additional atmospheric CO_2 transfer to the soil is likely to occur [49,60]. Existing CaCO_3 dissolution would result in losses of CO_2 to the atmosphere and, though CaCO_3 can reprecipitate, a net loss of carbonate rather than a net gain would be expected. In an arid environment, the primary source of Ca^{2+} deposition originates from limestone and igneous parent material [44,59,61,62], while in subhumid or semiarid regions, pedogenetic sources could be mainly limestone dissolution [62,63].

4. Role of Stable Isotopes in Pedogenic Carbonate Dynamics

Stable isotopes play an important role in soil carbonate formation, as they are considered to be useful tracers of climate influence on soil formation [64]. The composition of oxygen isotopes in meteoric water (water originating from precipitation) is especially related to the mean annual temperature and climate. Meanwhile, the composition of C isotopes of pedogenic carbonate is dependent upon the amount of CO_2 present in soil gases and the C_3 and C_4 plant proportions in the ecosystem [65]. Meteoric waters are

the controlling factor of oxygen isotopes, and soil CO₂ is the controlling factor in carbon isotopes found in sequestered soil C compounds. Since pedogenic carbonate formation requires an equilibrium relationship with the CO₂ in the soil atmosphere, sources of soil CO₂ depend upon organic matter, diffusional and atmospheric sources, as well as soil biological activity [62,66].

Plants are divided into three groups based on their metabolic CO₂ assimilation pathways, which influence their isotopic C values: C₃ plants, C₄ plants, and crassulacean acid metabolism (CAM) plants. Warm-season grass species generally make up the C₄ plant group, while C₃ plants consist of cool-season grasses, trees, shrubs, and herbaceous plants. The C₃ plants have δ¹³C values of around −26‰, C₄ plants have values of around −12‰, while CAM plants have intermediate values [65,66]. In addition, C₃ plants tend to have high water use, which makes their δ¹³C values positive for arid environments as compared to dry environments (water-stress conditions) [65]. Plants in the C₄ group have a more efficient photosynthetic pathway due to photorespiration, and have greater tolerance to water stress. Maize (*Zea mays* L.), sorghum (*Sorghum bicolor* (L.) Moench.), and prairie grasses are examples of North American C₄ plants. Succulent plants, like cacti and plants adapted to saline environments, are examples of CAM plants that have intermediate δ¹³C values, but are not specifically addressed in isotopic phenomena [64,65]. Cerling [64] showed a positive correlation between δ¹³C and δ¹⁸C due to the oxygen isotopic composition of meteoric water and the C₄ biomass proportion. The analysis showed that the difference in δ¹³C values in carbonates is due to microbial respiration in soil. Another reason for this change is due to the differences in the diffusion coefficients for ¹³CO₂ and ¹²CO₂.

Cerling and Quade [65] examined the isotopic composition of pedogenic carbonates in four different global climatic zones. The first, midwestern North America, is characterized by a monsoon climate supporting C₄ plant growth, which has good tolerance to high light and periodic water stress. The second region, located in the western US Great Basin Desert of Nevada and Utah, has a characteristically hot, dry growing season. Here, C₄ plants and some CAM plants, such as *Atriplex* sp., were found abundantly in lower elevations, but where meteoric water oxygen isotopes (δ¹⁸O) decrease with an increase in the elevation [65,66]. Sites from Bolivia and Kenya have an equatorial climate with a narrower annual temperature range. At these sites, root growth is insignificant below a 30 cm soil depth, limiting deeper biological activity to influence the isotopic composition. The final study sites were under the Mediterranean climates of southern Europe and southern Australia, dominated by dry summers and winter precipitation. With this seasonal pattern, the most active plant growth occurs in spring by C₃ vegetation, with very little production of C₄ plants. This study, utilizing isotopic diffusion equations, resulted in predictions indicating that the isotopic composition of pedogenic carbonates is reliably constant at soil depths due to the impacts of CO₂ changes being the greatest in the upper 20 cm of the soil, which are formed on a time scale of thousands of years. A 4.4‰ improved enrichment in CO₂ in the soil was observed as compared to the respired CO₂ in modern soils (developed in the last few thousand years). They concluded that the ratio of δ¹³C to δ¹⁸O values of pedogenic carbonates can be used to indicate an ecological change in paleosols [65,67].

Quade et al. [68] reported that local ecosystems in Pakistan (semiarid environment) showed a carbon isotope shift from C₃-dominated ecosystems to C₄-dominated ecosystems within 6 million years. Oxygen isotopes also showed a shift in an 8-million-year time period [65,68]. Stable isotope geochemistry of carbonate rock and marine clay soil studies have shown that nearly 50% of carbonates in upper carbonate rocks are newly formed, while, in marine clay soils, 100% of carbonates are newly formed due to a 10 and 30 percent dissolution or precipitation process efficiency [69]. Therefore, a balanced multiscale approach to carbonate measurement (biome scale, landscape scale, soil-profile scale, and rhizosphere scale) would provide an increase in the isotopic records of pedogenic carbonate formation [70]. The amount of newly formed carbonates can be calculated by using the isotopic mass balance equation (Equation (5)) [69,71]

$$\% \text{ New pedogenic C (PC)} = (\delta^{13}\text{C}_{\text{bulk}} - \delta^{13}\text{C}_{\text{parent}}) / (\delta^{13}\text{C}_{\text{pedogenic}} - \delta^{13}\text{C}_{\text{parent}}) \times 100 \quad (5)$$

According to this equation, the amount of newly formed pedogenic carbonate is estimated on a weight basis relative to the amount of total pedogenic carbonate. The $\delta^{13}\text{C}_{\text{parent}}$ is measured directly by the assumed parent material; $\delta^{13}\text{C}_{\text{bulk}}$ is measured separately from each soil horizon, which normally contains a mixture of parent and newly formed pedogenic carbonate [71].

5. Land Management and Its Effect on Inorganic Carbon Sequestration

Land management practices describe land use and land cover in terms such as native grasslands, cultivated lands, rangelands, and forests. Land management systems and crop cultivation affect the quantity of C stored in soils because vegetation is the major C accumulator in managed ecosystems [72]. However, soil erosion is less often considered as a factor, but it, too, plays an important role in the global C cycle [73] by reducing the stored SOC content of the topsoil, as well as reducing the pedogenic carbonates being formed as SIC. The conversion of natural ecosystems to agricultural lands reduces the SOC pool due to leaching and erosion, while altering the soil temperature and moisture regimes, resulting in the SOC for grassland ecosystems being higher than for croplands [7]. Olson et al. [74] reported decreasing organic C with an increase in the sediment transport and deposition process (wind and water erosion), which can transport SOC-rich particles to other agricultural lands. Eroding land can underestimate or overestimate the soil C values due to losses and additions caused by periodic erosion-induced changes, with similar effects on SIC being likely. It is a destructive process for soil C, as it alters and/or destroys the amount of both organic and inorganic C in soils. Hence, it is essential to consider land management and landscape elevation when studying soil C dynamics at specific locations. When studying soil C dynamics, three things need to be considered: (1) the eroding land unit; (2) the depositional land unit; (3) differing landscapes.

Soil erosion disrupts organic and inorganic C stocks due to runoff and C decomposition losses from the exposure of stored subsurface C to oxidation, dissolution, and leaching. Eroded soil moves C stocks from eroding landscapes to depositional landscapes, streams, and water bodies. Soil loss reduces both the SOC and SIC content in the soil profiles of eroded landscape positions, resulting in lesser amounts of C sequestered and stored, but can increase them in depositional lands. Depositional lands often have more than 0.5 to 1 m increases in soil from sediments derived and transported from eroded agricultural lands that are enriched in SOC and SIC [74]. Lal [13] noted that the soil erosion process occurs in four different stages, and the alteration of SOC stocks happens in each stage, creating different soil ecological conditions, including: (1) low soil quality and a decline in soil health, leading to a decrease in the net primary production of agricultural ecosystems; (2) a decrease in SOC stocks; (3) soil aggregate breakdown, leading to microbial vulnerability and reduced activity; (4) N immobilization/mineralization occurring in the depositional landscapes, giving rise to CH_4 and N_2O emissions.

Accounting for all the C in soils under varying management systems and landscapes is an approach to be considered to obtain a complete picture of soil C sequestration and storage. Mikhailova et al. [11] stressed the importance of land use and management in C sequestration, where the cultivation of grasslands in both the US northern Great Plains and the Russian chernozem led to a decrease in the SOC and an increase in the SIC. This report elaborated on the fact that native grasslands, known to have high C accumulation, will lose SOC with the length of time in cultivation, but in the examples cited, the SIC increased because the calcium-rich soil in the grassland ecosystems provided the substrates to precipitate SIC as the SOC deteriorated. When grasslands are disturbed, microbial respiration increases, resulting in higher CO_2 levels in the soil atmosphere. This, in combination with a potentially deeper infiltration of captured rainfall, creates an environment where CO_2 dissolved in the soil water has a greater opportunity to precipitate as Ca^{2+} and Mg^{2+} carbonates in the soil, rather than to be released back to the atmosphere.

To mitigate climate change and reduce CO₂ concentrations, in arid and semiarid areas, irrigation can be considered as contributing to C sequestration [75]. An increase in irrigation can impact the plant growth cycle and eventually provide root exudate, biological respiration, and root biomass C deposited in the soil [56]. Several studies [51,56,65] have reported more inorganic C as compared to organic C in arid and semiarid lands due to a lack of precipitation, which limits basic cations being able to leach from the system. Other studies show a null effect of irrigation on SIC increase or decrease [56,57]. Often, in arid environments, soils need to be remediated with gypsum or other Ca²⁺-containing materials to improve their productivity. Thus, proper land management, and the amount of irrigation according to environmental demands, is critical for changes in SIC. Anthropogenic activities can have a great impact on the amount of SIC accumulated in the soil profile. Recently, Dang et al. [76] stated that there was a significant increase of 6.55% and 9.25% in the SIC with anthropogenic activities, such as cultivation.

Yellajosula et al. [77] examined the organic, inorganic, and total C (SOC, SIC, and STC, respectively) in revegetated soils originating from a long-term cropped or native grassland in a 5-year study. The results found more STC and SOC, with little change in SIC, in native grasslands that had been tilled but immediately restored to grassland. The long-term (>90 years) cultivated lands had low initial C contents, but also had low C sequestration rates (as SOC, SIC, or STC) when restored to grassland. Bingham et al. [78] noted that many grass species had highly developed associations with specific mycorrhizal organisms that promoted their growth. In this study, the cropland appeared to be lacking the appropriate mycorrhizal populations as compared to the native grasslands, thus showing slow C sequestration activity and resulting in much lower changes in SOC, SIC, and STC. The soils in this study were an open system (alluvial sediments over fine gravel at 0.6 m) and showed a redistribution of SOC and SIC within the soil profiles due to water movement within the profiles. More data and research are needed to clarify the calcareous and noncalcareous source inputs to better quantify carbon stocks, and studies such as this can help explain how biotic and abiotic factors impact the formation of SIC. Tables A1 and A2 illustrate some of the methods used by scientists to study SIC.

6. SIC and Global C Sequestration

Soil inorganic carbon is estimated at 748 Pg (Table 1) when measured to a 100 cm depth. However, solid estimates of SIC beyond a 100 cm depth are generally lacking. When the data in Table 1 are examined closely, there is a doubling (2.15×) of the SOC mass observed when examining the SOC at a 100 cm depth rather than at a 30 cm depth, and nearly a second doubling (1.6×) when examined to a 200 cm depth. Table 1 also shows a tripling in the SIC mass (3.05×) from a 30 cm depth to a 100 cm depth. The question that remains is whether SIC triples again between 100 cm and 200 cm. If so, then the masses of the SOC and SIC would be nearly equivalent (~2250 Pg) at a 200 cm depth in the soil. Solid CaCO₃ has a density of 2.71 g cm⁻³, while preliminary data in an ongoing study in the northern Great Plains indicate that most soils in a semiarid environment have a bulk density of 1.2–1.4 g cm⁻³ (L. Cihacek, unpublished data). This difference can complicate the SIC estimation in soils due to the nature of the CaCO₃ (coatings, filaments, nodules, concretions, etc.) because these often get eliminated in the normal processing of soil samples (screening and/or crushing) after they are collected.

Research on soils having calcareous parent material, or the calcium from noncarbonate minerals contributing to the pedogenic carbonate formation, usually focuses only on limestone filaments or coatings present in the 15–30 cm soil depth, and are often not characterized as secondary/pedogenic carbonates [3,25,79]. Lal et al. [7] noted that most of the C present in a 1 m soil profile is found between 0.3 m and 1 m. This strengthens the argument that it is of a size large enough to be considered as a major C pool, but its potential to sequester carbon is still not clear [34]. Although often discussed, the lack of focused research on the quantity of C sequestered as SIC, and implementing proper techniques to determine the source of soil SIC, hampers our understanding of the role of SIC in the

overall picture of soil C sequestration and storage. Table A1 describes research methods used to determine the soil carbonates (lithogenic and pedogenic) most often associated as part of determining the SOC. These methods are not useful in identifying the contribution of newly formed pedogenic carbonates. Most of the methods utilize high-temperature combustion along with scanning electron microscopy (SEM) or mass spectrometry (MS). Table A3 shows the different studies carried out in different parts of the world that discuss the importance of SIC and its potential in C sequestration.

Most studies indicate pedogenic carbonates are due to CO₂ sequestration, calcareous dust deposition, the wet deposition of Ca²⁺ and Mg²⁺, or metamorphosis (primary carbonates later converting to secondary carbonates). Eswaran et al. [3] estimated that SIC, SOC, and STC in wet soils belong to nine different soil orders. The highest SIC was reported for Spodosols and Aridisols (21 Pg and 21 Pg, respectively). No SIC stock contribution was noted for Gellisols, Entisols, Ultisols, and Histosols. They also stated that the estimated SIC is less than 10% of the total SIC present, again indicating the difficulty of conducting research on SIC. Eswaran et al.'s [3] research indicated that higher SIC in Aridisols is due to the sequestration of atmospheric CO₂. However, in contrast, Gile and Grossman [28] concluded that most of the Ca sources in deserts are calcareous dust blown in from other places or the reprecipitation of carbonates from dust with the minimum involvement of atmospheric CO₂. Their hypothesis would then point to no contribution to the net transfer of CO₂ to soil, and SIC would not be considered as a carbon sink [47,60]. Monger et al. [25] pointed out that the complexity involving the atmospheric CO₂ sequestration potential of SIC may be resolved if attention is paid to the sources of Ca²⁺ involved in forming carbonates. If the source of Ca²⁺ is pre-existing carbonate leading the equilibrium reaction, it would be an unlikely contributor to sequestering C in the soil as compared to Ca²⁺ from silicate minerals in a unidirectional reaction, which will sequester C in the soil. So, the real answer to whether SIC contributes to the C sequestration potential of soil is to be found between the unknowns of the two above concepts. Currently, biological contributions to the CO₂ in the soil atmosphere and their role in soil SIC deposition are also poorly quantified.

Despite agreement about the large amounts of carbon that can be stored in soil as SIC, arguments still surround whether carbonates are considered a CO₂ sink or not. This controversy revolves around the following: (1) the mean residence time (MRT) of the C remaining as carbonate must be at least 35 years [40]; (2) climatic variations and land use are the main drivers of C stocks in any ecosystem, regardless of whether the stocks are SOC or SIC. Wet soils have low carbonates as compared to grasslands because of the continuous leaching of carbonates and bicarbonates from a wet soil system, but it may be considered an HCO₃[−] reservoir due to the dissolved CO₂ in the soil water. Eswaran et al. [3] concluded that SIC distribution varies highly among different ecological zones which also encompass many soil orders. Mermut et al. [79] reported an average estimated pedogenic carbonate rate of 33 kg C m^{−2} with a mean turnover time of 85,000 years globally, and a deposition rate estimated to be 1 to 3.5 g CaCO₃ m^{−2} yr^{−1} in arid regions. This rate is greater than the organic matter accumulation in arid lands. When comparing young soils to old soils, long-term carbon flux can vary from 0.35 g m^{−2} yr^{−1} to 0.015 g m^{−2} yr^{−1}, respectively.

Soil inorganic C sequestration occurs faster in young as compared to old soils on a time scale, but pedogenic carbonates in old soils appear to be more important. Soil IC is generally higher in temperate regions because many deserts occur in temperate regions, resulting in about 35% of the total SIC stores worldwide. On a time scale, age and turnover times are important in pedogenic carbonate formation [3,80]. Unfortunately, pedogenic carbonate estimation is not yet a part of the routine C sequestration analysis because of its occurrence at much deeper depths than is considered in most research, and C sequestration research tends to be focused in more humid areas of the globe.

Recent studies revealed radiocarbon (¹⁴C) as a reliable source of determining hydrothermal carbon fluxes instead of δ¹³C, which are highly sensitive to CO₂ outgassing. A study in the Changbaishan Volcanic area, Northeast China, reported the analytical results of hydrothermal fluids and their impacts on carbon isotopes [81,82]. These results indicate

that deep carbon flux in the volcanic area is much greater than the CO₂ consumption flux (silicate weathering), and deep CO₂ outgassing should not be underestimated [82]. Additionally, hydrologically variable conditions giving rise to dissolved inorganic carbon (DIC) play an important role in the global carbon cycle [82]. Liu et al. [82] investigated the associated chemical weathering processes and DIC response to the hydrological variability, and strengthened the claim from the [81] study, but $\delta^{13}\text{C}_{\text{DIC}}$ also depicts high sensitivity and highlights that hydrological variability and its impacts on the isotopic composition of carbonates can help to provide a more in-depth understanding of the global carbon cycle in the future.

Ecosystem services offered by C storage as SIC are important, but its exclusion in the framework of ecosystems can limit their apparent value. As the climate changes, soils also change, and since SIC is a component of a large terrestrial C pool, the contribution of SIC to ecosystem services should be acknowledged along with SOC [50]. Groshans et al. [83] also ranked the value of the highest amount of carbon stored by SIC in the upper 2 m depth of the soil profile on a currency basis (USD 10.42 ton⁻¹ of CaCO₃) as Mollisols > Aridisols > Alfisols > Entisols > Inceptisols > Vertisols, illustrating its importance as a supplier of supporting services.

7. Summary

This review provides an overview of SIC literature and highlights associated knowledge gaps due to a lack of SIC reporting in most C sequestration research. A sound understanding of primary and secondary carbonate occurrence, formation, and importance in the soil C pool is yet unclear as to their connection to the specific formation processes of carbonates and their role in soil C dynamics.

The challenge of accurately estimating C changes on landscapes on a large scale has prompted many researchers to suggest that accurate models be developed to provide these estimates [20,26,77]. However, in light of the current clear uncertainty of SIC as a major contributor to overall C sequestration and storage in soils, greater focus needs to be provided on the actual measurement of SIC to develop a more comprehensive SIC inventory to provide sound data for future modeling efforts.

When studying soil C sequestration, researchers need to ask: (1) Why are carbonates important in accounting for C sequestration in soils? (2) What processes are leading to CaCO₃ formation in different soil horizons? (3) Why are pedogenic carbonates neglected in the processes of soil C sequestration and storage? Considering these questions can help expand our understanding of SIC. Soil inorganic C as a major proportion of the total soil C is usually associated with arid and semiarid lands. Soil C dynamic changes due to anthropogenic activities, the amount of irrigation, soil management, and fertilization must be considered to grasp the complete understanding of the global C cycle. Future investigations are highly recommended to include concepts such as the evaluation of radiocarbon (¹⁴C) being a missing carbon sink, and the development and in-depth understanding of the effects of hydrological fluctuations in relation to the isotopic composition of DIC. Specific research needs include: (1) reporting SIC and STC, as well as SOC data, even where the SIC is not expected to build a more robust SIC and STC database; (2) the greater use of isotopic techniques to differentiate and quantify "new" versus "old" SIC; (3) the inclusion of more deep sampling in studies (up to 2 m or more) to obtain a clearer picture of the actual SIC stocks occurring in various soil orders and across landscapes; (4) the standardization of sampling and measurement protocols, which will provide the background information on SIC for the development of prediction models based on geology, geography, and climate. A multiscale approach accounting for SIC formation is suggested as a bridge to the future development of a better understanding of soil C dynamics.

This review emphasizes the need for information related to the SIC sequestration potential in understanding additional C sequestration potential, especially in regions such as the Great Plains of the US and Canada, which comprise about 2.9 million km² of the area, or about 290 million hectares, of both croplands and grasslands [78], representing a

potentially significant sink for C as SIC. Similar areas exist around the globe which can also contribute as sinks for atmospheric C, but have not received the attention that SOC has received [20,26,56,84,85]. Examples of SIC formation also exist in forestry environments [77], but the extent is not yet clearly defined. Expanding our research to fill the knowledge gaps illustrated above, as well as strengthening research databases to develop a clearer accounting of global soil C sequestration, will not only be helpful in academic and research areas, but will also help policymakers to make soil management decisions in favor of the Earth's environment.

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Appendix A

Table A1. Methods used to analyze both organic and inorganic soil C components commonly reported in the literature.

U.S State/Country	BD ¹	STC ²	SOC ³	SIC ⁴	Citation
Saskatchewan, Canada	N/D ⁵	HiTDC ⁶	HiTDC	IC ⁷	[48] ^a
Northeastern Italy	PTF ⁸	N/D	Dichromate oxidation and HiTDC	N/D	[86] [87] ^b
New Zealand	Claydon	A Leco WR-112 C analyser	fumigation extraction and dichromate oxidation	N/D	[88]
North Dakota, USA	Core method	N/D	N/D	Acid ⁹	[77] [89] [90] ^c
Kursk, Russia	Oven-dried	HiTDC spectrometry by RPT ¹⁰ system	HiTDC spectrometry by RPT system	IC	[14] [91]
Kursk, Russia	Oven-dried	N/D	HiTDC spectrometry by RPT	N/D	[92]
North Dakota, USA	Core method	HiTDC	OC=TC-IC	Acid	[93] [89] [94] ^d
Maryland, USA	Core method	N/D	HiTDC	N/D	[95]
North Dakota, USA	Core method	N/D	Modified Mebius method	Acid	[18] [96] [94]

Table A1. Cont.

U.S State/Country	BD ¹	STC ²	SOC ³	SIC ⁴	Citation
North Dakota, USA	Core method	HiTDC spectrometry by RPT System	HiTDC spectrometry by RPT system	Acid	[11] [90]
North Dakota, USA	Core method	HiTDC	HiTDC	Acid	[8] [94]
California	Oven-dried	Costech ECS 4010 CHNS-O elemental analyzer	Mass spectrometry	Acid fumigation	[96]

¹ Bulk density; ² Soil total carbon; ³ Soil organic carbon; ⁴ Soil inorganic carbon; ⁵ Not determined; ⁶ High-temperature dry combustion; ⁷ Inorganic C = Total C – Organic C; ⁸ Pedotransfer function; ⁹ Acid dissolution; ¹⁰ Robo-prep Tracemass System (Europa Scientific, Cheshire, UK). ^a First reference in the citation column indicates the primary article; ^b Second reference in the citation column indicates the cited article for the bulk density method; ^c Third reference in the citation column indicates the cited article for the SIC method; ^d Fourth reference in the citation column indicates the cited article for the SOC method.

Table A2. Methodology for the study of soil inorganic C.

Citation	Environment	Methods
Schaetzl et al. [46]	Temperate	Treating soil mixtures with HCl acid and measuring the evolved CO ₂ ; CaCO ₃ was determined, which is equivalent to a <2 mm fraction.
Rivadeneira et al. [44]	Semiarid	X-ray dispersive energy microanalysis; the formation of carbonate crystals by <i>Deleya halophila</i> .
Landi et al. [48]	Semiarid	Europa Tracer/20 Mass spectrometer analysis and mineralogical analysis.
Bruckman et al. [97]	Forest land	Fourier transform midinfrared spectroscopy and powder X-ray diffraction.
Kolosz et al. [98]	Multiple environments	Roth-C and century model.
Allison & Moodie [99]	Multiple environments	Vacuum distillation and titration, acid neutralization, volumetric calcimeter, and pressure calcimeter methods, and a gravimetric method for the loss of CO ₂ .
Mikhailova et al. [11]	Semiarid	Dry combustion mass spectrometry using the Robo-Prep Tracemass System.
Mikhailova & Post [14]	Semiarid	Electron microscope (SEM) model S-3500N for determining the elemental composition of CaCO ₃ .

Table A3. Recent studies from global sources discussing the secondary carbonate potential and the importance of soil C sequestration.

Country	Citation	Title of Study
Australia	Fitzpatrick and Merry [100]	Pedogenic Carbonate Pools and Climate Change in Australia.
Russia	Ryskov et al. [101]	The relationship between lithogenic and Pedogenic Carbonates Fluxes in Steppe Soils, and Regularities of Their profile dynamics for the last four millennia.
China	You et al. [102]	Profile storage and vertical distribution (0–150 cm) of soil inorganic carbon in croplands in Northeast China.
France	C. Grinand [103]	Prediction of soil organic and inorganic carbon contents at a national scale (France) using mid-infrared reflectance spectroscopy (MIRS).
China	Pan and Guo [104]	Pedogenic Carbonate of aridic Soils in China and its Significance in Carbon Sequestration in terrestrial system.

Table A3. Cont.

Country	Citation	Title of Study
India	Pal et al. [105]	Secondary Calcium Carbonate in Soils of arid and Semi-arid regions of India.
Turkey	Kapur et al. [106]	Carbonate Pools in Soils of the Mediterranean: A case study from Anatolia.
Japan	Nanko et al. [107]	Assessment of soil group, site, and climatic effects on soil organic stocks of topsoil in Japanese forests.
China	Nami et al. [108]	Soil inorganic carbon storage pattern in China.
Syria	Khalaf et al. [109]	Some calcareous soils Developed on Recent quaternary Basalt in Southeast Syria.
Tunisia	Houman [110]	Morphology, Distribution and Environmental Significance of Pedogenic Carbonates in Relict Soils of Tunisia.

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