Chapter | Four

Role of Mineralogy and Climate in the Soil Carbon Cycle

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MINERALOGY, WEATHERING, AND THE INORGANIC C CYCLE

When considering soils in the context of climate regulation, thoughts most often turn to soil organic carbon (SOC) stocks. However, over geologic time scales, a large part of the earth's C cycle is controlled by the weathering of silicate minerals and carbonates, as well as the formation of pedogenic carbonates. This is the role of mineralogy in the earth's inorganic C cycle.

Weathering and Consumption of CO_2

As parent material is transformed into soil, and primary minerals are dissolved or transformed into secondary minerals, cations are released into the soil solution. This process leads to the conversion of dissolved CO_2 to bicarbonate salts which are in turn sequestered over geologic time scales in the form of carbonate rock (Berner et al., 1983; Mackenzie and Lerman, 2006). The contribution of chemical weathering to atmospheric CO_2 consumption happens when base cations (Na, K, Ca, Mg) lost during soil development are charge balanced by bicarbonate in soil solution (Chadwick et al., 1994). One mole of base cation charge consumes 1 mol of bicarbonate (e.g., Eq. 4.1).

$$2(CO_2) + 3(H_2O) + CaSiO_3 \rightarrow Ca^{2+} + 2\left(HCO_3^-\right) + H_4SiO_4 \qquad (4.1)$$

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Bicarbonate salts are eventually leached to the ocean where oceanic organisms such as foraminifera, cocolithophorids, corals, and shellfish utilize dissolved bicarbonate salts to form their shells and skeletons, converting these salts to carbonate and carbonic acid. This process releases one of the previously fixed moles of C back into solution (Eq. 4.2). Solid carbonates will eventually be precipitated on the ocean floor and converted to rock.

$$Ca(HCO_3)_2(aq) \rightarrow CaCO_3(s) + H_2CO_3^-(aq) \tag{4.2}$$

Immediate weathering of carbonate parent materials in soils, as opposed to silicate parent materials, both releases and consumes CO_2. When Ca and Mg carbonate weather, they release 1 mol of CO_2 upon dissolution and consume 2 mol of CO_2 when recombining with bicarbonate in soil solution. For example, the C balance of dolomite weathering in soils:

$$\begin{aligned} 2H_2CO_3(aq) + Ca,Mg(CO_3)_2(s) &\rightarrow Ca^{2+}(aq) + Mg^{2+}(aq) \\ + 4HCO_3^-(aq) &\rightarrow Ca(HCO_3)_2 + Mg(HCO_3)_2 \end{aligned} \tag{4.3}$$

The importance of mineral assemblage in determining atmospheric CO_2 consumption during pedogenesis is emphasized by several authors (Amiotte-Suchet and Probst, 1993; Bluth and Kump, 1994; Edmond et al., 1995; Garrels and Mackenzie, 1971; Meybeck, 1986), who also highlight the importance of mineral weatherability in determining rates of inorganic C consumption during pedogenesis. Weathering of base-rich extrusive basaltic and ultramafic materials will consume a larger amount of CO_2 per mass unit than weathering of more siliceous granitic and andesitic parent materials. For example, across a lithosequence under pine forest, development of soils on basalt parent material consumed 60 kg CO_2 m^{-2}, in comparison with only 5 kg CO_2 m^{-2} consumption during pedogenesis on granite parent material (Heckman and Rasmussen, 2011). Weathering of carbonate materials is a carbon neutral process in the long term, even though it consumes CO_2 on shorter time scales (see Eq. 4.2).

The inorganic C cycle in soils is also strongly influenced by formation and/or deposition of pedogenic carbonates. High concentrations of pedogenic carbonates commonly occur in soils of arid and semiarid regions. These carbonates may originate from eolian deposition, dissolution of Ca-containing primary minerals, or deposition of Ca-rich rainwater. In contrast to carbonate formation in oceans, pedogenic carbonate formation is mostly an abiotic process, with the reaction being driven by high concentrations of Ca^{+2}, CO_3^{2-}, or HCO_3^-. Low mean annual precipitation rates, warm temperatures, and dry soil moisture regimes limit water penetration depth and frequency in soils, thereby restricting the dissolution of pedogenic carbonates. These climatic conditions lead to the buildup of significant carbonate deposits over time which can dominate the morphology and function of these soils

(Kraimer et al., 2005; Schlesinger et al., 2008). Carbonate deposits in arid soils also often represent a larger C stock than organic C. For example, in the arid and semiarid soils of Arizona, soil inorganic C storage was nearly three times greater than organic C storage (Rasmussen, 2006).

Inorganic C Stock Sizes and Fluxes

The size of inorganic C stocks involved in the weathering and transformation of minerals in soils and sediments can be equivalent or larger than atmospheric and organic C stocks (Table 4.1).

The fluxes involved in soil inorganic C cycling are smaller than that of terrestrial organic C cycling but are significant over long time scales. Soil carbonate deposits can have residence times in the order of 10,000 years or more (Schlesinger, 1985) and have shown little sensitivity to shifts in climate, suggesting a stable long-term stock (Monger and Martinez-Rios, 2000). In comparison, SOC stocks cycle more rapidly, typically on a decadal to centurial scale (Amundson, 2001). The Fifth Assessment Report of the IPCC estimates only 0.3 Gt of C is consumed each year due to mineral weathering in soils, in comparison with an estimated flux of 2.6 ($\pm$1.2) Gt of C sequestered in terrestrial organic reservoirs per year (although the distribution of this sink between aboveground vegetation and soils is not known).

In summary, the weathering of primary minerals in parent material and soil acts as an active short-term sink of atmospheric CO_2 through formation of aqueous bicarbonates but also acts over geologic time scales to regulate earth's climate through formation of sedimentary carbonaceous rocks and long-term sequestration of C.

Table 4.1 Carbon Masses in Some Global Reservoirs

Reservoir	Mass of Carbon	
	Gigatons C	Moles C
Atmosphere		
CO_2 (preindustrial 280 ppm)	600	5×10^{16}
CO_2 (current 400 ppm)	829 ± 10	6.9×10^{16}
Land		
Soil organic matter	1920	1.6×10^{17}
Litter and peat	25	2.08×10^{16}
Inorganic soil ($CaCO_3$)	720	6×10^{16}
Ocean $CaCO_3$ surface sediment	65,300,000	5.44×10^{21}

Adapted from Mackenzie, F.T., Lerman, A., 2006. Carbon in the Geobiosphere — Earth's Outer Shell. Springer, Dordrecht, The Netherlands; with data from IPCC, 2013. Climate change 2013: the Physical Science Basis. In: Stocker, T.F., Qin, D., Plattner, G-K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M., (Eds.), Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

CLIMATE, MINERAL ASSEMBLAGE, AND SOIL ORGANIC CARBON ARE INTRINSICALLY LINKED THROUGH WEATHERING PROCESSES

Globally, soils develop and evolve across a continuum of climate regimes and parent materials. The interactions of climate with mineral substrates across time produce a myriad of soil morphologies with contrasting physiochemical environments. These unique suites of physiochemical matrices drive many of the differences observed in SOC storage, the mechanisms controlling C stabilization, and interactions among soil biotic and abiotic components. Pedogenesis and the SOC cycle are both affected by, and linked through, the interactions of climate and mineral substrates.

Climate Versus Physiochemical Control of Soil and Organic C Stock Development

The development of mineral soils is driven by energy and mass fluxes constrained by temperature, precipitation, primary production, soil production, and sediment redistribution (Jenny, 1941). The availability of these resources varies widely based on latitude. From a geomorphological perspective, a convenient way to illustrate the consequences of climate for soil profile characteristics is the Strakhov diagram (Fig. 4.1). This diagram summarizes the broad trends in soil depth and mineral character with latitude. In the tropics, where moisture is generally abundant and temperatures are high, chemical weathering rates are at their maximum. The soil weathering zone reaches depths of tens of meters. High precipitation rates produce highly leached soils characterized by high concentrations of Fe and Al oxides. At the opposite side of the spectrum are the taiga and tundra regions of the Arctic. Freezing temperatures limit chemical weathering by keeping water locked up in ice for most of the year. Physical weathering dominates soil development in these regions but

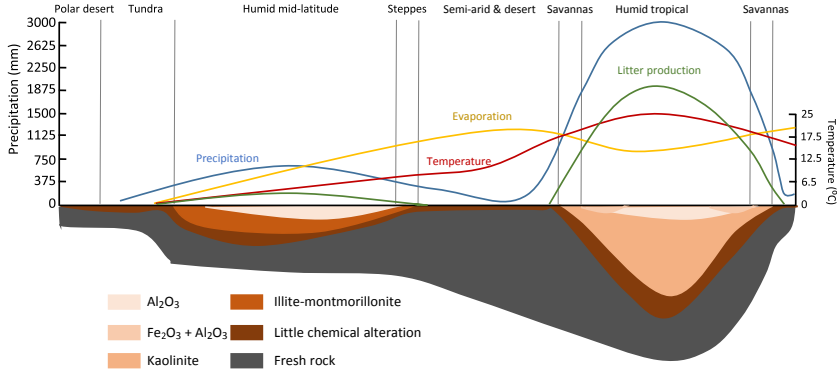

FIGURE 4.1 Strakhov model (Strakhov, 1967). Reproduced from Rutter (2009) with permission.

produces little in the way of mineral transformation or morphological development. Here soils are shallow and similar to their parent material in mineral character. In the midlatitudes, factors determining the depth and intensity of the weathering zone are more complex, and relationships between temperature and soil development are less direct. In arid desert regions, temperatures are high, but water limits weathering reactions, and soils remain mostly static in mineral character. In the forests and plains of temperate latitudes, a broad diversity of soil weathering regimes exist which give rise to a high diversity of soil morphology and mineral assemblage.

From a pedologic perspective, soil development, here characterized by categorization into one of the 12 soil orders, may be said to follow one of several pathways, or to rephrase, that the degree of soil development is dominated by one of the soil-forming factors: climate, vegetation, topography, parent material, or time (Fig. 4.2). As outlined above, climatic extremes such as tropical, Arctic, and hyperarid regimes give rise to either extremely high or low rates of soil development. In temperate systems, the mineral assemblage of the parent material may be the determining factor in the character of the resulting soil. High amounts of expandable clays in the parent material may result in a vertisol with characteristic shrinking and swelling, resulting in large cracks and constant movement and sheering of large soil aggregates within the soil. Sandy parent materials deposited by glacial retreat in northern temperate zones may develop characteristic spodic horizons due to high water infiltration rates, acidic vegetation, and hydrologic properties of the parent material.

SOC stocks, and the stability of those stocks, are dictated by the same soil forming factors that shape soils into their unique morphological and chemical matrices. Interactions among SOC and soil minerals act to decrease the bioavailability of SOC, thereby slowing degradation rates and leading to the preservation of SOC belowground. Extreme climatic conditions lead to extremes in SOC stocks and their turnover. SOC stocks can vary from as little as <25 tons ha^{-1} in arid deserts and dry arctic soils to >300 tons C ha^{-1} in boreal systems where decomposition is limited by soil saturation and low temperatures (Scharlemann et al., 2014). Soil respiration also varies by an order of magnitude or more across the globe, from 80 g C m^{-2} $year^{-1}$ in deserts to 800–2000 g C m^{-2} $year^{-1}$ in a tropical forest (Torn et al., 2009). In desert soils, not only are SOC stocks small, they are generally unstable even when there is an abundance of reactive mineral surfaces. However, large C stocks of inorganic C may be present in these soils and sequestered for long time periods as carbonate minerals. Here, mineralogy (in the form of carbonate minerals) plays a large part in inorganic C deposition and stabilization, but not in organic C stabilization. In arctic and boreal systems, the opposite is true. SOC stocks are generally large and turnover slowly (Fig. 4.3). The preservation of C in these soils is generally mostly dependent on climatic factors, however, not interactions with the minerals, making these C stocks highly vulnerable to future warming.

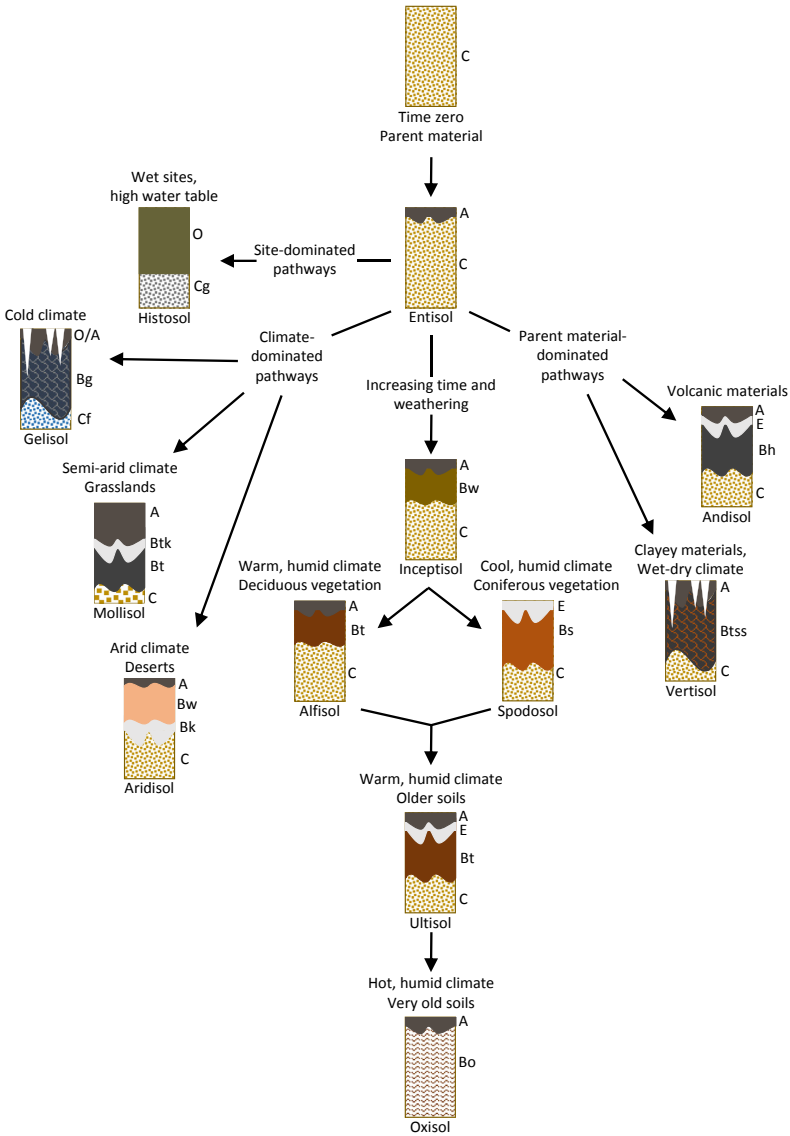

FIGURE 4.2 Soil order development pathways. Reproduced with permission from Schaetzl, R.J., Anderson, S., 2005. Soils: Genesis and Geomorphology. Cambridge University Press, New York, 917 pp.

The mineral matrix has received substantial attention in regard to C cycling and stabilization in temperate and tropical regions, where decomposition rates of soil organic matter are thought to be tightly linked to mineralogical parameters. The details and interdependencies of these links between soil C degradation and mineral assemblage are still not fully understood, nor are

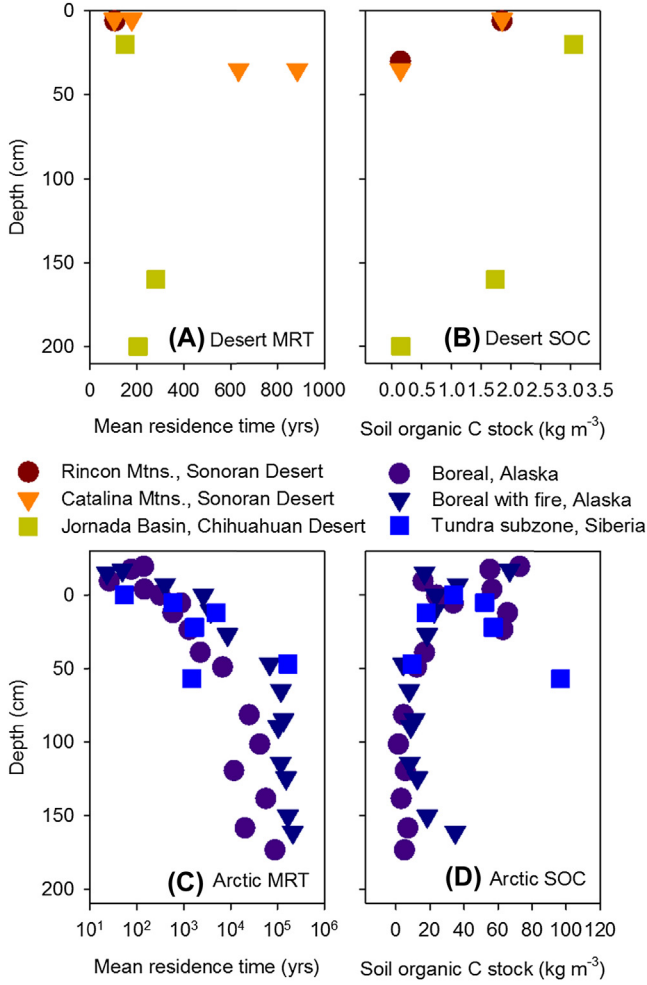

FIGURE 4.3 Comparison of soil organic carbon (SOC) stock density (kg C per m^3 of soil) and SOC mean residence time (MRT) between arid dry ecosystems (desert) and cold moist ecosystems (arctic). These profiles are not meant to be all encompassing but are meant to give some typical examples of the extremes of SOC stocks and stability. Data was taken from Connin, S.L., Virginia, R.A., Chamberlin, C.P., 1997. Carbon isotopes reveal soil organic matter dynamics following arid land shrub expansion. Oecologia 110, 374–386; Lybrand, R.A., Rasmussen, C., 2015. Quantifying climate and landscape position controls on soil development in semiarid ecosystems. Soil Science Society of America Journal 79, 104–116; Lybrand, R.A., Heckman, K., Rasmussen, C., 2018. Soil organic carbon partitioning and residence time variation in desert and conifer ecosystems of southern Arizona. Biogeochemistry (in review); O'Donnell, J.A., Harden, J.W., McGuire, D.A., Kanevskiy, M.Z., Jorgenson, M.T., Xu, X., 2011. The effect of fire and permafrost interactions on soil carbon accumulation in an upland black spruce ecosystem of interior Alaska: implications for post-thaw carbon loss. Global Change Biology 17, 1461–1474; Kaiser, C., Meyer, H., Biasi, C., Rusalimova, O., Barsukov, P., Richter, A., 2007. Conservation of soil organic matter through cryoturbation in arctic soils in Siberia. Journal of Geophysical Research: Biogeosciences 112(G2), doi:10.1029/2006JG000258.

the vulnerabilities of these relationships to climate change. However, a comparison among tropical soils can illustrate how the role of the mineral matrix in protecting SOC stocks from biodegradation varies with mineral assemblage within a climate regime. Andisols are among the most organic matter–rich mineral soils on the planet, whereas oxisols often have little organic matter that is easily lost after disturbances such as cultivation. The contrast of C density in these tropical soils is one of the most drastic examples of mineral assemblage determining C stock size and stability. Globally, andisols contain nearly three times the C per unit area as oxisols (0.028 vs. 0.010 Pg 1000 km^2) (Eswaran et al., 1993). This difference in C content arises from a combination of the unique mineral properties inherited from both parent material and transformation of those minerals by weathering processes. Andisols develop from volcanic parent material containing an abundance of highly weatherable amorphous volcanic glass. The unique chemistry of the parent material, in combination with a wet and warm tropical climate, produces soils enriched in secondary minerals with high specific surface area and charge, capable of binding large amounts of organic material. Tropical oxisols may develop from a number of parent materials, but regardless of the attributes of the parent material, it is time which defines the mineral character of these soils (see Fig. 4.2). Oxisols contain highly weathered materials that have often been eroded and redeposited multiple times prior to morphological development in their current locations, leaving few weatherable mineral phases. Thus the mineral matrix of oxisols is composed mostly of quartz, iron oxides, and aluminum oxides (Van Wambeke et al., 1983; Buol and Eswaran, 1999). Although oxides generally have high specific surface area and pH-dependent charge, pH conditions in the soils lead to low cation exchange capacity (CEC). This low CEC in combination with weathering-induced base cation leaching leads to low fertility and low organic matter contents (Buol et al., 2003). This is only one example of how mineral assemblage can influence SOC stocks within a particular climate regime.

The Chronosequence: Linking SOC Stocks and Mineral Weathering Over Time

The current mineral character and C loading of a particular soil is the result of climate acting on parent material over a period of decades to millions of years. Weathering of primary minerals into secondary phases is largely driven by interaction with water and organic acids over time (Huang and Keller, 1972; Drever and Vance, 1994; Dontsova et al., 2014). Organic matter accumulation is concomitant with these weathering processes, itself being driven partially by the creation of new mineral binding sites. Chronosequences can be used to track the coevolution of the mineral matrix and SOC stocks. Perhaps one of the first chronosequences to link C stabilization and the accumulation of reactive secondary mineral phases came from a series of lava flows on the islands of Hawaii, Molokai, and Kauai (Torn et al., 1997). This chronosequence on

quickly weathering volcanic substrate tracked the accumulation and eventual loss of reactive noncrystalline mineral phases and SOC stocks over a period of approximately 4 million years. SOC and noncrystalline mineral phases reached a mutual maximum concentration at approximately 150,000 years of soil development, then jointly declined as progressive weathering led to the dissolution and leaching of reactive noncrystalline mineral phases. Similar patterns of accumulation and loss of secondary mineral phases and SOC stocks over geologic time scales can also be seen across chronosequences in temperate climates (Fig. 4.4). The types of secondary mineral or colloidal phases formed over time are necessarily constrained by the parent material, but the importance of Al- and Fe-oxyhydroxide and amorphous phases is a common theme in the long-term accumulation and stabilization of SOC stocks

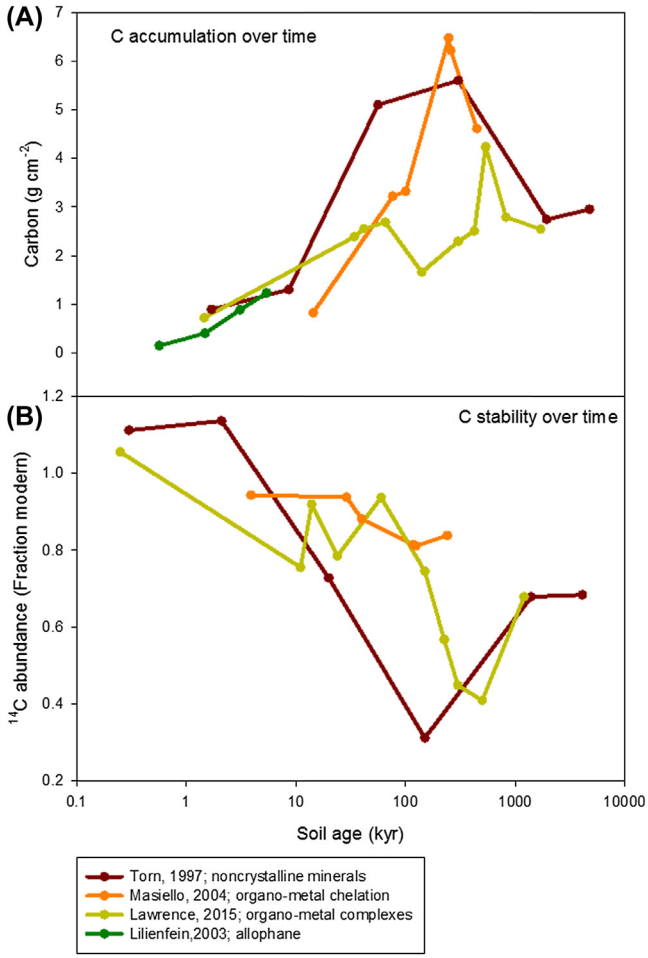

FIGURE 4.4 Variance in (A) C stocks and (B) stability across a series of chronosequences. Figure legend indicates primary authors and mineral corollary variables.

across chronosequences on a range of parent materials. Chronosequences from a grassland over arkosic sedimentary materials (Masiello et al., 2004) and a mixed deciduous forest over loess-mantled glacial outwash (Lawrence et al., 2015) both identified accumulation of organometallic complexes as the strongest determinant of SOC accumulation. A young chronosequence formed through the retreat of the Damma glacier in Switzerland found a close association of SOC stocks and allophane accumulation (Dümig et al., 2012). These chronosequences illustrate the links between SOC abundance and reactive mineral abundance across geological time scales.

MINERAL STABILIZATION OF SOIL ORGANIC C—BONDING MECHANISMS

Soil minerals vary widely in their elemental composition, degree of crystallinity, and charge characteristics, and therefore in their capacity to form and preserve bonds with organic matter. Most primary minerals are assumed to be fairly unreactive, and therefore not expected to exert a large influence on soil organic matter retention. Secondary mineral phases formed during pedogenesis have received a much larger degree of examination, both in natural soils, artificial soil mixtures, and as pure phases. Secondary phyllosilicates, hydroxides, and short-range order phases are often the focus of most investigations due to their ubiquitous nature in soils and their reactive surface chemistry. Although each secondary mineral has a large range in charge and surface characteristics due to variance in formation conditions among soils, general trends in reactivity and amount of surface area available for sorption are still observable (Table 4.2). Expandable phyllosilicate phases such as smectites have larger surface area and permanent charge than nonexpansible phyllosilicate phases such as kaolinite. Hydroxide phases exhibit higher reactivity than phyllosilicates, and finally short-range order phases, ferrihydrite, allophane, and imogolite, show the highest potential for sorption of organic matter.

Organomineral bonding occurs over a spectrum of bond types and strengths. The type and strength of the organomineral bond as well as the organic matter functional groups involved varies based on the mineral phase characteristics outlined above (Mikutta et al., 2007; Wattel-Koekkoek et al., 2001). Bonding mechanisms include (Essington, 2003) (1) Cation exchange, where negatively charged N-containing moieties (quaternized N atom in an aliphatic chain or heterocyclic ring) of the organic matter form a bond with a negatively charged site on the mineral surface; (2) Anion exchange, where protonated mineral surface sites bond with anionic organic groups; (3) Water bridging, the formation of weak H bonds between negatively charged organic functional groups and waters of hydration on a mineral surface; (4) Cation bridging, in which a cation from soil solution acts as a bridge between negatively charged

Table 4.2 Reactive Properties of Common Secondary Soil Minerals

	Layer Charge (mol per 1/2 Unit Cell)	PZNC	SSA ($m^2\ g^{-1}$)	Cation Exchange Capacity (cmol kg^{-1})	Density
Halloysite	~0	na	21–43	2–60	2.5–2.65
Kaolinite	~0	5.25	5–20	3–15	2.6
Illite	0.6–0.8	3.5–8.5	100–200	10–20	2.6–2.9
Vermiculite (high activity)	0.6–0.9	na	300–500	100–150	2.3–2.7
Smectite	0.2–0.6	na	700–800	80–150	2.0–2.7
Goethite	na	7–9	8–200	0–5	3.3–4.3
Gibbsite	na	9	32 (varies widely)	0–5	2.3–2.4
Ferrihydrite	na	~7.9	100–700	~0	3.8
Allophane	na	5.5–6.9	700–900	10–40	2.3
Imogolite	na	8.4	900–1100	50	2.3

Values taken from Brady and Weil, 2002; Dixon and Schulze, 2002; Cornell and Schwertmann, 2003; Essington, 2003; Joussein et al., 2005; Schaetzl and Anderson, 2005; Karamalidis and Dzombak, 2010; Ma and Karube, 2013; Kleber et al., 2014.

groups on the organic and mineral structures; (5) Ligand exchange, when at low pH, organic matter carboxylate and phenolate groups replace the hydroxyls of protonated mineral surface groups to form strong bonds; (6) Hydrogen bonding, where weak bonds are formed due to the interaction between basal oxygens of mineral surfaces and hydrogens of organic functional groups; (7) van der Waals bonding, when bonds are formed when the fluctuations of the organic and mineral polarizations are correlated; (8) Hydrophobic interaction, when organics precipitate out of soil solution onto mineral surfaces due to their hydrophobic nature.

These bonding mechanisms are assumed to be in operation in synthetic and naturally occurring soils, with their relative importance varying with mineral structure, soil solution ionic strength, and pH. Any variance in the susceptibility of these different organomineral complexes to changes in climate has yet to be identified. Outer sphere and electrostatic bonds are assumed to be more vulnerable to disruption, given an increase in temperature, while ligand exchange reactions are thought to be the most stable. Field-scale evidence reflecting changes in SOC stability due to the varying strengths of particular organomineral bonds at the microscale has yet to be presented in a robustly defensible manner.

MINERAL STABILIZATION OF SOIL ORGANIC C—FIELD AND LAB-BASED EVIDENCE

Data from observational field experiments, lab-based manipulative experiments utilizing field-harvested and artificial soils, as well as batch sorption experiments all suggest a significant influence of the mineral matrix on the binding and preservation of soil organic matter. However, a general agreement among these results has not been reached in regard to the relative importance of the suite of identified mineral—organic interactions to the preservation of soil organic matter and its interaction with climate.

Lab-Based Studies: Batch Sorption and Incubation Experiments

Basic and advanced spectroscopic techniques in combination with batch sorption and incubation studies have allowed for insight into the formation of organomineral bonds. Due to differences in functional groups on the surfaces of minerals and organics, certain organic compounds are hypothesized to bond preferentially to certain mineral phases or certain functional groups on mineral surfaces. As a result of this preferential bonding, when a heterogeneous mixture of organics is reacted with a mineral surface, a phenomenon referred to as "sorptive fractionation" occurs whereby the bulk composition of the mixture of organics is changed after reaction with the mineral. A recent review of the association of organics with mineral particles by Kleber et al. (2014) indicated some trends in the types and strengths of organomineral bonds summarized from lab-based sorption experiments. Fitting with theory, metal oxides formed strong ligand exchange bonds with organic carboxyl groups, whereas weaker bonds such as outer sphere complexation and H bonding were generally observed for reactions of organics with phyllosilicates, although cation bridging was also observed between phyllosilicate surfaces and organic compounds. These results have been achieved through reaction of individual mineral phases with a single organic compound, under controlled conditions. In naturally forming soils, a multitude of complex mineral phases and organic compounds coexist under conditions of fluctuating moisture and organic matter input which leads to swings in pH, organic compound reactivity, soil solution ionic strength, and oxygen availability.

Studies Utilizing Natural Soils: Linkage of Soil Mineralogical and Organic Properties Through Observational Measurements

The question remains as to the importance of the above reactions within the context of climatic influence on SOC cycling. The increased retention and stability of soil organic matter due to adsorption on mineral surfaces is well established (e.g., Baldock et al., 2000; Lutzow et al., 2006). However, the relative influence of specific mineral phases in the protection of SOC against

biodegradation is not. There are few studies offering observations of differences in SOC characteristics or bonding as associated with mineral phases in naturally formed soils. Density separation has been employed to separate natural soils into fractions of varying mineral assemblage (Sollins et al., 2006, 2009). This separation scheme utilizes the differences in density among mineral phases (Table 4.2). However, this approach is confounded by the fact that the amount of organic matter associated with the particular mineral fraction decreases the density of the organomineral complexes by an unpredictable degree. Therefore the denser the isolated mineral fraction, the lower the organic matter content. Even considering this complication, separation by density has allowed for the comparison of naturally formed organomineral complexes that differ significantly in their mineral assemblage. Separation of soil fractions dominated by secondary phyllosilicates (less dense) from fractions composed of (assumed to be unreactive) mainly primary minerals (higher density) gave no evidence of mineralogical control over the stability or composition of their associated organics (Sollins et al., 2006). Total C decreased with increasing particle density, but C stability (approximated from radiocarbon content) increased with increasing density. A similar study indicated both increased and decreased stability of C with increasing organomineral complex density (Baisden et al., 2002). In a subsequent investigation by Sollins et al. (2009), again no role of mineral surface chemistry control on SOC stability could be identified in the soils examined, with exception of mineral Fe concentration. Data suggested that Fe oxide phases did protect organic matter from microbial attack for longer periods of time than the other isolated organomineral fractions, evidenced by the relatively unprocessed character and long mean residence time of organics associated with mineral fractions dominated by Fe-dense phases. The question remains, Why does the variance in organomineral bond type and strength observed under laboratory conditions remain so difficult to observe in natural systems?

One moderately well-accepted exception to this question occurs in andisols. Andisols and soils with andic properties are perhaps the longest recognized and most studied example of regulation of soil C cycling by mineral and amorphous/sesquioxide phases. Andisols are unique in their high concentrations of allophane and imogolite and poorly crystalline minerals with high reactivity. The high specific surface areas and abundance of reactive surface functional groups of these minerals are thought to be the major driver of SOC accumulation and stabilization in these C dense soils (Harsh et al., 2002; Lilienfein et al., 2004; Rasmussen et al., 2005). Recent publications have used quantification of these poorly crystalline minerals to draw statistical relationships between the abundance of these mineral phases and SOC in andisols (Giardina et al., 2014; Garrido and Matus, 2012). Andisols are a unique case, however, and account for only 3% of soil coverage worldwide (Eswaran et al., 1993). Elucidating the role of mineral surface chemistry in soils of differing morphology remains a challenge.

Recent Advances in the Understanding of Mineral Control of Soil Organic Matter at the Landscape Scale

On a broad scale, some very general relationships between soil texture, as a proxy for the mineral matrix, and SOC have been in use for decades. Given steady-state inputs of C to the soil, soil texture is generally understood to determine the length of time required for SOC stocks to achieve equilibrium levels (Jenny, 1941). Soil texture is also widely used as an ecosystem scale predictor of SOC stocks in terrestrial biogeochemical models (e.g., CENTURY), with some degree of success. However, significant evidence of mineralogical control of SOC abundance and turnover at the field scale remain difficult to detect due to the influence of confounding environmental factors. New ecosystem- and continental-scale investigations into the importance of soil mineral assemblage in regulation of the SOC cycle are currently under way. Although some trends are emerging, studies are still offering conflicting conclusions.

Field studies have begun testing the predictive capacity of soil texture against other soil physiochemical parameters. In a survey of 62 plots on the central US plains, SOC abundance was more strongly related to silt content than clay content. The authors attribute this to the greater water holding capacity of silt-dominated soils which yields better growing conditions and consequently greater C inputs to soils (Augustin and Cihacek, 2016). In a survey of Chilean volcanic soils, texture was not correlated with SOC concentration. Allophane and C complexed with colloidal Al (pyrophosphate extractable Al) explained most of the variation in C content, with the abundance of allophane and C−Al complexes directly dependent on soil pH (Garrido and Matus, 2012). Many times, spatial variability prevents the detection of even general dependencies of C on mineralogical properties. In a recent study of SOC stability and turnover across 13 forests in Switzerland, patterns of turnover (^{14}C abundance) and variance were not related to clay content but exhibited no direct relationship to climatic or geologic variation either. Additionally, in these plots, microtopographical variance in ^{14}C abundance was similar in magnitude to regional-scale variance (van der Voort et al., 2016).

The attention of modelers has also turned to the physiochemical characteristics of the soil including mineral assemblage, elemental composition, and chemistry (Bradford et al., 2016). These factors are being introduced as bonding and/or sorption hysteresis reactions which act to modify the cycling rate of soil organic matter pools. The Microbial Efficiency-Matrix Stabilization framework (Cotrufo et al., 2013) suggests that the cycling of microbial decomposition products is explicitly limited through sorption reactions with soil oxides and cation exchange surfaces. No models currently include mineral assemblage explicitly, although efforts toward this end are emerging from exploration of compiled data sets as well as creation of large-scale field observational experiments.

Recently, examination of top soils (0−10 cm) across a transect of 24 grassland and shrubland sites found significant evidence that adsorption to mineral surfaces drives C accumulation and resistance to biodegradation. Although climatic factors have long been assumed to drive turnover of surface soils, precipitation and temperature were only secondary predictors of C stocks and turnover; geochemical predictors (Si, Al, Fe, concentrations, and base saturation) were more robust predictors (Doetterl et al., 2015). Additionally, some data suggest that mineral assemblage may play more of a role in regulating the stability and turnover of "deep" soil C (>30 cm below the surface). A statistical exploration of 122 soil radiocarbon profiles from all over the world by Mathieu et al. (2015) indicated a strong dependence of soil C turnover on soil morphological characteristics as opposed to climate or land use.

SUMMARY

The mineral component of soils is often the largest by mass and volume, with a strong influence over the soil physiochemical conditions under which C preservation and degradation take place. Although it is a well-recognized fact that the mineral matrix of the soil plays a part in the global C cycle, how exactly that part stands to be altered under future climate conditions is not known. Soils contain substantial inorganic and organic C stocks, both of which represent a substantial proportion of the terrestrial C pool. Evidence to date indicates low sensitivity of inorganic C stocks to climate change but has not reached a consistent conclusion in regard to SOC stock vulnerability to changing climate. Modelers and experimentalists alike are currently examining the role of mineral assemblage in regulating the cycling of SOC, but to date no consensus has been reached.

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