Chapter 3
Soils as Generators and Sinks of Inorganic Carbon in Geologic Time

H. Curtis Monger

Abstract Soil is a continuum in geologic time. Like today, pedogenesis in the geologic past altered soils by transformations, translocations, additions, and losses as continents drifted and collided across global climatic zones. One of the major biogeochemical systems operating in soils across geologic time is the carbonic acid system, which includes gaseous $CO_{2(g)}$, dissolved $CO_{2(aq)}$, carbonic acid $H_2CO_{3(aq)}$, bicarbonate $HCO_3^-{}_{(aq)}$, carbonate $CO_3^{2-}{}_{(aq)}$, and solid-phase calcium carbonate (mainly calcite). These chemical species, collectively referred to as inorganic carbon, increased in the Silurian when vascular plants colonized the continents and began pumping atmospheric CO_2 into soils via photosynthesis and root respiration, which accelerated mineral weathering and made soils "generators" of bicarbonate. In humid regions soils are "flushing" and bicarbonate enters groundwater, streams, and is transported to the oceans. In arid regions soils are "non-flushing" and bicarbonate is not linked to the hydrological system, but precipitates in soil as pedogenic carbonate, making arid soils sinks of inorganic carbon. Pedogenic carbonate is documented in paleosols throughout the Cenozoic, Mesozoic, and back into the Silurian of mid-Paleozoic time. Paleogeographic maps from Present to Precambrian are useful for revealing where arid regions were located in geologic time and how they expanded and contracted; thus, propounding the question of how (and if) a currently expanding "Aridosphere" will impact the global carbon cycle.

Keywords Pedogenic carbonate • Paleosols • Carbon sequestration • Deserts

H.C. Monger (✉)
MSC 3Q Plant and Environmental Science, New Mexico State University,
Las Cruces, NM 88003, USA
e-mail: cmonger@nmsu.edu

Introduction

Why is soil organic carbon studied more than soil inorganic carbon? A word-search of the IUSS Global Soil Carbon Conference Program & Abstracts (Madison, Wisconsin 2013), for example, found six abstracts that mentioned inorganic carbon in contrast to 65 abstracts that mentioned organic carbon. The Intergovernmental Panel on Climate Change chapter on biogeochemistry does not mention soil inorganic carbon, in contrast to soil organic carbon which is mentioned 18 times (Denman et al. 2007). Perhaps because soil inorganic carbon is restricted to sparsely populated arid and semiarid climates, in contrast to humid regions where soil organic carbon covers every continent in varying amounts and is important for agriculture. Perhaps soil inorganic carbon is studied less, especially as a method of carbon sequestration, because it is viewed as mineralogy, unresponsive to management, in contrast to soil organic carbon which is dynamic and capable of being manipulated.

Soil inorganic carbon is, however, widely recognized as being a large pool (940 PgC), exceeded only by the amount of carbon in oceans (38,000 PgC) and soil organic matter (1,530 PgC) (Eswaran et al. 2000; Sarmiento and Gruber 2002). It is less widely recognized that inorganic carbon is biological, at least in part, and therefore might be more dynamic than previously thought (Phillips et al. 1987; Monger et al. 2009). It is least widely recognized that, unlike organic carbon which has a concentration level controlled by its vegetative community, inorganic carbon can continue to accumulate to highly concentrated levels, such as those in petrocalcic horizons (Fig. 3.1).

Overall, the role of inorganic carbon as a method for carbon sequestration is viewed as being insignificant (Schlesinger 2000). This view is the result of at least three reasons. First, in order for soil carbonate to actively sequester atmospheric carbon the source of calcium must be from silicate minerals, not pre-existing carbonate, and tracing calcium to its silicate or carbonate source is difficult. Second, quantifying sequestration by soil carbonate is also difficult because many soils contain both pedogenic carbonate and lithogenic carbonate, which cannot be differentiated using routine measurements of "calcium-carbonate equivalents" (Rabenhorst et al. 1984). Third, carbonate accumulation rates are on times scales of thousands of years (Monger and Gallegos 2000). Such low influx values give rise to long mean residence times, such as 85,000 years (Schlesinger 1985).

However, progress has been made to track the source of Ca by using Sr isotopes as a proxy indicator (Capo and Chadwick 1999; Naiman et al. 2000). Progress has also been made to differentiate pedogenic from lithogenic carbonate using carbon isotopes and micromorphology (Nordt et al. 1998; Kraimer and Monger 2009). Likewise, progress has been made to refine mean residence times using artifacts and meteorites of known age to refine accumulation rates (Barrat et al. 1998; Pustovoytov 2003; Monger and Cooke 2013).

The objective of this paper is to construct a broad-scale context—both spatially and temporally—for viewing the generation, loss, and accumulation of inorganic carbon in soils. It focuses on the major pathways along which carbon moves through the inorganic system and makes inferences about pedogenic carbonate
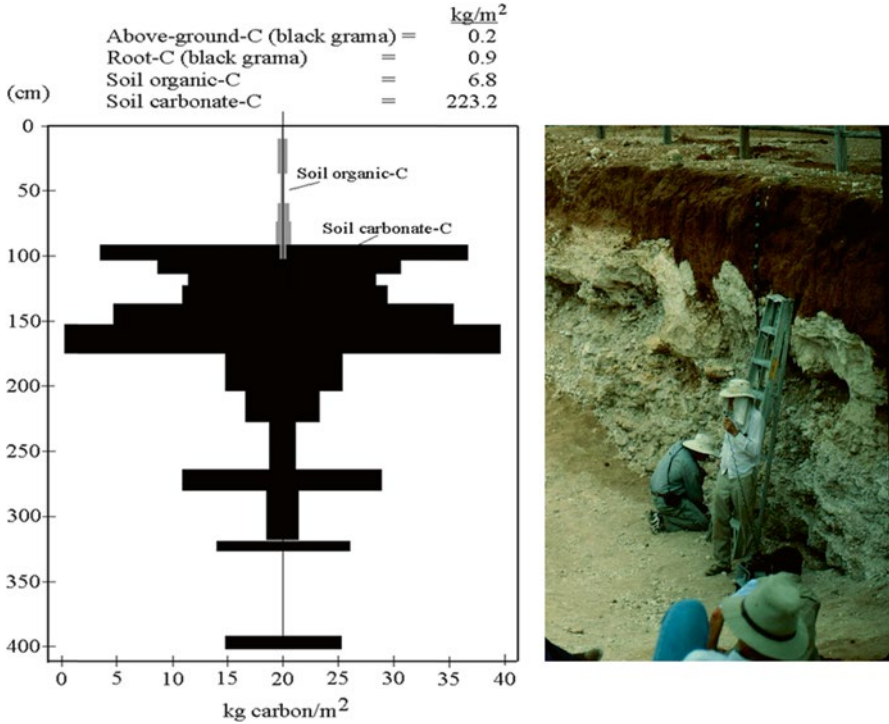
Fig. 3.1 Comparison of amounts of carbon stored as inorganic carbon versus organic carbon in a desert soil with a petrocalcic horizon at the USDA-ARS Jornada Experimental Range in the northern Chihuahuan Desert in New Mexico. The site illustrates the huge amount of carbon that can reside in some desert soils. The soil is an Argic Petrocalcic (USDA-NRCS soil survey number S95NM-013-004). Black grama data are from Xing (2002) (Picture was taken in May 2000 during a tour of the Desert Soil-Geomorphology Project (Gile et al. 1981))

through geologic time. The purpose for this broad-scale context is to help us conceptualize how the global carbon cycle might be impacted if the "Aridosphere" expands as the result of global warming.

Inorganic Carbon Generators and Sinks

There are two end-members for soils as generators and sinks of inorganic carbon—humid soils in which profiles are "flushing" (Rode 1962) and arid soils in which profiles are "non-flushing" (Fig. 3.2). Between these end-members is a continuum of sub-humid through semiarid soils whose profiles are periodically flushing. Humid soils are linked to groundwater and rivers. This hydrological connection provides a conduit whereby bicarbonate, which is generated in soil, travels to the oceans. In contrast, arid non-flushing soils lack the moisture required to leach bicarbonate downward out of the profile and into the phreatic groundwater-river-ocean system.
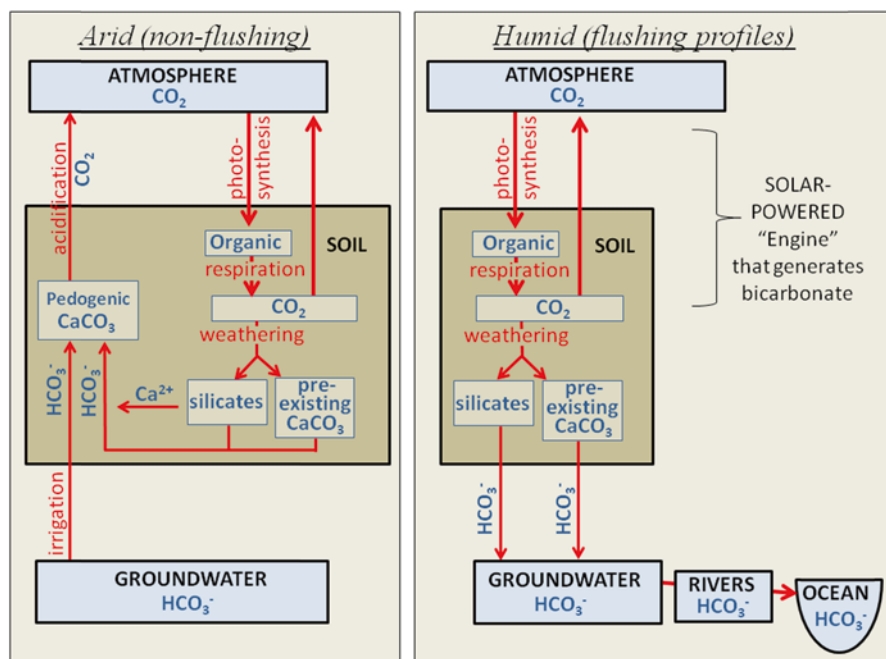
Fig. 3.2 Pathways of modern inorganic carbon arid versus humid climates illustrating how inorganic carbon enters and exits soils, how it is transformed while in soils, and how it is hydrologically connected to groundwater, rivers, and oceans

Humid soils, and to a lesser extent arid soils, generate bicarbonate during the weathering of silicates and pre-existing carbonates. Silicate minerals are chemically weathered via their reaction with carbonic acid (Reaction 3.1). This results in the production of one mole of Ca and the consumption of two moles of carbon dioxide (Berner 2004).

$$2CO_2 + 3H_2O + CaSiO_3 \rightarrow Ca^{2+} + 2HCO_3^- + H_4SiO_4 \qquad (3.1)$$
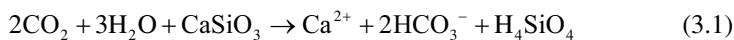
When Ca and bicarbonate from silicate minerals precipitate as calcite, one mole of carbon is sequestered and one mole is released as CO_2 (Reaction 3.2).

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \qquad (3.2)$$

Thus, there is a net sequestration of one mole of carbon. Pre-existing carbonates in soil are also chemically weathered via carbonic acid (Reaction 3.3). In this case, however, one of the two moles of carbon in bicarbonate is from the pre-existing carbonate, and the other mole is from carbon dioxide (Krauskopf and Bird 1995). Thus, the carbon dioxide consumed during the formation of carbonic acid ($H_2O + CO_2 \leftrightarrow H_2CO_3$) is released upon the re-precipitation of calcium carbonate. Therefore, no sequestration has occurred.

$$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3^- \tag{3.3}$$
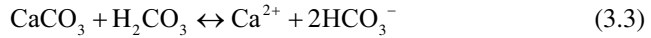
On the global scale, bicarbonate generated in humid "flushing" soils travels to oceans, precipitates as calcium carbonate, and sequesters one mole of atmospheric CO_2—if the Ca is derived from silicates. If, however, the Ca is derived from pre-existing carbonates, no carbon is sequestered. Similarly, in "non-flushing" soils atmospheric carbon is sequestered in pedogenic carbonate if Ca is derived from silicates. On the other hand, if Ca is derived from pre-existing carbonate, then no carbon is sequestered. The same stoichiometry would apply to irrigated agricultural soils—sequestration depends on the source of Ca (Fig. 3.2).

Throughout geologic time high concentrations of carbon dioxide in soil air have been a consequence of root and microbial respiration made possible by photosynthesis. Without plants and photosynthesis soils would contain less carbon dioxide, which was the case in pre-Silurian time before the evolution of land plants (Berner 1992). Post-Silurian soils, however, are *generators* of inorganic carbon because of the bicarbonate-mineral-respiration-photosynthesis system that is driven by the sun's energy (Fig. 3.2). The amount of bicarbonate-C generated in soils is at least 0.40 Pg per year, which is the amount of carbon as HCO_3^- in the world's rivers (Schlesinger and Bernhardt 2013). Of this, about 37 % is from silicate weathering (Reaction 3.1) and 61 % from pre-existing carbonate weathering (Reaction 3.3) (Berner and Berner 1996). In addition to being generators of bicarbonate, soils are also *sinks* of inorganic carbon in the form of pedogenic carbonates in arid, semiarid, and subhumid soils.

Geologic Time and the Formation of Inorganic Carbon

Figure 3.3, in a single view, provides a broad-scale temporal and spatial framework for thinking about how inorganic carbon has changed in geologic time. This figure compares modern soil carbonate (USDA-NRCS 2000) with paleogeographic maps showing deserts and semiarid regions as tan to light brown, in contrast to humid vegetated regions that are shown as green and dark green. The upper two maps in Fig. 3.3 show the correlation of soil carbonate with deserts and semiarid regions of the present.

Assuming uniformitarianism, deserts and semiarid regions in the geologic past would have resulted from the following three conditions that create modern deserts and semiarid regions (Dick-Peddie 1991). First, they are located between 25° and 35° latitude where dry air from the Hadley cells, as viewed in cross-section, descends on the continents. Second, deserts and semiarid regions result from rain shadows on the leeward side of mountain ranges that scavenge precipitation from air cooled as it rises over lofty terrain. Third, deserts and semiarid regions form because they are located great distances from oceans, such as the drylands of central Asia. In addition to these hot and warm drylands, cold deserts also exist in polar zones (e.g., Antarctica) and in high elevation terrain (e.g., Tibetan Plateau).
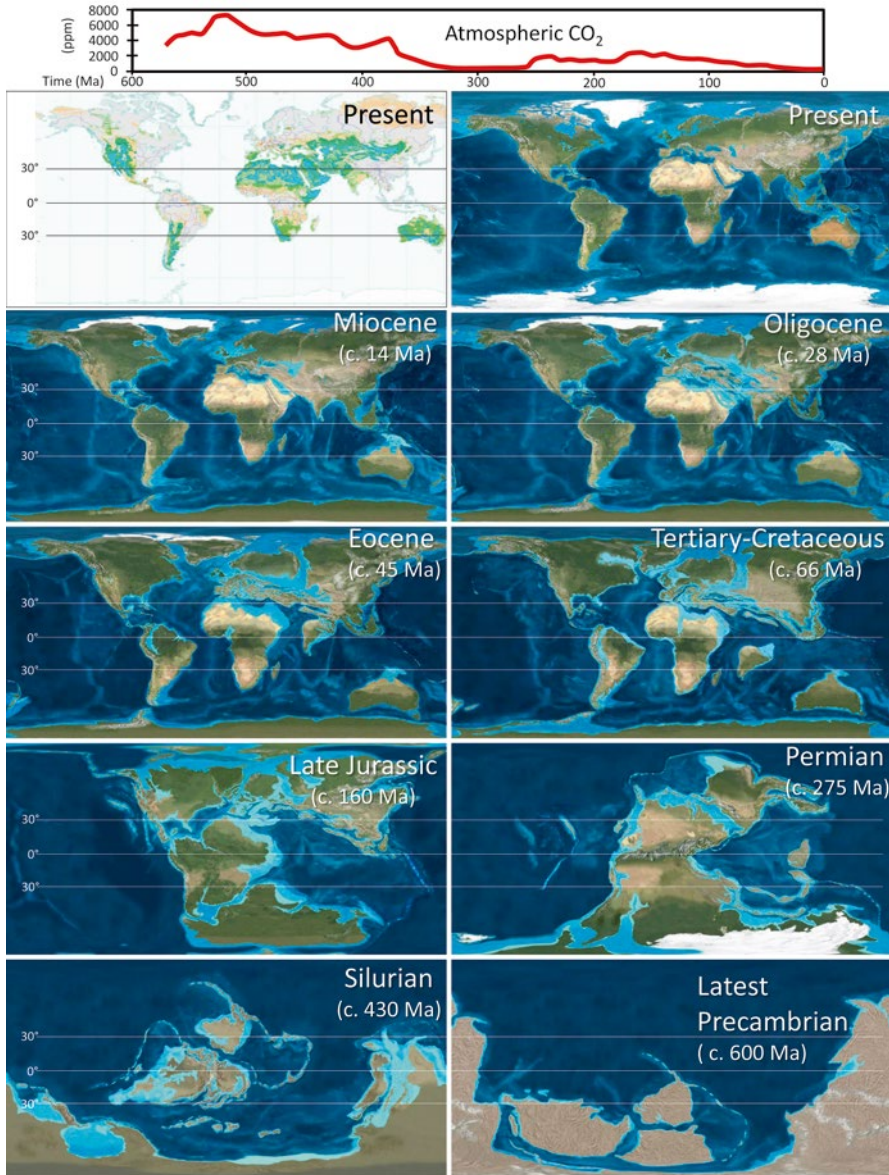
Fig. 3.3 Paleogeographic maps in which tan and brown colors correspond to zones with pedogenic carbonate, thus illustrating how pedogenic carbonate might have changed across geologic time. Dates are approximate mid-points of each era. Images courtesy of Colorado Plateau Geosystem, Inc. (http://cpgeosystems.com/paleomaps.html) (Images used with permission)

For pedogenic carbonate to be generated in modern soils (and presumably ancient soils) four conditions must be met. (1) The soil must have an alkaline pH. (2) There must be an active source of CO_2, namely root and microbial respiration, which is necessary for HCO_3^- production. (3) There must be available Ca^{2+}.

(4) The soil must occasionally contain moisture; but not too much moisture. That is, the formation of calcium carbonate is an aqueous phenomenon. Some deserts, like the driest zones of the Atacama, are too dry for pedogenic carbonate (Ewing et al. 2006). On the other hand, when rainfall increases above 500–760 mm, pedogenic carbonate does not typically form in soil profiles (Birkeland 1999; Royer 1999).

By starting with the oldest and working toward the youngest, we can see in Fig. 3.3 that the Precambrian map is unlike the younger paleogeographic maps because it lacks green colors on any continent, despite latitude, since land plants had yet to evolve—a phenomenon that occurred during the Late Silurian and Devonian (Kenrick and Crane 1997). The Precambrian landscape, therefore, was likely barren and gullied with abundant rock outcrops. On gentle slopes a chemically-weathered regolith, in some areas with an argillic horizon, probably resided atop bedrock. The landscape was probably not totally devoid of life based on carbon isotopes in pedogenic goethite (Yapp and Poths 1993). A cyanobacterial crust similar to certain types of modern soil biological crusts might have covered the soil surface.

By Silurian time when the continents were being progressively covered by vascular plants the conditions became increasingly suited for pedogenic carbonate formation. Carbon dioxide would have been pumped into soils by plants and soil air would have reached higher CO_2 concentrations than those in the atmosphere. Calcium would have been increasingly controlled by vascular land plants, as it is today (Yanai et al. 2005), in contrast to pre-plant times when it would have traveled with water controlled exclusively by gravity and evaporation. By late Silurian and Devonian time, pedogenic carbonates were forming in soils based on paleosol evidence (Mora et al. 1991, 1996). Several studies show that later in Paleozoic and Mesozoic time, pedogenic carbonates were widespread and provide evidence for climate change and concentrations of atmospheric CO_2 (e.g., Mack et al. 1991; Ekart et al. 1999; Lee and Hisada 1999; Tanner et al. 2001; Ziegler et al. 2002; Cleveland et al. 2008).

By late Cretaceous-early Tertiary time, continents began taking on their recognizable shapes including the formation of major deserts in Africa, North and South America, and central Asia (Fig. 3.3). Australia began its slow drift northward into the arid 30° latitude zone in the Cretaceous which continued through the Eocene, Oligocene, Miocene, and to the Present. Thus, the major deserts of today have generally existed for at least 60 million years. Pedogenic carbonates preserved in paleosols of these deserts and semiarid lands have provided important clues about paleoecology, especially the rise of C_4-photosynthesis (e.g., Quade et al. 1989; Cerling et al. 1993; Magioncalda et al. 2004).

Currently Earth is experiencing an abrupt rise in atmospheric CO_2 caused by fossil fuel burning and land use that is unprecedented during human evolution and modern ecosystems (Schlesinger and Bernhardt 2013). During the Phanerozoic, however, carbon dioxide in Earth's atmosphere was generally more concentrated than today's levels (Fig. 3.3). How did such high concentrations impact the formation of pedogenic carbonate? During the Cambrian, for example, atmospheric CO_2 levels were likely to have been almost 8,000 ppm (Berner 2004). Therefore, diffusion into soils would have caused those plant-free soils to also have been 8,000 ppm. Pedogenic carbonate, however, does not appear in Cambrian paleosols (based on

literature searches by the author). Is the lack of Cambrian pedogenic carbonate the result of high CO_2 levels of that era? Probably not since CO_2 concentrations of 8,000 ppm are within the range of soil CO_2 in which modern pedogenic carbonate forms (e.g., Parada et al. 1983). Instead, the absence of pedogenic carbonate might be the result of an absence of land plants and their associated microorganisms. In the dries zones of deserts today, where there is an absence of plants, there is an absence of pedogenic carbonate (e.g., Bespalov 1964).

Conclusions

Vast amounts of research are being focused on understanding the consequences of higher levels of atmospheric carbon dioxide. Paleosols, both lithified (i.e., petrosols, McSweeney and Fastovsky 1987) and unlithified, provide a means to study the ecology and biogeochemistry in a higher-CO_2 world. Based on the paleosol record, inorganic carbon has been an important component of the global carbon cycle throughout the Phanerozoic, especially the weathering of Ca silicates that have resulted in massive amounts of carbon being stored as marine limestone (Berner 1999). Likewise, pedogenic carbonate that began forming after land plants evolved must have played a significant role in the global carbon cycle.

Carbon sequestration by inorganic carbon requires that the source of Ca be derived from silicates. However, carbon can also be sequestered as bicarbonate via the dissolution of pre-existing carbonate until it re-precipitates and releases CO_2 back into the atmosphere. There may be great potential for promoting carbon sequestration as inorganic carbon. It requires a manipulation of Ca from silicates, water, alkaline pH, and CO_2 (i.e. root respiration). In addition, because soil fungi and bacteria are agents of calcite biomineralization, they might also be manipulated to enhance inorganic sequestration. Inorganic carbon, unlike organic carbon which reaches an equilibrium with crops or native vegetation, can, in theory, be made to accumulate carbon up to the petrocalcic horizon stage. Another important aspect of inorganic carbon is its role in future climate change. That is, given the importance of a shrinking Cryosphere to the global carbon cycle, how would an expanding Aridosphere impact the global carbon cycle?

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