

The Potential of U.S. Grazing Lands to Sequester Carbon and Mitigate the Greenhouse Effect

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CHAPTER 4

Inorganic Carbon Sequestration in Grazing Lands

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Introduction

Carbonate C as CaCO_3 (also termed soil inorganic C, or SIC) is a principal component of many arid and semiarid soils throughout the world (Dregne, 1976). In reference to soil profiles in southern New Mexico, for example, Ruhe (1967, p. 55) said that the subsoil horizon of calcium carbonate is so prominent that it is the first feature to catch an observer's eye. The amount of carbonate that forms in an arid or semiarid soil depends highly on soil age (Gile et al., 1966; Hawley et al., 1976). In young soils of Holocene age, only enough carbonate has formed to make filaments or coatings composed of silt and clay sized CaCO_3 crystals. With increasing age, the amount of carbonate crystals progressively accumulates, plugging soil pores, engulfing other soil particles, and eventually forming calcic and petrocalcic horizons (Soil Survey Staff, 1998).

In terms of C sequestration from the atmosphere, soil carbonate C is important because it is the third largest pool of C, containing approximately 750 to 950 Pg of C (Schlesinger, 1985; Eswaran et al., 1999). Only the oceanic (38,000 Pg C) and soil organic (1,550 Pg C) pools are larger (Schlesinger, 1997, p. 359).

Many uncertainties exist, however, about the role of soil carbonate C in the global C cycle. First, is the formation of soil CaCO_3 a sink for atmospheric CO_2 or does it only represent a lateral transfer of C from one location to another (Grossman et al., 1995)? Second, if soil CaCO_3 does sequester CO_2 , would the rate of sequestration be rapid enough to play an important role in mitigating the greenhouse effect? Third, instead of being a CO_2 sink, is the carbonate C pool more im-

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The Potential of U.S. Grazing Lands to Sequester Carbon and Mitigate the Greenhouse Effect

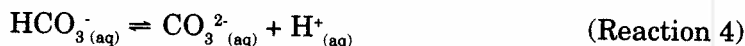
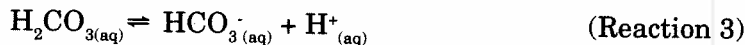
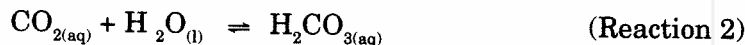
portant as a CO₂ source when exhumed calcic and petrocalcic horizons are exposed to the dissolving effects of acidic rain and microbiotic crusts?

Although grazing occurs on various patches of land across the U.S., this chapter focuses on carbonate C in grazing lands of the drylands regions of the West and Midwest — that is, soils with aridic, ustic, and xeric moisture regimes (Soil Survey Staff, 1998). In this sense, our use of the term *grazing lands* is synonymous with *rangelands* (Holechek et al., 1989), except we exclude forests of the West that are used for grazing and browsing. We assess carbonate C in these western grazing lands in three categories: woodlands, shrublands, and grasslands. Within this context, this chapter:

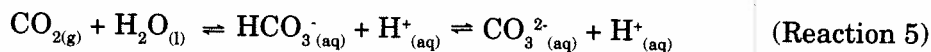
1. reviews processes of soil CaCO₃ formation
2. estimates the amount of soil carbonate C in the woodlands, shrublands, and grasslands of the U.S.
3. estimates the annual sequestration rates of carbonate C
4. discusses the potential for promoting C sequestration as soil carbonate C in grazing lands.

Types of Inorganic Carbon

Inorganic C refers to the chemical species involved in the carbonic acid system (Morse and Mackenzie, 1990). These species include gaseous CO₂ (CO_{2(g)}), dissolved CO₂ (CO_{2(aq)}), carbonic acid (H₂CO_{3(aq)}), bicarbonate (HCO_{3(aq)}⁻), and the carbonate ion (CO_{3(aq)}²⁻). We can represent the relationships among these chemical species with these reactions:



In the soil solution, as with other natural waters, we can illustrate the interaction of atmospheric CO₂ with the carbonic acid system by combining the above reactions into this one:

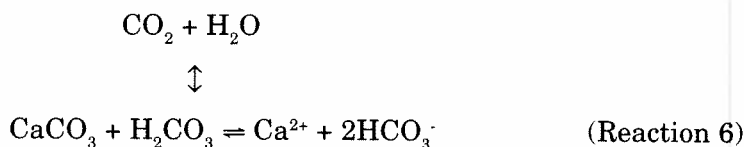


Increasing CO_{2(g)} drives the reaction to the right. In contrast, the addition of acid (H_(aq)⁺) drives the reaction to the left.

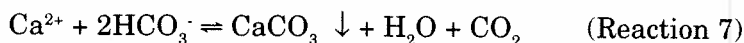
Another important part of the inorganic C system is its mineral component. In soil, the overwhelming carbonate mineral is calcium carbonate (CaCO₃), occurring mainly as calcite (Doner and Lynn, 1989). In fact, in terms of C sequestra-

tion, the phrase *soil inorganic carbon* progressively has become synonymous with *soil carbonate* (e.g., Lal et al., 1999).

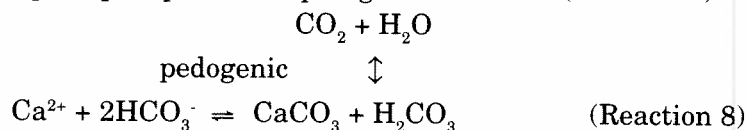
We can represent the interaction of soil carbonate minerals with the carbonic acid system in Reaction 5 in two ways. First, Reaction 6 represents the dissolution of preexisting soil carbonates by carbonic acid and its reprecipitation (Krauskopf, 1967):



Second, Reaction 7 represents the precipitation of soil carbonate in a system supplied with Ca released by chemical weathering of non-carbonate minerals, such as Ca feldspars, and the production of bicarbonate from root and microbial respiration (Schlesinger, 1997, p. 115):



In many arid and semiarid regions, large amounts of pedogenic carbonate have been produced in soils formed in parent materials without preexisting CaCO_3 . For these dryland soils, we can write a precipitation-dissolution reaction by combining the reaction representing the dissolution of carbonate (Reaction 6) with the reaction representing the precipitation of pedogenic carbonate (Reaction 7):



For example, supplying ample Ca^{2+} from weathering, from atmospheric additions, or from plant litter decomposition drives the reaction to the right, provided enough HCO_3^- is available. Likewise, providing ample HCO_3^- from respiration under suitable pH conditions drives the reaction to the right as long as enough Ca^{2+} is available. Conversely, depleting Ca^{2+} by leaching or plant uptake, or depleting HCO_3^- by leaching or acidification, drives the reaction to the left, causing CaCO_3 to dissolve. An increase in the amount of CO_2 and H_2O also drives the reaction to the left, also causing CaCO_3 to dissolve.

Much of what we know about carbonate equilibria as expressed in the above reactions has been developed for marine systems (e.g., Bathurst, 1975; Morse and Mackenzie, 1990). Nevertheless, these principles appear valid for the soil biogeochemical system even though it differs from the marine system in several important ways. Most notably, unlike the marine system, the soil system is alternately wet and dry. Moreover, it is a porous system, consisting largely of silicate minerals, organic particles, gases and solutions, and a vast variety of organisms, including roots, arthropods, nematodes, fungi, and bacteria. In this environment, CO_2 can reach concentrations hundreds of times greater than atmospheric CO_2 .

In this environment, carbonate precipitates in the ephemeral aqueous zones of the soil, which are areas where the soil solution resides in pores and surrounds particles. Carbonate also precipitates in the aqueous environments associated with root and microbial tissue (Monger et al., 1991). Carbonate, because of its low solubility of 0.0014 g/100 mL (Weast, 1986), is one of the first minerals to precipitate when the soil dries, which consumes Ca^{2+} and HCO_3^- from the soil solution. Again, due to its low solubility in alkaline conditions, carbonate does not readily dissolve upon subsequent wettings but accumulates with time, progressively plugging the soil porosity and, eventually, pushing apart framework grains (Gile et al., 1966; Machette, 1985).

Soil carbon dioxide

The biological processes of root and microbial respiration produce soil CO_2 . In addition, some atmospheric CO_2 may enter the upper soil profile if soil respiration rates are low (Cerling and Quade, 1993). The link between atmospheric CO_2 and soil CO_2 exists because plant C, which photosynthesis previously fixed from the atmosphere, generates respired soil CO_2 .

Several methods, of which the most common are adsorption by alkali and soda lime, gas chromatography, and infrared, can measure soil CO_2 (Anderson, 1982; Cropper et al., 1985). These techniques reveal that soil CO_2 is seasonally dynamic. It generally reaches highest concentrations in the rooting zone during warm growing seasons. Afterwards, pulses of CO_2 propagate downward through the soil profile (Reardon et al., 1979).

In some cases, concentrations of soil CO_2 can reach levels of 8% in cropland soils (Buyanovsky and Wagner, 1983), which is over 200 times greater than the atmosphere concentration of about 0.036%. Lower concentrations are reported for desert soils. In stony desert soils of Nevada, for example, seasonal levels of soil CO_2 range from 0.03% (near atmospheric levels) in January to 0.25% in April (Terhune and Harden, 1991).

Bicarbonate

Bicarbonate (HCO_3^-) is produced when CO_2 dissolves in water, making carbonic acid, which subsequently dissociates into H^+ and HCO_3^- (Reactions 1, 2, and 3). Bicarbonate is one of the major anions in soil (Bohn et al., 1985) as well as one of the dominant anions in rivers (Schlesinger, 1997, p. 94). It is more common than CO_3^{2-} in natural waters except in solutions above pH 10.3 (Morse and Mackenzie, 1990, p. 8).

Measurements of HCO_3^- most commonly are based on its amount in saturated soil extracts determined by titration to a pH end point with a chemical indicator (Soil Survey Staff, 1996). Because this process destroys the three-dimensional

architecture of the soil-root-microbial infrastructure, and because the amount of HCO_3^- in the saturation paste extract depends highly on the water content used to make the extract, it seems likely that these HCO_3^- data are only partially useful for understanding its exact role in CaCO_3 precipitation and C sequestration.

Origin and classification of soil carbonate (CaCO_3)

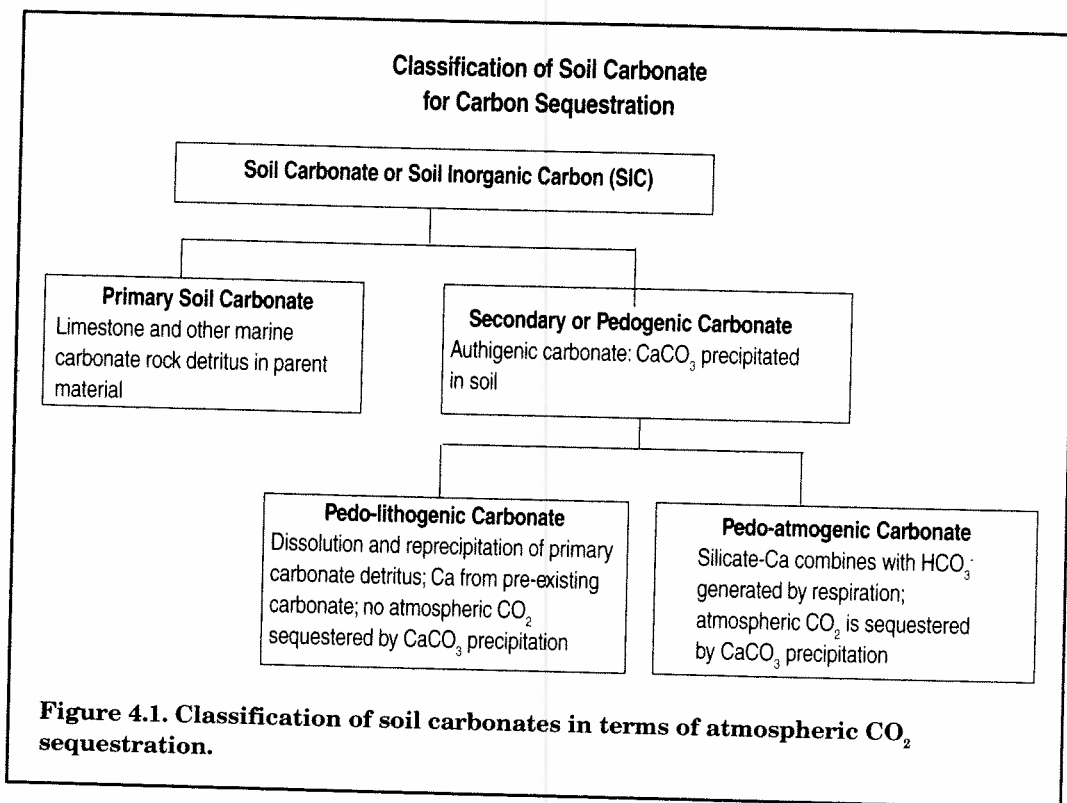
The pedologic literature has discussed the origin of soil carbonate for several decades (e.g., Dokuchaev, 1883). Depending on local conditions, soil carbonate can originate from one or more of these sources: (1) parent material, (2) atmospheric additions, (3) biogenic precipitation, and (4) groundwater.

In much of the midwestern U.S., for example, researchers largely have attributed the origin of soil carbonate to its loess and glacial till parent materials (Aandahl, 1982), and they commonly have viewed carbonate concentration in the subsoil of these parent materials as the result of its dissolution in the upper profile and its reprecipitation after downward leaching (Jenny and Leonard, 1934; Arkley, 1963). In many limestone terranes, the *in situ* dissolution and reprecipitation of limestone bedrock is another example of carbonate derived from parent material (Rabenhorst and Wilding, 1986).

However, research on soil carbonates that formed in non-calcareous parent materials made clearer the importance of an external source of carbonate (Bretz and Horberg, 1949; Gile et al., 1965, 1966). In this case, Ca in rain and calcareous dust were important sources of carbonate. Russian scientists, who observed that decomposed plant rootlets leave behind carbonate minerals, also offered biogenic precipitation of carbonate as a source of soil carbonate (Lobova, 1967). Moreover, lab studies have shown carbonate precipitation by soil microorganisms (Monger et al., 1991). Carbonate from calcareous groundwater, in contrast to other sources of soil carbonate, occurs in localized areas where water tables are shallow (Dregne, 1976).

Researchers have measured the amount of soil carbonate mainly by applying acid to soil and determining the amount of evolved CO_2 or the sample weight loss or measuring a titration end point (Soil Survey Staff, 1996). These procedures give the total amount of carbonate in soil, which would include limestone detritus plus secondary carbonate, if both were present.

For the purpose of understanding the role of soil carbonate in sequestering atmospheric CO_2 , soil carbonate can be classified into three pools: *primary*, *pedo-lithogenic*, and *pedo-atmogenic* carbonate (Fig. 4.1). The *primary soil carbonate*, as defined here, is the mineral fraction composed of marine or lacustrine carbonate detritus, such as limestone and dolostone particles. It is *allogenic* and includes CaCO_3 dust. *Lithogenic carbonate*, as in Rabenhorst et al. (1984), West et al. (1988), and Nordt et al. (1998), is synonymous with our *primary carbonate*.



In contrast to primary carbonate, *secondary* or *pedogenic carbonate* is formed *in situ* and is *authigenic*. Pedogenic carbonate, in turn, can be subdivided into two groups: *pedo-lithogenic* and *pedo-atmogenic* (Fig. 4.1). Pedo-lithogenic carbonate is the result of dissolution and reprecipitation of primary carbonate. Pedo-lithogenic soil carbonate includes not only marine carbonate detritus that dissolved and reprecipitated, but also CaCO₃ dust that dissolved and reprecipitated, as well as carbonate formed from Ca in rain derived from CaCO₃ dust. Monger and Gallegos (1999) formerly termed pedo-lithogenic carbonate *lithogenic carbonate*.

With respect to C sequestration, pedo-lithogenic carbonate would not sequester additional atmospheric CO₂, given the premise that the amount of CO₂ consumed by dissolution of primary carbonate would be released by its reprecipitation as pedo-lithogenic carbonate (Reaction 10). This concept, however, depends on scale. Over long geologic time periods (millions of years), the C in marine carbonates also can be attributed to an atmospheric origin (Berner, 1999).

If the source of Ca during the precipitation of soil carbonate is non-carbonate minerals (e.g., Ca silicates), a second type of pedogenic carbonate forms. This form has been termed *atmogenic soil carbonate* (Monger and Gallegos, 1999), reflecting the sequestration of atmospheric CO₂. In this chapter, we have updated the term to *pedo-atmogenic carbonate* in order to emphasize its pedogenic origin

and relation to pedo-lithogenic carbonate (Fig. 4.1). In addition to Ca from Ca silicate weathering in the soil profile, pedo-atmogenic carbonate forms when the source of Ca is gypsum or when rain or groundwater provides Ca from non-carbonate sources.

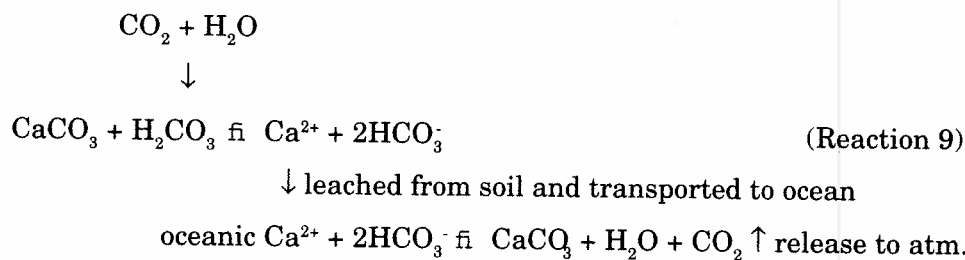
Sequestration of Atmospheric Carbon Dioxide by Soil Carbonates

Sequestration of atmospheric CO₂ depends on the timescale of the C cycle and parent material. The short-term timescale occurs over decades to centuries and involves the exchange of C in the surficial system, consisting of the atmosphere, biota, soils, and ocean. The long-term timescale operates over millions of years and involves the slow exchange of C between rocks and the surficial system (Berner, 1999). Parent material is important because of its role in supplying Ca. The two dominant parent materials for grazing land soils of the western U.S. are sediments from marine carbonates and igneous rock (cf., Hunt, 1986; Raisz, 1995).

Carbonate weathering and the consumption or release of atmospheric carbon dioxide

The following cases can illustrate whether or not the weathering of CaCO₃, either primary or pedogenic, consumes or releases atmospheric CO₂:

Case #1: Transport of bicarbonate from carbonate weathering via river water to the oceanic reservoir

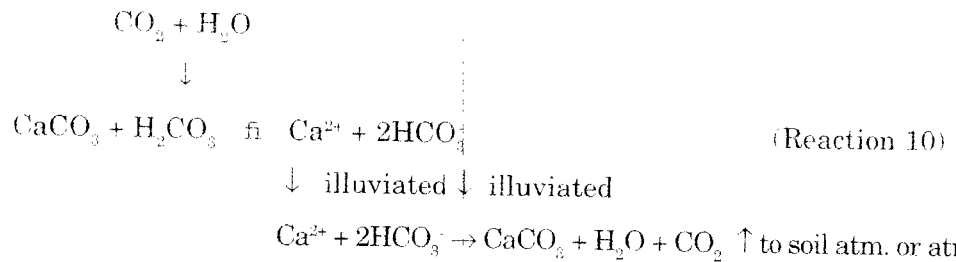


Adams (1993) argued that weathering of caliche (CaCO₃) would take up CO₂ from the atmosphere and contribute the resulting hydrogen carbonate (bicarbonate), via river water, to the oceanic reservoir. But as Case #1 (Reaction 9) illustrates, this process only temporarily consumes CO₂, because calcium carbonate precipitation in the oceans liberates CO₂ back into the atmosphere (Berner and Lasaga, 1989).

Also, during the journey of bicarbonate to the ocean, any drop in pH below about 6 would cause bicarbonate to release CO₂ via Reaction 5 (Morse and Mack-

enzie, 1990, p. 8). Moreover, this case would be most common to the weathering of limestone and soil carbonates in regions with enough rainfall to leach Ca and bicarbonate from soil profiles into phreatic water, but it would be of limited importance in arid regions. In terms of C sequestration, this long-term process operates at a timescale greater than the scale important for management designed to offset anthropogenic CO₂ emissions.

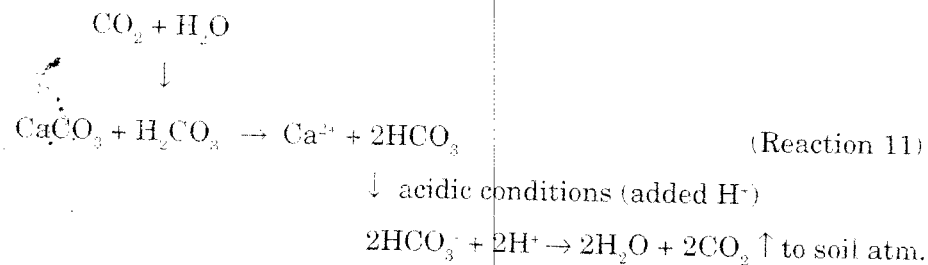
Case #2: Dissolution and reprecipitation of carbonate in aridland soil profiles



In Case #2, carbonate weathers, dissolves, and is illuviated from the upper profile to the subsoil. Yet, rainfall is insufficient to flush Ca and bicarbonate from the soil profile, so they reprecipitate. Note that, in this reaction (10), one of the two C moles in 2HCO₃⁻ is from atmospheric CO₂ and the other is from CaCO₃ (Krauskopf, 1967). Therefore, the CO₂ used to form carbonic acid is released with the precipitation of CaCO₃.

If the released CO₂ goes back into the atmosphere, no C has been sequestered. If the released CO₂ remains in the soil, it could be recycled to produce more carbonic acid and be re-released upon the reprecipitation of CaCO₃. Therefore, as in Case #1, the weathering of existing carbonate and its reprecipitation in soil is both a sink and source of C, and therefore neutral in terms of CO₂ sequestration. Unlike the first case, however, Case #2 would occur at the short-term C cycle scale.

Case #3: Congruent dissolution of carbonate

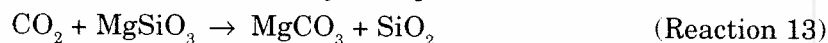
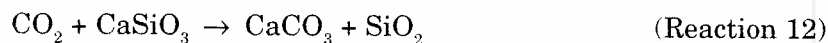


In Case #3, sufficiently low pH causes the complete (or congruent) dissolution of carbonate. As a result, the two moles of C in 2HCO₃⁻ of Reaction 11 are released as two moles of CO₂, following the path Reaction 5 illustrates. This is the reaction

that would occur in acid soils that have received lime, and it is the reaction that would occur, to some extent, in the rhizosphere microenvironments in arid soils. In terms of greenhouse gases, this reaction would occur when exhumed soil carbonate is exposed to acids in rain and from microbiotic crust. In this case, weathering of CaCO_3 would be a source of CO_2 and may be important to managing grazing lands in the U.S. and elsewhere.

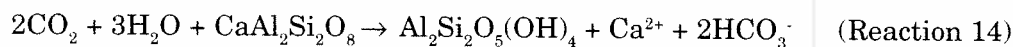
Consumption of atmospheric carbon dioxide by calcium silicate weathering

In contrast to carbonate weathering, the weathering of Ca silicate minerals is an unidirectional sink for atmospheric CO_2 . Berner (1993) expressed the consumption of atmospheric CO_2 , in general terms, by the weathering of Ca Mg silicates using these reactions:

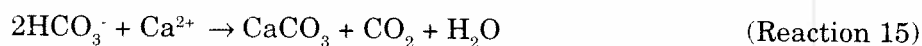


A more detailed form of Reaction 12 can be written as (Berner, 1992):

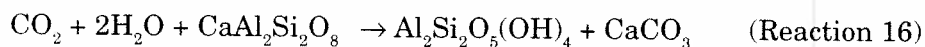
Weathering



Carbonate precipitation in oceans



Overall reaction

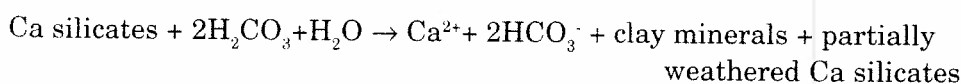


These same reactions of global weathering and marine carbonate precipitation also apply to the weathering of Ca silicates in arid and semiarid soils. In arid and semiarid soils, because of limited leaching, the Ca is not removed from the profile. Instead, Ca combines with bicarbonate generated by root and microbial respiration in the soil profile.

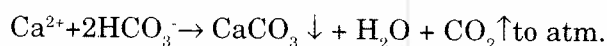
This reaction may be represented best in a general stoichiometric form, where various clay minerals and partially weathered Ca silicates are produced:



↓



↓ in soil fl in soil



Roots and microbes play a major role in this process for two reasons. First, they elevate the concentration of CO_2 by respiration. Second, they provide an aqueous environment of rhizosphere films and mucilaginous sheaths where carbonate precipitation can occur (e.g., Monger et al., 1991; Monger and Gallegos, 1999).

Model of carbon sequestration processes within limestone and igneous soils

Figure 4.2 illustrates potential sources of atmospheric additions that lead to soil carbonate formation and processes occurring internally in soil among the three carbonate pools — pedo-atmogenic, pedo-lithogenic, and primary carbonates. The block diagrams of limestone and igneous soils are hypothetical and referred to as soils at point B (Fig. 4.2). They illustrate the relationships between the carbonate pools, the atmosphere, parent material, and rainfall. In theory, the pedo-atmogenic carbonate pool would be small in the limestone soil but large in the igneous soil.

Limestone is used in this theoretical treatment, but other marine carbonate rocks also would pertain, such as dolostone, marl, and calcareous sandstones. Similarly, igneous rock is used in this model, but other rocks composed of Ca silicates would pertain equally, such as many metamorphic rocks, arkosic sandstones, and shales, as well as gypsiferous parent material containing Ca from igneous sources.

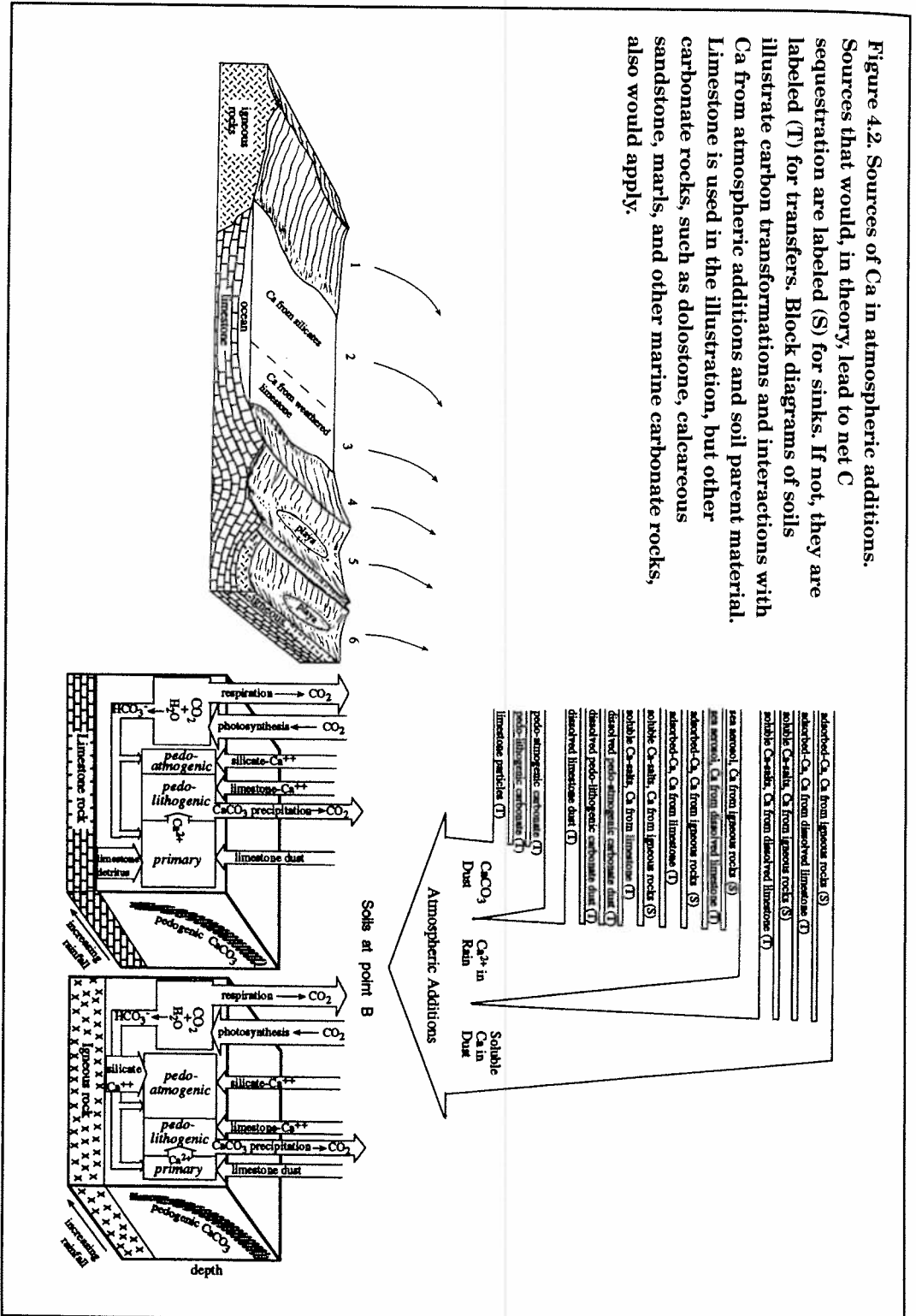
Limestone soil

The limestone soil, like all soils with vascular plants, contains CO_2 brought into the soils via a two-step process (see Fig. 4.2 and read it, beginning on the left side of the limestone soil diagram, left to right). First, photosynthesis removes CO_2 from the atmosphere to make plant biomass. Second, C in biomass is released into soil by respiration, either directly as root respiration or subsequently as microbial decomposition of plant material.

A small portion of soil CO_2 combines with water and dissociates to make HCO_3^- . This amount may be only a very small fraction of the total amount of CO_2 that fluxes through soil (Chadwick et al., 1994). If HCO_3^- encounters Ca^{2+} from a silicate source, as from an atmospheric addition of silicate Ca^{2+} , it precipitates as CaCO_3 and contributes to the pedo-atmogenic carbonate pool. On the other hand, if HCO_3^- encounters Ca^{2+} released by the dissolution of primary carbonate from limestone detritus or limestone dust, it precipitates as pedo-lithogenic carbonate and releases CO_2 .

The third carbonate pool, the primary carbonate pool, is composed of limestone detritus and limestone dust (Fig. 4.2). The C in this pool was atmospheric during

Figure 4.2. Sources of Ca in atmospheric additions. Sources that would, in theory, lead to net C sequestration are labeled (S) for sinks. If not, they are labeled (T) for transfers. Block diagrams of soils illustrate carbon transformations and interactions with Ca from atmospheric additions and soil parent material. Limestone is used in the illustration, but other carbonate rocks, such as dolostone, calcareous sandstone, marls, and other marine carbonate rocks, also would apply.



some previous geologic era (Berner, 1993), with respect to mitigating the greenhouse gases, it is considered here as a C reservoir.

The right side of the diagram illustrates the climatic effect of rainfall. As rainfall increases, the amount of pedogenic CaCO_3 (i.e., the combined pedo-atmogenic and pedo-lithogenic pools) decreases and becomes deeper in the profile (Jenny and Leonard, 1934). When pedogenic carbonate ceases to exist as the result of humid climates, the soils have changed from Pedocals to Pedalfers (Marbut, 1928). In humid regions, the effect of rainfall is so prevalent that primary carbonates are flushed from soils overlying limestone, leaving only insoluble residues dominated by quartz and clay minerals (Monger and Kelly, in press).

With respect to C sequestration, the pedo-atmogenic carbonate pool is the C sink, because one of the two moles of CO_2 required to weather Ca silicates is sequestered by CaCO_3 (Reaction 17). In contrast, the pedo-lithogenic carbonate pool does not sequester C during its formation. This is because one mole of CO_2 used to dissolve primary CaCO_3 is released during the precipitation of pedo-lithogenic CaCO_3 (Reaction 10).

Igneous soil

Soils formed in igneous parent material also could contain all three pools of soil carbonate (Fig. 4.2). In theory, the pedo-atmogenic pool would be the largest if chemical weathering released Ca^{2+} that precipitated with HCO_3^- generated by respiration. Any silicate Ca^{2+} supplied via atmospheric additions also would contribute to the pedo-atmogenic pool.

The primary and pedo-lithogenic carbonate pools in igneous soils could result from atmospheric additions. The primary carbonate pool would be composed of limestone dust or other airborne CaCO_3 particles. If such dust dissolved and reprecipitated, it would become pedo-lithogenic carbonate and release CO_2 . Pedo-lithogenic carbonate also would form from any Ca^{2+} , dissolved in rain, that originated as limestone Ca^{2+} .

The effect of rainfall on pedogenic carbonate in igneous soils is similar to its effect in limestone soils. As rainfall increases, pedogenic carbonate deepens and diminishes. Unlike limestone soils, however, igneous soils lose pedogenic carbonate more readily in humid environments. This is apparent when tracing soils up slope from arid lowlands into forested udic moisture regimes of the mountainous Southwest. In these situations, limestone soils have calcic horizons extending farther into progressively wetter climates than do neighboring igneous soils.

In terms of C sequestration, the igneous soil Figure 4.2 illustrates contains the greater potential for sequestering atmospheric CO_2 , provided chemical weathering makes a supply of Ca^{2+} available. To this end, the "mining" of Ca^{2+} from silicate minerals by plant roots and associated mycorrhizae may greatly hasten and increase the amount of Ca^{2+} available for CaCO_3 precipitation. In comparison to

the size of the pedo-atmogenic pool, the size of pedo-lithogenic and primary pools theoretically would be small in igneous soils. An exception, however, is where igneous soils received abundant amounts of calcareous dust.

Atmospheric additions

Atmospheric additions can be a major source of Ca in pedogenic carbonate (Gile et al., 1981; Reheis et al., 1995). Understanding the source of Ca in atmospheric additions is important for knowing whether or not atmospheric CO₂ is sequestered as CaCO₃. As Figure 4.2 shows, "atmospheric additions" is a broad category composed of multiple subcategories. The three major subcategories are CaCO₃ dust, soluble Ca in dust, and Ca²⁺ in rain (Gile and Grossman, 1979).

For purposes of this hypothetical discussion, the same two soils at point B, representing the two major parent materials, are considered the recipients of atmospheric additions. Atmospheric additions are labeled transfers (T) if no C sequestration is expected, or sinks (S) if C sequestration is expected.

All of these cases depend on the timescale. We can differentiate transfers and sinks on the short-term C cycle timescale. On the long-term C cycle timescale, the C in limestone was originally a sink for atmospheric CO₂.

Calcium carbonate dust

In theory, CaCO₃ dust has at least three sources. The first source is limestone particles derived from limestone terrane. As Figure 4.2 illustrates, their transport by wind originated from source 4. If the limestone particles landed on the soil surfaces, were translocated in suspension, and accumulated in the soils, no net C sequestration would occur. Therefore, the soil carbonate is a transfer (Grossman et al., 1995). Similarly, if the limestone dust, upon landing on the soils at point B, dissolved and reprecipitated, as Reaction 10 illustrates, no sequestration would occur because reprecipitation would release the CO₂ dissolution consumed (Reaction 10).

The second source of CaCO₃ dust is pedo-lithogenic carbonate. The same reasoning also applies to pedo-lithogenic carbonate dust blown from soils at source 4 (Fig. 4.2). The third source of CaCO₃ dust is pedo-atmogenic carbonate. Pedo-atmogenic carbonate, although having sequestered C initially during its formation at source 1, for example (Fig. 4.2), also would represent a transfer.

Soluble calcium in dust

A second major category — soluble Ca in dust — is that fraction of Ca resolved from dust samples contained in water extracts (Gile and Grossman, 1979). The origin of this Ca could be (1) soluble Ca minerals or (2) water soluble Ca adsorbed on the cation exchange complex of the dust particles.

If the Ca in the Ca minerals came from limestone weathering and, for example, moved downslope to a playa as at source 5 (Fig. 4.2), then Reaction 10 is most applicable. However, the first part of this reaction would occur in the weathering of limestone at source 5, while the second part of Reaction 10 would occur in the soil at point B. Consequently, the CO_2 consumed during the weathering of limestone at source 5 would be released during the formation of CaCO_3 in the soils at point B and would be a transfer.

If, however, the Ca in soluble Ca minerals came from igneous weathering, as at source 6 (Fig. 4.2), the situation would be different. In this case the Ca, after travelling on windblown dust to the soils at point B, would combine with bicarbonate generated by respiration, and C sequestration would occur. Reaction 17 represents this case, where the formation of CaCO_3 sequesters one of the two moles of C required to dissolve Ca silicates.

Ca adsorbed on dust particles follows the same sequences. If the adsorbed Ca comes from limestone weathering, as at source 5 (Fig. 4.2), then Reaction 10 is most applicable, and no net C sequestration occurs from any subsequent CaCO_3 precipitation in soils at point B. In contrast, if adsorbed Ca is from the weathering of igneous rocks, as at source 6 (Fig. 4.2), C sequestration occurs with subsequent CaCO_3 precipitation.

Calcium in rain

A third, and probably the most important, source of atmospheric Ca is Ca dissolved in rain, represented in its cationic form — Ca^{2+} — in this discussion. For example, dust trap and rainwater analysis in southern New Mexico strongly suggests that Ca^{2+} in rain could produce roughly two to three times more soil CaCO_3 than would result from the combined amounts of CaCO_3 dust and soluble Ca in dust (Gile et al., 1981, p. 63).

The source of Ca^{2+} in rain largely comes from droplets containing dissolved Ca dust. Therefore, the potential sources of Ca^{2+} in rain are the same as those for dust and soluble Ca in dust. Whether or not the precipitation of CaCO_3 in soils at point B sequesters C depends on those Ca sources:

1. Ca^{2+} from dissolved limestone dust is a transfer.
2. Ca^{2+} from dissolved pedo-lithogenic soil carbonate is a transfer.
3. Ca^{2+} from dissolved pedo-atmogenic soil carbonate also is a transfer, but its initial formation was a sink.
4. Ca^{2+} from soluble Ca minerals derived from limestone is a transfer.
5. Ca^{2+} from soluble Ca minerals derived from igneous rocks is a sink.
6. Ca^{2+} from adsorbed Ca derived from limestone is a transfer.
7. Ca^{2+} from adsorbed Ca derived from igneous rocks is a sink.

In addition to these Ca^{2+} sources in rain, two other sources of Ca^{2+} are possible, and both are sea aerosols from ocean waters (Bohn et al., 1985). First, if the Ca^{2+}

in aerosols comes from the dissolution of terrestrial limestone, as at source 3 (Fig. 4.2), then the precipitation of CaCO_3 in soils at point B is a transfer. In this case, Reaction 9 is most applicable. Instead of CaCO_3 precipitating in a marine environment, however, CaCO_3 precipitates in soils at point B. In the second case, Ca^{2+} comes from the weathering of igneous rocks, as at source 2 (Fig. 4.2). In this situation, Reaction 17 is most applicable. Of the two moles of CO_2 used to weather Ca silicates, one is sequestered by CaCO_3 precipitation in soils at point B and therefore is a sink.

Differences between inorganic and organic carbon sequestration

C sequestered as carbonate C differs from C sequestered as OC, in at least three ways. SOC exists to some extent in most soils, but pedogenic CaCO_3 is limited to dryland soils. As annual rainfall climbs above 50 to 70+ cm per year, soil CaCO_3 progressively ceases to exist (Jenny and Leonard, 1934; Arkley, 1963). This boundary is the Pedocal-Pedalfer boundary (Marbut, 1928).

Figure 4.3 illustrates the processes occurring across this boundary. In the three ecosystems it shows, photosynthesis and subsequent root and microbial respiration bring atmospheric CO_2 into the soil. Pools of C storage include the aboveground C pool, root C pool, soil organic C (SOC) pool, and CaCO_3 pool. As rainfall increases and climate changes from dry to intermediately dry to humid, the relative sizes of the pools change. For example, the aboveground C pool is smallest in the desert scrub system and greatest in the forest system (e.g., Dick-Peddie, 1993). In contrast, the CaCO_3 pool is greatest in desert scrub systems (Schlesinger, 1982) and nonexistent in humid forest systems.

A second difference between organic and carbonate C sequestration is that CaCO_3 formation requires additional steps. Photosynthesis converts the C in organic matter (OM) from gaseous CO_2 to solid phase C, but the C in CaCO_3 passes from the solid phase OM to the gaseous CO_2 phase by respiration, then to the aqueous HCO_3^- phase by dissolution and dissociation, and then to the solid CaCO_3 phase by crystallization. This requires a dry climate, because Ca^{2+} and HCO_3^- progressively leach out with increasing rainfall (Fig. 4.3). It also requires suitable pH and wet-dry cycles for carbonate precipitation. Consequently, C sequestered by CaCO_3 captures only a small portion of photosynthetic C that passes through the soil (Chadwick et al., 1994).

A third difference is the temporal scales of the two processes. Plant photosynthesis brings OC into the soils, and microbial decomposition returns it to the atmosphere, at turnover rates ranging from a few to a few thousand years (Trumbore et al., 1996; Paul et al., 1997). In contrast, CaCO_3 may remain in the soil for hundreds of thousands of years (Gile et al., 1981). The annual movement of CO_2 from the atmosphere into the soil carbonate pool may be only 0.023 Pg C/yr, yielding a turnover time of 85,000 years (Schlesinger, 1997, p. 365).

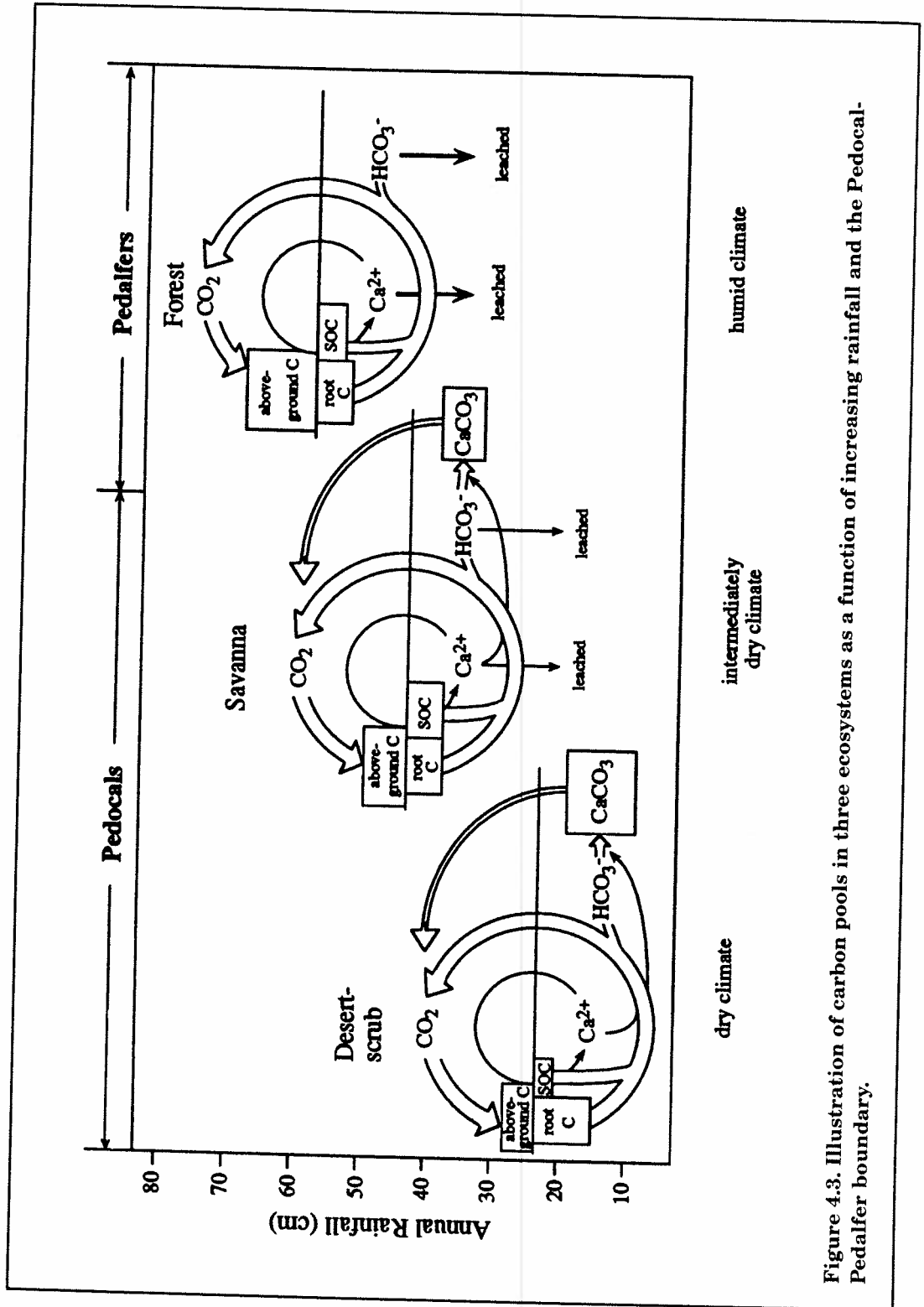


Figure 4.3. Illustration of carbon pools in three ecosystems as a function of increasing rainfall and the Pedocal-Pedalfer boundary.

However, although this may be true as a long-term global average, the possibility lingers that, like OC, carbonate may have both a recalcitrant pool (slow turnover) and a labile pool (fast turnover), the latter because of the involvement of roots and soil microbes in carbonate formation. In lab experiments, for example, soil bacteria and fungi can precipitate carbonate crystals in days to months (Monger et al., 1991). Furthermore, mesquite shrubs (*Prosopis glandulosa*) on the Jornada Experimental Range in New Mexico, known to be under 75 years old, have carbonate crystals on their roots (Gallegos, 1999).

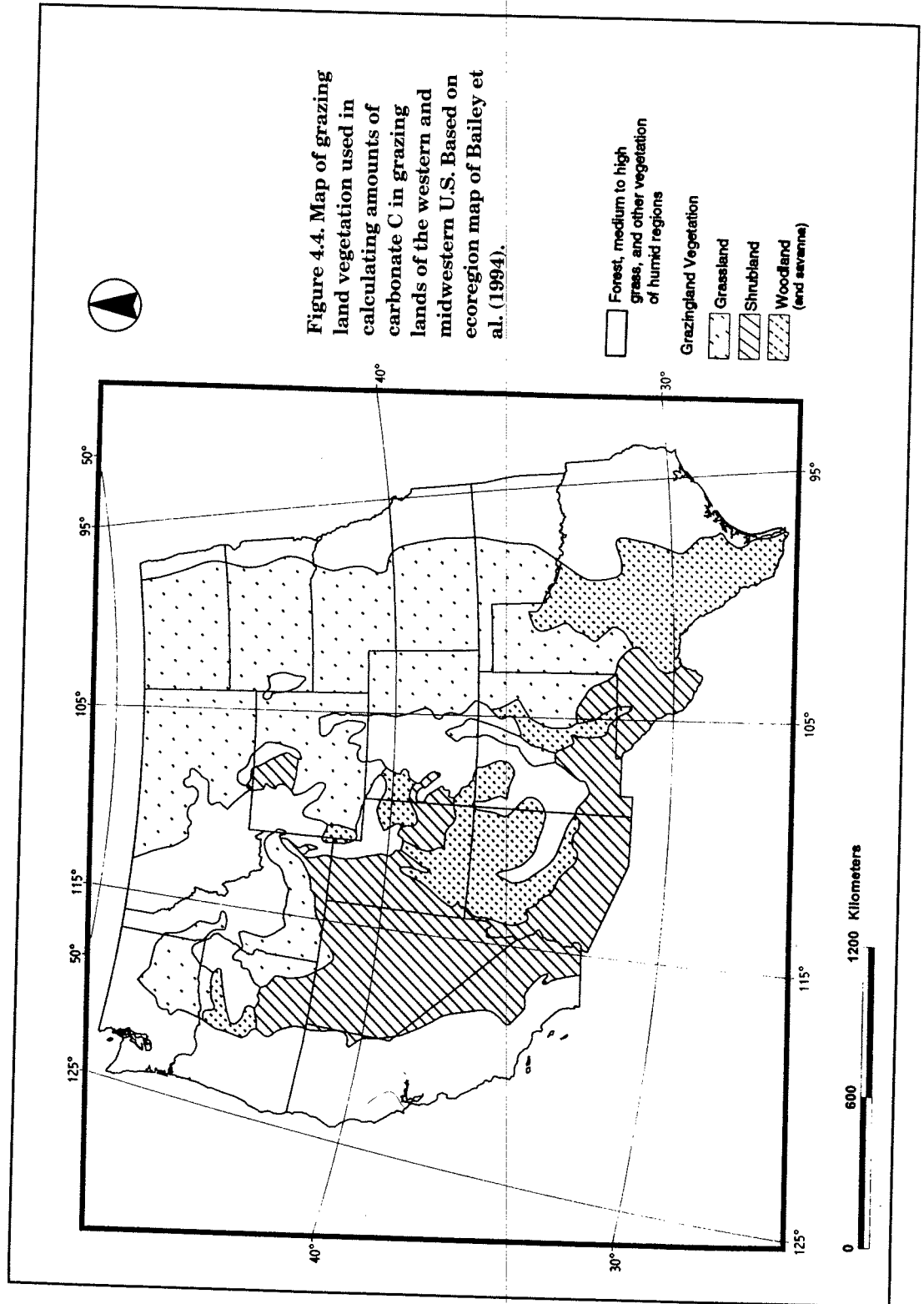
Amount of Soil Carbonates in Grazing Lands

Estimating method

We estimated the amount of soil carbonate in grazing lands by calculating its individual amounts in woodlands, shrublands, and grasslands that occur within arid, ustic, and xeric moisture regimes of the U.S. The ecoregion map of Bailey et al. (1994) provided these ecoregion categories, based on dominant species. For example, their unit 315C of the rolling plains section of central Texas (mesquite-buffalo grass) was grouped into the woodland category because mesquite was listed first. In contrast, its neighboring unit to the west, 315B (grama-buffalo grass, shinnery oak), was grouped into the grassland unit because grama grass was listed first. Woodlands, as used in this study, are mainly areas dominated by pinyon and juniper, but they also include the central Texas savannas of medium grass and mesquite (Küchler, 1995).

We excluded ecoregions in the udic moisture regime because udic soils generally do not contain pedogenic carbonate except when the parent material contains high amounts of limestone or other marine carbonate parent material. For the same reason, and because of their small size, we excluded aquatic moisture regimes. After grouping the ecoregions into woodlands, shrublands, and grasslands, we digitized each ecoregion, using ARC/INFO GIS software as a vector layer. We then converted this layer to raster format (grid), using raster-based GIS software, assigning a size of 1,068,705.6 m² per grid cell (a square of approximately 1,000 m per side). Figure 4.4 presents the map of the three ecoregion categories and Table 4.1 presents their areas.

We estimated soil carbonate in the woodland, shrubland, and grassland categories in three ways. First, we digitized Machette's (1985) calcic soil map (Figure 4.5), encoding the calcic soils and marginal areas in the vector layer, then converting it to raster format. Using random sampling for at least 25 sites per ecoregion on Machette's map, we determined the mean concentration of CaCO₃ (Table 4.1) based on the National Soil Survey Center database and the STATSGO database.



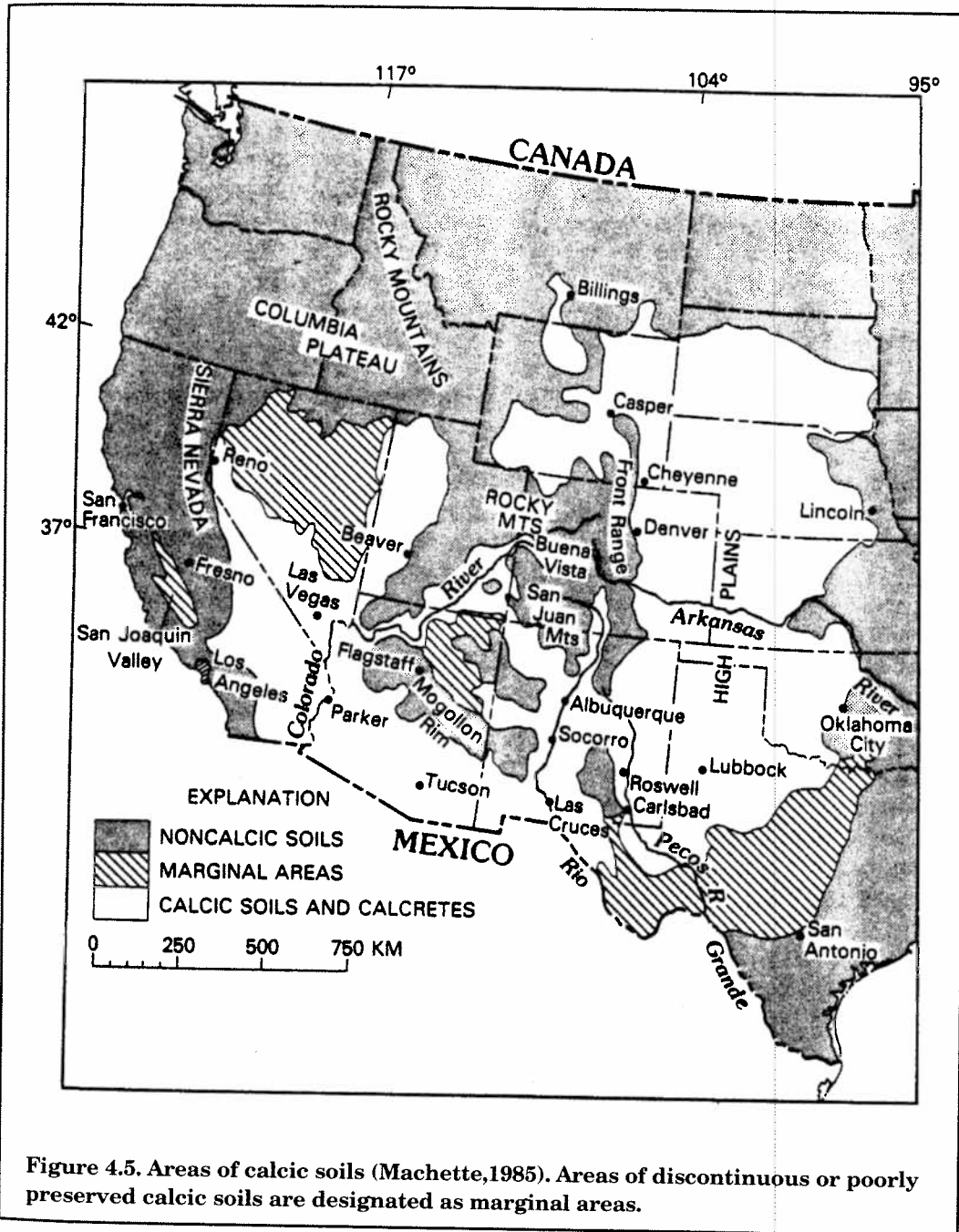


Table 4.1. Estimated amounts of carbonate C in grazing land soils of ecoregions that lie within aridic, ustic, and xeric moisture regimes of the western and midwestern U.S.

Grazing Land Ecoregions	Carbonate C Area (Mha)	Carbonate Concentration (MTC/ha)	C (Pg)
<i>Based on Machette's (1985) map and the Ecoregion map (1994)</i>			
woodland	35.6	177	6.3
shrubland	73.9	225	16.6
grassland	<u>100.1</u>	273	<u>27.3</u>
	Total 209.6		Total 50.2
<i>Based on Schlesinger's 1982 concentrations and Ecoregion map (1994)</i>			
woodland	58.0	50	2.9
shrubland	89.0	310	27.6
grassland	<u>158.0</u>	223	<u>35.2</u>
	Total 305.0		Total 65.7
<i>Based on STATSGO concentrations and Ecoregion map (1994)</i>			
woodland	58.0	183	10.6
shrubland	89.0	207	18.4
grassland	<u>158.0</u>	145	<u>22.9</u>
	Total 305.0		Total 51.9

Second, we estimated soil carbonate C in the woodland, shrubland, and grassland ecoregions by multiplying the areas of each category (Fig. 4.4) by the concentrations of carbonate C that Schlesinger (1982) derived for Arizona soils.

Third, we determined average SIC amounts state by state, using STATSGO, and then multiplied them by the total areas of the three ecoregion categories (Fig. 4.4 and Table 4.1).

Sources of error

Several assumptions and simplifications may have introduced error into the estimated carbonate C amounts in grazing lands. First, we based the results on general maps that oversimplify vegetation inclusions and ecotones. For example, many isolated mountain ranges occur in the shrubland category. Grassland typically skirts these ranges, and woodland caps them. At this scale, however, these categories do not show.

Second, we greatly underestimated the vertical distribution of CaCO_3 . The soil databases do not represent adequately the massive calcretes in many parts of

the Southwest, such as those of the Llano Estacado in eastern New Mexico and west Texas. They also do not represent adequately the stacked sequences of buried soils containing pedogenic carbonate (Grossman et al., 1995). Neither do they account for groundwater carbonate, despite its importance in the terrestrial C cycle and its dependence, in part, on soil processes (L. Wilding, personal communication, 1999).

Third, listing CaCO_3 content by ecological categories oversimplifies the great variability that exists because of differences in soil age. For example, grassland soils of the middle Pleistocene Dona Ana geomorphic surface near Las Cruces have $453 \text{ kg CaCO}_3/\text{m}^2$ (Gile et al., 1981). In contrast, nearby grassland soils of the late Holocene Organ geomorphic surface have less than $1 \text{ kg CaCO}_3/\text{m}^2$ (cf., pedons 59-1 and 60-12 in Gile and Grossman, 1979).

Fourth, measuring areas represented on a two-dimensional map does not account for the topographical third dimension. This can be important for the mountainous regions of the arid Southwest. Without accounting for the greater surface area resulting from arid mountains, we will underestimate CaCO_3 by as much as 20% in some mountainous regions.

Fifth, many steep slopes have been mapped Entisols-Rockland with little significance given to the degree of pedogenic development, including CaCO_3 accumulation, that can occur there. In fact, many steep alluvial fans draping the sides of mesas in the west have well developed calcic and petrocalcic horizons, as do soils occurring as pockets in mountain bedrock outcrops. Therefore, we again underestimate CaCO_3 .

Sixth, we excluded the central valley of California, which contains some grazing land areas, from either the grassland or woodland categories because of the dominance of agriculture. In contrast, we included large areas of dryland and irrigated agriculture in the High Plains in the grassland category.

Seventh, we grouped the sagebrush steppes that occur in parts of eastern Oregon, southern Idaho, and Wyoming (Bailey et al., 1994; Küchler, 1995) with the grasslands instead of the shrublands, for three reasons. First, they were classified as steppes, so we kept them grouped with the other steppes, which are grasslands. Second, they contain large amounts of Mollisols, which also fit best with grasslands. Third, they largely occur outside the desert boundary MacMahon defined (1985), which also fit better with the grasslands than the shrublands. We also grouped most of central Texas into the woodland category, based on Bailey et al. (1994), when much of that region, especially the western part, is considered grassland (Küchler, 1995).

Amounts

Table 4.1 presents three estimated amounts of C (as carbonate C) for the three grazing land ecoregions. Method #1 (the amounts derived using Machette's map) is considered least accurate of the three methods. This is because the calcic and marginal units of that map omit large areas of calcic soils in Montana, North Dakota, and Washington. As the result, the ecoregion areas are smaller than those used in the other two methods. Using this method, however, woodlands contain 6.3 Pg of carbonate C, shrublands contain 16.6 Pg of carbonate C, and grasslands contain 27.3 Pg of carbonate C, for a total of 50.2 Pg of carbonate C.

Method #2 (extrapolating Schlesinger's 1982 C concentrations) is more accurate because it does not omit large areas of calcic soils. Based on this extrapolation, woodlands in the U.S. contain about 2.9 Pg of carbonate C, shrublands contain about 27.6 Pg of carbonate C, and grasslands contain about 35.2 Pg carbonate C, for a total of 65.7 Pg of carbonate C in grazing lands (Table 4.1).

Method #3 (STATSGO) is most accurate because the data come from soil survey information and, therefore, have received the most groundtruthing. Based on the STATSGO method, woodlands in the U.S. drylands contain about 10.6 Pg of carbonate C, shrublands contain about 18.4 Pg of carbonate C, and grasslands contain about 22.9 Pg carbonate C, for a total of 51.9 Pg of carbonate C (Table 4.1).

Schlesinger's estimates for the woodland category are smaller than STATSGO's estimates, probably because Schlesinger included forest with his woodland category. Schlesinger's (1982) shrubland and grassland categories are higher than STATSGO's, perhaps because shrublands and grasslands in Arizona contain more CaCO_3 because of greater aridity.

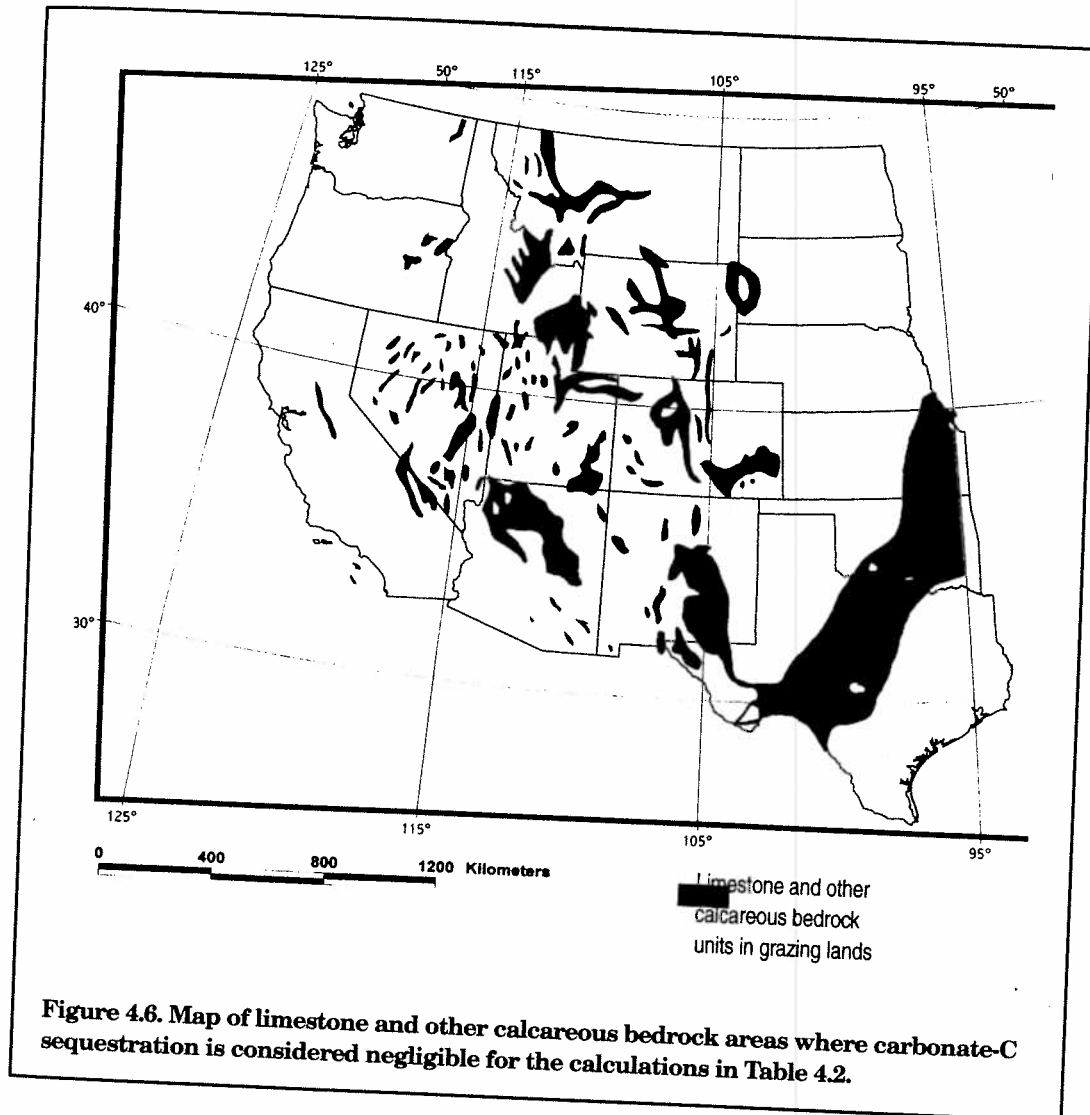
Annual Rates of Soil Inorganic Carbon Sequestration in U.S. Grazing Lands

To estimate the annual rate of C that soil carbonate sequesters, we assumed that no CO_2 is sequestered as carbonate C in calcareous bedrock terrain (Reaction 10). Therefore, we digitized areas of the western and midwestern U.S. dominated by limestone, dolostone, marls, and calcareous sandstones (Fig. 4.6). We based the location of these areas of calcareous bedrock on geologic maps by Oetking (1966, 1967), Feray (1968), Renfro and Feray (1972), Bennison (1973), Renfro (1973), Bennison (1984), and Raisz (1995). Next, we subtracted the areas of calcareous bedrock from the grazing land ecoregions (Fig. 4.4) to give the ecoregion areas with non-calcareous bedrock parent material (Table 4.2).

To obtain a range of sequestration rates, we used low-end and high-end ranges of CaCO_3 accumulation rates that the pedologic and geologic literature reported. For the low end, we used 1 g $\text{CaCO}_3/\text{m}^2/\text{yr}$ (Gile et al., 1981; Schlesinger,

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1985). For the high end, we used $12 \text{ g CaCO}_3/\text{m}^2/\text{yr}$ (Gile et al., 1981; Reheis et al., 1992, 1995). Furthermore, for the low end we assumed that 90% of the pedogenic carbonate that formed in grazing land soils was from limestone dust (Chadwick et al., 1994). Therefore, only 10%, or $0.1 \text{ g CaCO}_3/\text{m}^2/\text{yr}$ is pedo-atmogenic carbonate. Of that amount, C sequestration would be 12% of the CaCO_3 accumulation rate (i.e., 12 molar grams of C per 100 molar grams of CaCO_3), or $0.012 \text{ g carbonate C}/\text{m}^2/\text{yr}$ (Table 4.2).

For the high end, we assumed that only 10% of the pedogenic carbonate was from limestone dust. Thus, 90% of the $12 \text{ g CaCO}_3/\text{m}^2/\text{yr}$ (i.e., $10.8 \text{ g CaCO}_3/\text{m}^2/\text{yr}$) is pedo-atmogenic carbonate. Of that amount, C sequestration would be 12% of the CaCO_3 accumulation rate, or $1.3 \text{ g carbonate C}/\text{m}^2/\text{yr}$ (Table 4.2).

Table 4.2. Estimated annual rates of carbonate C sequestration by grazing land soils in the western and midwestern U.S.

Grazing Land Ecoregions	Ecoregion Areas	Area of Calcareous Bedrock within each Ecoregion	Ecoregion Area with Noncalcareous Parent Material	Low End	High End
				0.012 (g carb-C/m ² /yr)	1.3 (g carb-C/m ² /yr)
	(Mha)	(Mha)	(Mha)	(Pg C/yr)	(Pg C/yr)
woodland	58.0	22.5	35.4	4.3×10^{-6}	4.6×10^{-4}
shrubland	89.0	10.7	78.4	9.4×10^{-6}	1.0×10^{-3}
grassland	<u>158.0</u>	<u>9.4</u>	<u>148.6</u>	<u>1.8×10^{-5}</u>	<u>1.9×10^{-3}</u>
Total	305.0	42.6	262.4	3.2×10^{-5}	3.4×10^{-3}
Total% of U.S. 1442 MMTCE/yr ¹ =				0.032 MMTC/yr	3.4 MMTC/yr
Total% of global carbonate C sequestration rate ² =				0.002%	0.2%
				0.1%	15%

¹ Annual carbon emission rate from Lal et al. (1998, p. 4).
² 0.023 Pg carbonate-C/yr (Schlesinger, 1997, p. 365).

After subtracting the areas of calcareous bedrock from the grazing land ecoregions, the low-end estimate is 3.2×10^{-5} Pg carbonate C/yr (or 0.032 MMTC/yr), which is only 0.002% of the annual C emissions in the U.S. (Table 4.2). The high-end estimate is 3.4×10^{-3} Pg SIC/yr (or 3.4 MMTC/yr), which is 0.2% of the annual C emissions in the U.S. (Table 4.2). In comparison with the estimated global sequestration rate of 0.023 Pg SIC/yr (Schlesinger, 1997, p. 365), the low-end estimate suggests that grazing lands in the U.S. sequester 0.1% of the global SIC amount, whereas the high-end estimate suggests that U.S. grazing lands sequester 15% of the annual global SIC (Table 4.2).

Sources of error in these estimates include:

1. We subtracted only calcareous bedrock areas from grazing land areas. Figure 4.6 does not include Quaternary calcareous deposits, such as calcareous loess, glacial till, and fluvial deposits, especially in the upper Midwest (e.g., Aandahl, 1982, p. 206). However, even if we had adequate maps of these unconsolidated deposits in the West and Midwest, we still would be uncertain whether the CaCO_3 would be primary carbonate or recycled pedogenic carbonate.
2. Similarly, we did not subtract alluvial fans skirting calcareous bedrock mountain peaks, especially those in the Basin and Range.
3. The assumption that calcareous bedrock soils do not contain pedo-atmogenic carbonate may be wrong. Pedo-atmogenic carbonate would form in such soils if Ca from igneous sources was added as dust, rain, or irrigation.

4. We did not treat irrigated agricultural areas of the High Plains and elsewhere as special cases.
5. The accumulation rates reported in the literature may be over simplified. They are based on soil ages spanning a couple to tens of thousands of years. These accumulation rates assume a unidirectional buildup of carbonate and may overlook dynamic biogenic carbonate that occurs on roots and microorganisms.

Management to Sequester Atmospheric Carbon Dioxide as Soil Inorganic Carbon

Fostering SIC sequestration by altering the supply of calcium and bicarbonate

Under natural conditions, most carbonate forms at a rate of 1 to 12 g $\text{CaCO}_3/\text{m}^2/\text{yr}$ (Gile et al., 1981; Machette, 1985; Schlesinger, 1985). If management is to promote this process to sequester C as CaCO_3 , several conditions are important.

First, this process is limited to the Pedocal zone of low rainfall and high pH (i.e., pedogenic carbonate C is not an option in humid regions). Second, a non-carbonate source of Ca is required, as shown by Reaction 10 versus Reaction 17 and Figure 4.2. This source could be from Ca silicates or some other non-carbonate source, possibly gypsum.

The question, then, is how could a non-carbonate source of Ca be obtained? One possibility is irrigation with groundwater residing in igneous terrane. For instance, large areas of the West meet this requirement, such as the Sierra Nevada groundwater recharge system, as well as many other mountain ranges in the Basin and Range in both the U.S. and Mexico. Regions dominated by limestone would have a lower potential for management to sequester C as CaCO_3 unless one could pump in a non-carbonate source of Ca.

Third, the HCO_3^- supply, generated by biotic respiration, is also important. Therefore, by increasing biotic respiration, possibly by adding manures and sludges, the HCO_3^- supply might be increased. However, based on isotope studies (e.g., Nordt et al., 1998), the amount of HCO_3^- derived from soil CO_2 greatly exceeds the amount of Ca needed to form CaCO_3 . Therefore, Ca, not HCO_3^- , would be the limiting factor in sequestering C by CaCO_3 formation. Overall, an optimum amount of silicate Ca, HCO_3^- from respiration, water, and pH is required to sequester carbonate C.

Release of carbon dioxide from soil inorganic carbon

Grazing land soils are important not only as a potential sink for atmospheric CO_2 , but also as a potential source of CO_2 . Pedogenic CaCO_3 forms in the subsoil. Its exhumation and exposure to acidic rain and organic acids might release CO_2 as the result of congruent dissolution (Reaction 11). However, for this reaction to occur, enough acidity is necessary not only to dissolve CaCO_3 and produce HCO_3^- , but also to cause HCO_3^- to convert to CO_2 and H_2O , as Reaction 5 represents. In theory, congruent dissolution might occur not only where acidic rain contacts CaCO_3 but also where microbiotic crusts grow and excrete organic acids on exposed CaCO_3 .

Moreover, erosion promotes the loss of OM (SOC) from soil because it disrupts plant growth that would otherwise bring C into the soil system via photosynthesis (Lal et al., 1998). The same process could apply to carbonate C, because erosion destroys root-microbial infrastructure. If roots and microbes precipitate a significant amount of carbonate (Lobova, 1967; Monger et al., 1991), the demise of this bio-pedologic system curtails CaCO_3 precipitation.

Conclusions

Processes of soil carbonate formation potentially leading to carbon sequestration

In contrast to C sequestration by OM, which involves a one-step process whereby C is converted from gaseous CO_2 to plant tissue C by photosynthesis, C in pedogenic CaCO_3 requires three additional steps. After C has been fixed by photosynthesis, it passes from OM back to gaseous CO_2 by respiration, then to aqueous HCO_3^- by dissolution and dissociation, and then to solid CaCO_3 by crystallization.

Depending on parent material, the formation of pedogenic carbonate can be grouped into two categories: (1) dissolution-reprecipitation of preexisting carbonate (Reaction 10) or (2) silicate Ca combining with HCO_3^- generated by respiration (Reaction 17). The important difference between these two reactions is that one mole of CO_2 is used to dissolve preexisting CaCO_3 in Reaction 10 and one mole is released during the reprecipitation of CaCO_3 . Hence, no C is sequestered. In contrast, two moles of CO_2 are consumed to weather Ca silicate in Reaction 17, yet only one mole is released to the atmosphere with precipitation of CaCO_3 . Therefore, one mole of C is sequestered by CaCO_3 .

Whether or not pedogenic carbonate sequesters atmospheric CO_2 depends on the timescale. On the short-term timescale of decades and centuries, we can differentiate transfers and sinks based on whether the source of Ca is preexisting

carbonates (transfers) or Ca silicates (sinks). On the long-term timescale of millions of years, even marine carbonate rock is a sink for atmospheric CO₂ (Berner, 1999).

Amount of soil inorganic carbon in U.S. grazing lands

Soil carbonate C, based on the STATSGO database and ecoregions of Bailey et al. (1994), totals, in woodlands in the western U.S., about 10.6 Pg C; in shrublands, about 18.4 Pg C; and in grasslands, about 22.9 Pg C; for a total of 51.9 Pg carbonate C (Table 4.1). If we extrapolate soil characterization data derived for Arizona ecosystems (Schlesinger, 1982) to larger regions of the West, then U.S. woodlands contain about 2.9 Pg C, shrublands contain about 27.6 Pg C, and grasslands contain about 35.2 Pg C, for a total of 65.7 Pg carbonate C. Furthermore, if we take a value of 930 Pg carbonate C as the global amount (Schlesinger, 1997; Eswaran et al., 1999), then U.S. grazing lands contain about 6 to 7% of the total carbonate C in world soils.

Annual rates of soil inorganic carbon sequestration in U.S. grazing lands

If we look at a range of carbonate C sequestration rates based on the low-end and high-end CaCO₃ accumulation rates that the literature reports, and subtract calcareous bedrock terrane from grazing lands based on the assumption that no carbonate C sequestration occurs there, we find sequestration rates ranging from 3.2×10^{-5} to 3.4×10^{-3} Pg carbonate C/yr. This range represents, on the low end, 0.002% of the annual U.S. C emission of 1442 MMTC (Table 4.2) to, on the high end, 0.2% of the annual U.S. C emissions.

Globally, if we assume a carbonate C sequestration rate of 0.023 Pg/yr (Schlesinger, 1985), then, on the low end, the U.S. sequesters 0.1% of the annual global amount and, on the high end, 15% of the annual global amount.

Soil inorganic carbon sequestration potential in U.S. grazing lands

In theory, soils with a high potential to sequester carbonate C are those in arid and semiarid lands that could be irrigated economically with water containing Ca from non-carbonate sources (Reaction 17). These soils are in areas with groundwater residing in sediments derived from igneous rocks, such as the Sierra Nevada system. Such igneous terranes occur in many areas of the western U.S. and Mexico.

Adding biosolids to certain grazing land soils also might increase respiration, and, consequently, bicarbonate content. If Ca from non-carbonate sources were available, the formation of pedogenic carbonate, and thus carbonate C, might be increased.

Needed research

An important point about the soil carbonate pool in terms of C sequestration is that it is not a homogeneous pool. Instead, it is composed of at least three sub-pools: primary carbonates, pedo-lithogenic carbonates, and pedo-atmogenic carbonates (Fig. 4.1). Before we can understand the potential of grazing land to sequester atmospheric CO₂, we need to measure the size and better understand the nature of the pedo-atmogenic carbonate pool.

The greatest error in estimating annual sequestration rates might be in the carbonate accumulation rates used (Table 4.1). Although these values are probably accurate on a timescale covering thousands of years, the rates may overlook more dynamic accumulations that occur on the decadal scale. This may be especially important when carbonates are formed biogenically in grazing land soils.

We need to understand if degradation of grazing lands contributes to the greenhouse effect as the result of erosion and the exposure of soil carbonates to acid conditions. If so, preventing grazing land degradation and restoring lands already degraded may be the best contribution that carbonates in grazing lands can make to mitigating the greenhouse effect. Research data also are needed on the impact of liming on the release of CO₂.

Acknowledgments

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