

CARBON BALANCE IN THE
MAJOR SOIL ZONES
OF SASKATCHEWAN

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2002

Carbon Balance in the Major Soil Zones of Saskatchewan

A Thesis

Submitted to the College of Graduate studies and Research in Partial Fulfillment of the
requirements for the Degree of

Doctor of Philosophy

in the

Department of Soil Science
University of Saskatchewan
Saskatoon, Saskatchewan, Canada

by

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Fall 2002

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ABSTRACT

Soil organic matter and carbonates are the two major C pools in the pedosphere, which are interconnected to the biosphere and atmosphere. The objectives of this study were to determine the present storage and accumulation rates of pedogenic carbonate and organic C using stable isotope geochemistry in a series of zonal (Brown through Gray) soils representing a gradient of time and environment in the Prairie Ecozone of Saskatchewan.

The mass of organic C was 9.1 kg C m^{-2} for Brown, 11.7 kg C m^{-2} for Dark Brown, and 14.9 kg C m^{-2} for Black soils, decreasing to 9.6 kg C m^{-2} for Gray soils. A Rego Black Chernozem soil (carbonated phase) contained 21.0 kg C m^{-2} . The $\delta^{13}\text{C}$ values of organic C was -22.9‰ for Dry Brown soils, -24.3‰ for Brown soils, -24.8‰ for Dark Brown soils, -25.3‰ for Black soils, and -26.8‰ for Gray soils.

The storage of pedogenic carbonate increases from 133.9 kg m^{-2} in Brown soils to 164.5 kg m^{-2} in Gray soils, with corresponding rates of pedogenic carbonate accumulation of 8.3 to $14.3 \text{ g m}^{-2} \text{ yr}^{-1}$. Values for the $\delta^{13}\text{C}$ of pedogenic carbonates decrease from semiarid to humid soils, representing a decrease in the proportion of C_4 plants in the vegetation. The depth of carbonate-free solum, the total pedogenic carbonate storage, and the rate of pedogenic carbonate accumulation all increase with increasing annual precipitation.

In a landscape of Dark Brown and Black Chernozem soils on hummocky moraine, stores of C in soil organic matter and pedogenic carbonate were higher in soils

on north-facing slopes than those on south-facing slopes. Soil organic C stores were larger in concave area in comparison to level areas with profiles > 1 m depth. Pedogenic carbonate stores to 1 m depth varied considerably over the landscape studied. Pedogenic carbonates were highest in rego soils on convex or planar slopes adjacent to leached depressions and in shoulder soils. Mean values of C accumulation in the form of pedogenic carbonate and soil organic C for the whole landscape were 14.1 and 15.0 kg C m⁻², respectively.

The results show that in addition to C sequestration in the form of organic C, substantial amounts of C are stored as pedogenic carbonate. Soils of grasslands and forests of the boreal regions have considerable potential to store C in organic forms in the short to medium term, and a long term potential as pedogenic carbonate.

ACKNOWLEDGMENTS

I would like to express my sincere appreciation and thanks to my supervisors Drs. A. R. Mermut and D. W. Anderson for their understanding, advises, criticisms, unvaluable suggestions and comments, and support and encouragement throughout my study. I would also like to thank the members of my advisory committee, Drs. K.J.C. Van Rees, D. J. Pennock, J.D. Knight, G. Koehler, and D. deBoer for their constant advice and suggestions. My sincer thanks are extended to Dr. L. Wilding, who served as the external examiner on my Ph.D. defense examination, for his thought provoking criticisms and unvaluable suggestions.

I also would like to thank individuals who assisted me to carry out my research successfully. I appreciate the help that received from Mr. M. Solohub for survey of the landscape, Ms. A. B. Haughn for soft wear programs, Mr. D. Cerkowniak for GIS program, Mr. M Stocky for stable isotope measurement, Mr. B. Goetz for Atomic Absorption work. I would like to acknowledge the graduate students in our team, Mr. W. I. I. Mella, Ms. C. S. S. Masutti, and Mr. F. M. Debela who shared their ideas with me and provided their help and assistance whenever I was needed. I will remember their friendship in the rest of my life.

The financial support of this study by the Iranian Ministry of Science, Research and Technology, and Natural Sciences and Engineering Research Council (NSERC) is greatly appreciated.

Most of all, my most sincere gratitude goes to my wife, Forough and my two lovely daughters, Behnaz and Sara for their patient, encouragement, sacrifice and their love. Without them, none of this would have been possible. I would like to dedicate this thesis to my wife and daughters.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND INFORMATION

A better knowledge of the magnitude and dynamics of organic C and the C in carbonates is important for a more complete understanding of the global C cycle, and to evaluate the storage and fluxes between the atmosphere, the biosphere, and the pedosphere (Lal et al., 2000). The soils of the cool and dry boreal regions are known to contain large stores of both organic matter and carbonates. Although the size of the organic storage is reasonably well known, carbonate storage, especially pedogenic carbonate, has received only limited attention (Wang and Anderson, 2000).

Carbonates, as a more stable pool than organic C, can sequester substantial amounts of C and are important constituents of many soils. In general, carbonates are characteristic of relatively dry soils where grasses or mixed grasses and shrubs are the dominant vegetation (Cecring, 1984). Soil carbonate may originate from the parent material by solution-precipitation mechanisms that result in the formation of secondary or pedogenic carbonates. Whereas some forms of pedogenic carbonate such as concretions, pendants, and laminar caps are readily identifiable, in soils formed from carbonate-rich parent materials it can be difficult to distinguish between carbonates inherited from the parent material (lithogenic) and those formed *in situ* (Rabenhorst et al., 1984). The marked differences in the relative content of ^{13}C in relation to ^{12}C ($\delta^{13}\text{C}$)

between carbonates of lithogenic origin and those of biogenic origin (reflecting present and past vegetation) makes stable isotope geochemistry particularly relevant to identifying and estimating the amount of pedogenic carbonates.

Stable C and O isotopes in soil carbonates provide a record of past environments that may include shifts in vegetation, climate, and atmospheric circulation patterns (Cerling, 1984; Quade et al., 1989; Amundson et al., 1996). The good correlation between the $\delta^{18}\text{O}$ value of pedogenic carbonate and local meteoric water has been used to reconstruct past environments (Cerling and Hay, 1986; Cerling et al., 1988; Quade et al., 1989).

The ecoregions of Saskatchewan largely coincide with the major soil zones, reflecting the effects of latitude and diminishing energy from the southwest to the northeast of Saskatchewan. The zonal relationships between climate, soils and the distribution of native species is clearly displayed from the warmer but still cool, dry native grasslands of the southwest through the cool, sub-humid (still comparatively dry) parkland area, to the cold, dry lichen woodlands in the northeast (Acton et al., 1998).

1.2 HYPOTHESES

The hypotheses of this study were:

- 1) The amount of pedogenic carbonate and its rate of accumulation increase along the environmental gradient from the Dry Brown to the Gray soil zones.

- 2) The $\delta^{13}\text{C}$ value of pedogenic carbonate will decrease regularly along the environmental gradient from Dry Brown to Gray soils, as will the $\delta^{13}\text{C}$ of the soil organic matter, reflecting the average long-term contribution of C_4 and C_3 plants.
- 3) The conversion of organic C to pedogenic carbonate is of greater magnitude in boreal soils than in the soils of desert environments.
- 4) Unusually high amounts of pedogenic carbonates and organic C in Rego Black Chernozem (Wooded Calcareous) are likely due to regional hydrological flows, bringing Ca into the soil environment which is dominated by CO_2 from soil respiration.

1.3 OBJECTIVES

The objectives of this thesis are to:

- 1) Assess the size of the pool and rate of accumulation of pedogenic carbonates in non-cultivated lands of the different soil zones of Saskatchewan and to estimate the transformation rate of organic C to pedogenic carbonate.
- 2) Obtain, in a systematic way, a consistent data set that describes for the major climatic zones across Saskatchewan, $\delta^{13}\text{C}$ values for organic matter, pedogenic carbonate, and bulk soil, providing a baseline for further studies.

CHAPTER 2

LITERATURE REVIEW

2.1 GLOBAL CARBON POOLS

2.1.1 Estimates of Soil Carbon Pools in Relation to Global Carbon Pools

Of the three major active reservoirs, the oceans contain approximately 38,000 Pg (10^{15} g) of C, the terrestrial system about 2,500 Pg, and the atmosphere about 720 Pg C (Fig. 2.1). Geologic C, including C in fossil fuels contains 5,000 to 10,000 Pg C. Soil organic C together with inorganic C or pedogenic carbonates are estimated to be about 2,500 Pg C and both play important roles in the global C cycle. Although short-term C cycling (photosynthesis and soil respiration) has been documented for many ecosystems (Raich and Schlesinger, 1992), there are few reliable estimates of long-term net C fluxes from the atmosphere to the soil (Schlesinger, 1990; Harden et al., 1992).

Most of the estimated values of the mass of organic C in soils fall in the range of 1,400-1,600 Pg C, regardless of whether the global pool is estimated from an aggregation of vegetation biomes (Schlesinger, 1977), climate-life zones (Post et al., 1982), or soil orders (Eswaran et al., 1993; 2000). Approximately 55 Pg C of the total resides in the fresh litter or detritus on the soil surface. Because this value is similar to the net primary production (NPP), the mean residence time of surface litter globally is

considered to be about one year (Schlesinger, 2000).

Because of the complexity of processes involved in atmosphere-vegetation-soil-landscape relationships, it is difficult to estimate the pool of secondary or pedogenic carbonate in the world's soils, and the long-term net C fluxes from atmosphere to carbonate by way of plants and soil organic matter (Lal et al., 2000).

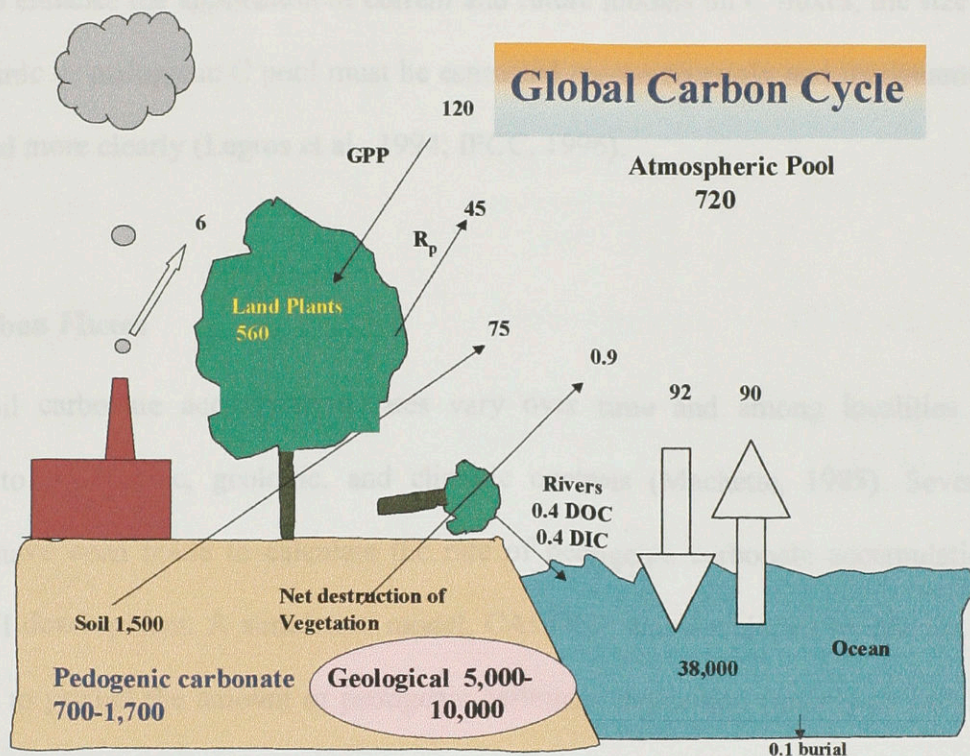


Figure 2.1 The present-day global carbon cycle, showing the reservoirs (in Pg) and fluxes (in Pg) (modified and redrawn from Schlesinger and Andrews, 2000).

Pedogenic carbonate has been estimated globally to be about 800 Pg in Aridisols and Entisols of arid regions, mainly in the caliche layers (Schlesinger, 1982). Other estimates of total pedogenic carbonates in world soils include 720 Pg C by Sombroek et al. (1993), 1738 Pg by Eswaran et al. (1995), 695 to 748 Pg by Batjes (1996), and 750 to 947 Pg Eswaran et al. (2000). The differences among estimates are due at least in part

to the difficulty of differentiating between primary carbonates (lithogenic carbonates) and carbonates of secondary origin (pedogenic carbonates). Some of the rock fragments (lithogenic carbonates) may be present in the silt and clay fractions of soils, and incorrectly considered to be pedogenic carbonates (Eswaran et al., 1995; Mermut et al., 2000).

To enhance the application of current and future models on C fluxes, the size of the inorganic or pedogenic C pool must be estimated more accurately and its dynamics understood more clearly (Legros et al., 1994; IPCC, 1996).

2.1.2 Carbon Fluxes

Soil carbonate accumulation rates vary over time and among localities in response to geographic, geologic, and climatic controls (Machette, 1985). Several attempts have been made to calculate the rate of pedogenic carbonate accumulation during soil development. A simulation model, CALDEP, was developed by Marion et al. (1985) to predict the amount of pedogenic carbonate deposition (mainly as caliche layers) in the soils of the southwestern deserts of the USA. The model assumed that most pedogenic carbonate formed during the Pleistocene under a climate with cool and wet winters. The calculated CaCO_3 deposition rate was 1 to 5 $\text{g m}^{-2} \text{yr}^{-1}$. Calculations included an atmospheric dust input of CaCO_3 of 0.51 $\text{g m}^{-2} \text{yr}^{-1}$. The model also predicted that an increase in rainfall caused an increase in CaCO_3 precipitation.

The ages of calcic horizons in Aridisols of the Mojave Desert were determined using ^{14}C , ^{230}Th and ^{234}U methods, and the rate of pedogenic carbonate formation was

calculated to be between 1.0 to 3.5 g CaCO₃ m⁻² yr⁻¹ (Schlesinger, 1985). The rates calculated by Schlesinger are similar to those calculated using a variety of approaches, as compared in Table 2.1.

Table 2.1 Rates of pedogenic carbonate deposition in the soils of the southwestern deserts of the USA (Schlesinger, 1985).

Location	Rate of Deposition g CaCO ₃ m ⁻² yr ⁻¹	Approach	Reference
Nevada, Mormon Mesa	1.73-10.85	CaCO ₃ content of each layer divided by the estimated time for its formation.	Gardner (1972)
California, Whipple Mountain alluvium	1.0	Chronosequence	McFadden (1982)
Arizona, Avra Valley	3.87- 5.67	CaCO ₃ contents of layers divided by C-14 age.	Buol and Yesilsoy (1964)
New Mexico, Rio Grande Valley	1.0- 12.0	CaCO ₃ contents in soils on alluvial terraces of known age.	Gile et al. (1981)
New Mexico, Rio Grande Valley	2.2- 5.1	CaCO ₃ contents in soils on alluvial terraces of known age	Bachman and Machette (1977)

The C stored in the soil organic matter of terrestrial ecosystems represents the long-term net balance of photosynthesis and total soil respiration, including mainly CO₂ from organic matter decomposition. During soil development, organic matter often shows an initial period of rapid increase for up to 3,000 years, followed by a lower rate of accumulation that may continue for millennia (Birkeland, 1984). The soil, in a sense, is at equilibrium where inputs of C by photosynthesis are more or less balanced by C released as CO₂ as organic matter decomposes. In upland ecosystems, the long-term rate

of C storage varies from $0.2 \text{ g C m}^{-2} \text{ yr}^{-1}$ in some polar deserts to $> 10 \text{ g C m}^{-2} \text{ yr}^{-1}$ in some forests (Schlesinger, 1990). The size of the C pool in soils (3000-10000 year old) developed on Holocene glacial deposits showed that the average accumulation rate of C was about $2.4 \pm 0.7 \text{ g C m}^{-2} \text{ yr}^{-1}$.

Biological processes strongly control the global C cycle over yearly timescales because atmospheric CO_2 consumed during photosynthesis is nearly balanced by CO_2 released during soil respiration (Chadwick et al., 1994). During each photosynthesis-respiration cycle, however, a small amount (2% on average) of C is not returned to the atmosphere, but is held in the living plants or as soil organic matter, leached as dissolved organic matter, or diverted into the inorganic C phase during chemical weathering. Chadwick et al. (1994) estimated the rates of C transfer from the atmosphere to organic and inorganic C in moist temperate grassland and desert scrubland ecosystems in the USA. For the soils of moist grasslands, cumulative conversion of atmospheric CO_2 to bicarbonate increases and begins to level off after a total C transfer of 10 to 15 kg m^{-2} . The long-term C flux decreases from $0.11 \text{ g m}^{-2} \text{ yr}^{-1}$ for relatively recent soil profiles to about $0.06 \text{ g m}^{-2} \text{ yr}^{-1}$ for the oldest profiles. Conversion of atmospheric CO_2 to organic C in grassland soils levels off following cumulative C transfer of about 150 kg m^{-2} after about 120 ky. Initial net C flux into organic matter is about $7.4 \text{ g m}^{-2} \text{ yr}^{-1}$.

For desert scrubland soils, the cumulative mass of carbonate C reaches about 25 kg m^{-2} after 1,700 ky. The gross long-term C flux (not corrected for external carbonate input) ranges from 0.02 to $0.035 \text{ g m}^{-2} \text{ yr}^{-1}$ for recent soils to $0.015 \text{ g m}^{-2} \text{ yr}^{-1}$ for the oldest soil profiles. Cumulative conversion of atmospheric CO_2 to organic C results in

small amounts of C transfer with maximum values of about 7.5 kg m^{-2} . Initial rate of C flux to form soil organic matter is $0.19 \text{ g m}^{-2} \text{ yr}^{-1}$, but in the oldest soil profiles the flux decreases to about $0.005 \text{ g m}^{-2} \text{ yr}^{-1}$. The conversion of CO_2 to pedogenic carbonate become more important as the soil matures, especially in desert scrubland soils (Chadwick et al., 1994).

2.2 CALCIUM CARBONATE IN SOILS

Carbonates are important constituents of many soils, especially those of arid to sub-humid environments. Soil carbonates originate from several sources or combinations of sources, either directly in the form of carbonates, or by solution-precipitation mechanisms (Fig. 2.2). The most common carbonate minerals in the soil are calcite (CaCO_3), Mg-calcite [$\text{Ca}_x\text{Mg}_{1-x}(\text{CO}_3)$], dolomite [$\text{CaMg}(\text{CO}_3)_2$], occasionally aragonite (CaCO_3), and siderite (FeCO_3) (Doner and Lynn, 1989). The formation of siderite is consistent with the conditions of a reducing environment and high CO_2 partial pressure. Calcite is the most abundant carbonate species in the soil (Salomon and Mook, 1976).

2.2.1 Common Sources of Soil Carbonate

1) Parent material. The most direct source of soil carbonates is inheritance from the parent material. The principal requirement for retaining lithogenic or parent material carbonates in soil is insufficient leaching (low intensity or short time) to remove carbonate from the solum (Doner and Lynn, 1989). The provenance of the carbonates in most soils is ancient marine carbonate rocks. Glacial erosion of calcareous rocks,

especially the dolomitic limestone of east-central Saskatchewan, is the source of most CaCO_3 in the glacial drift parent materials of the province. Carbonate contents were found to be highest in the eastern section (25%) of the Saskatchewan and lowest (10%) in those areas in which the glacial deposits are thin and overlie non-calcareous bedrock, although in local areas some values may fall below or above this range (St. Arnaud, 1976).

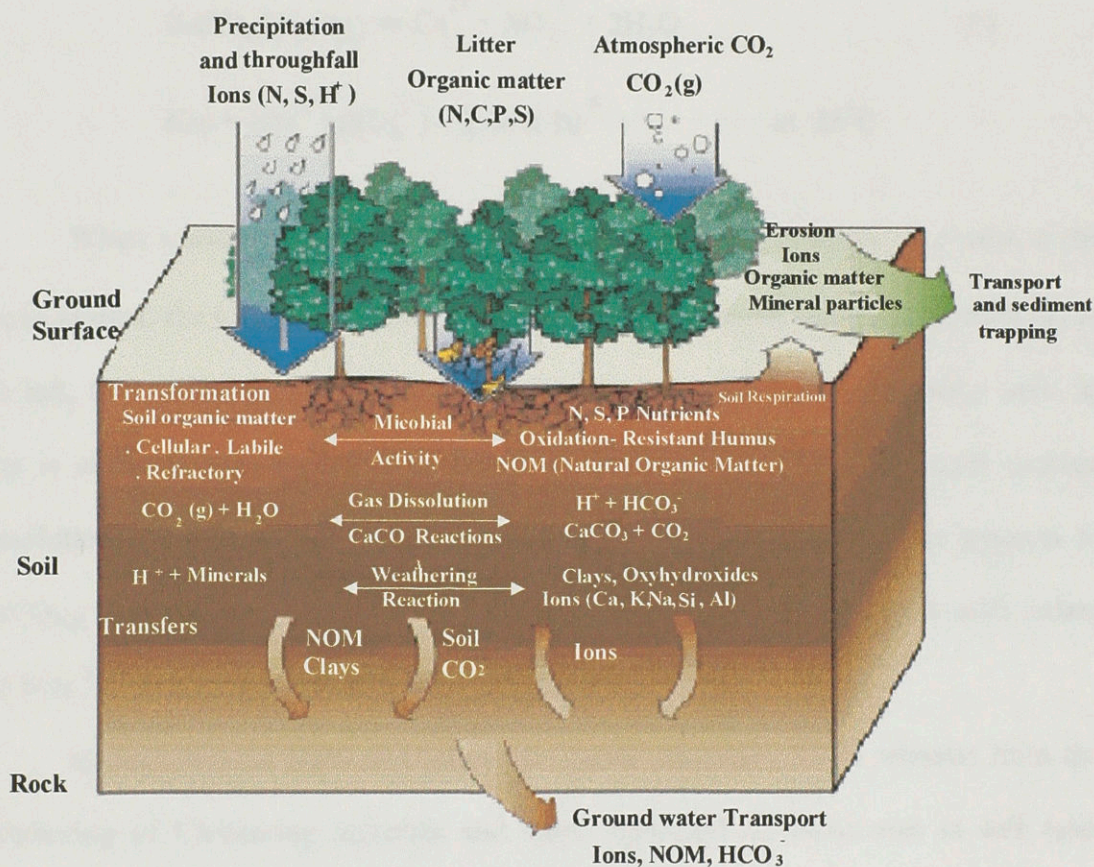


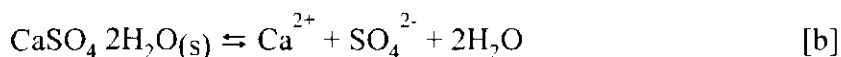
Figure 2.2 The dynamics of carbon transformation and transport in the soil (United States Department of Energy, 2002).

2) Dissolution of Ca-bearing minerals. The common source of Ca for CaCO_3 formation is dissolution of easily soluble minerals such as gypsum and calcite/dolomite, or easily weathered minerals such as anorthite (Ca-feldspar) within the immediate soil (Doner

and Lynn, 1989). Through the common ion effect, all of the gypsum in a particular system may be converted to $\text{CaCO}_{3(s)}$ in the presence of excess CO_3^{2-} in soil solution (Berigari and Al-Any, 1994) as indicated in the following reactions:



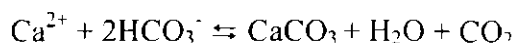
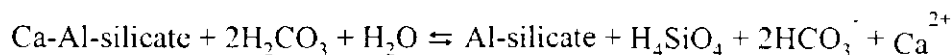
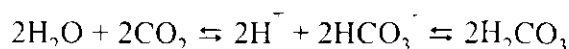
$$K_{\text{sp}} = (\text{Ca}^{2+})(\text{CO}_3^{2-}) = 5.03 \times 10^{-9} \quad \text{at } 25^\circ\text{C}$$



$$K_{\text{sp}} = (\text{Ca}^{2+})(\text{SO}_4^{2-}) = 2.44 \times 10^{-5} \quad \text{at } 25^\circ\text{C}$$

When a water-soluble carbonate salt such as Na_2CO_3 is added in excess to the above system, the CO_3^{2-} in solution increases instantly causing a shift in reaction [a] to the left, thus reducing the Ca^{2+} concentration through $\text{CaCO}_{3(s)}$ precipitation until its K_{sp} is attained. This reduction in Ca^{2+} will drive reaction [b] to the right causing dissolution of gypsum. The net effect is total conversion of the Ca^{2+} in gypsum to $\text{CaCO}_{3(s)}$ (Berigari and Al-Any, 1994). Gypsum is too soluble to persist in soils unless the SO_4^{2-} concentration approaches 10^{-2} M (Lindsay, 1979).

In soils derived from non-carbonatic parent materials, Ca is released from the weathering of Ca-bearing minerals and when deposited as carbonates in soil must represent a sink for C from the atmosphere. The major portion of bicarbonate and ultimately carbonate for calcite precipitation may be supplied by CO_2 from plant respiration or the decomposition of organic residues (Roy et al., 1969; Smith and Drever, 1976).



3) Biocycling by plants. Plants take up Ca from deeper horizons and return it to the surface horizons in plant litter. Calcium released as plant residues decompose react with CO_2 in the soil to form $\text{Ca}(\text{HCO}_3)_2$ and ultimately CaCO_3 . The origin of secondary calcite in the surface horizons of some Rego Black Chernozem soils may be at least partly related to the ability of poplar (*Populus sp.*) to cycle Ca from the subsoil (Fuller et al., 1999). High concentrations of soluble Ca in the litter horizon of a Rego Black Chernozem soil suggest that Ca is being returned to the surface from a source at depth, then reacting to form pedogenic carbonate.

4) Wind deposition. Carbonate materials may be suspended in air, transported some distance and then deposited on the surface as dust. Subsequent reaction within the soil by solution and precipitation is possible. Gile et al. (1966) reported that calcareous dust has been deposited in all surfaces of the desert and desert grasslands adjacent to the Rio Grande of southern New Mexico. The dust added to the surface was partly dissolved by rainfall, with the Ca entering the soil to react and form CaCO_3 .

5) Rain. Calcium ions enter the soil in rainwater and subsequently combine with HCO_3^- and precipitate as CaCO_3 (Rabenhorst et al., 1984a). The Ca^{2+} in precipitation is considered to contribute much more to the pedogenic carbonate than does the carbonate in the dry dust, perhaps by a factor of two to three. Wolaver and Leith (1972) reported

that, in the central part of the USA (from Arkansas to southern Michigan and Wisconsin), between 2000 to 3400 mg m⁻² yr⁻¹ of Ca²⁺ is added in rainfall, whereas eastern Montana, with much less rain, receives less than 250 mg m⁻² yr⁻¹ of Ca²⁺.

6) Surface water. Natural surface water or irrigation water can contain Ca that reacts with H₂CO₃ and precipitates as CaCO₃ (Doner and Lynn, 1989).

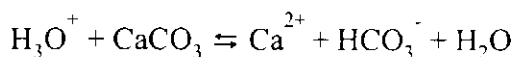
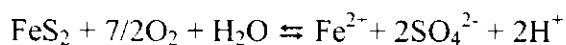
7) Ground water. Ground water may move through carbonate-containing soils or strata and bring either Ca²⁺ or HCO₃⁻ ions into the soil, where they combine to form CaCO₃ when the soil dries or its temperature rises (Sobecki and Wilding, 1983).

2.2.2 Dissolution and Precipitation of Calcium Carbonate

The dissolution and precipitation of carbonates during soil development are strongly influenced by two factors: Geological C released as CO₂ upon dissolution of lithogenic carbonate and dolomite within the solum, and the CO₂ from respiration within the zone of maximum root concentration and microbial activity. Generally the HCO₃⁻, Ca²⁺ and Mg²⁺ ions are leached downward and precipitate as calcite in the subsoil. The calcite precipitate is poorly crystalline initially, recrystallizing later to form larger crystals (Hallet, 1976; Ducloux et al., 1984). Most of the pedogenic carbonates in the soil matrix are in the size range of clay and fine silt, unless present as coatings on larger grains. Wang (1997) study shows that most of the pedogenic carbonate in medium and coarse silt size fractions form coatings on particles.

Dissolution of carbonates in soils is caused mainly by the action of biogenic CO₂ derived from decaying organic matter and root respiration (Salomon and Mook,

1976). Salt marsh sediments generally contain large amounts of sulfides, the oxidation of which release sulfuric acid (Brummer et al., 1976). This also may cause dissolution of the carbonates according to the following reaction (Salomon and Mook, 1976):

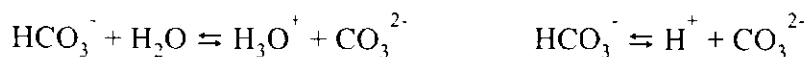
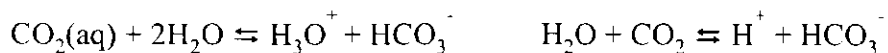
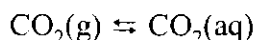


Pedogenic carbonate commonly forms in soils of arid and semi-arid regions. Carbonate precipitation is particularly active in areas of carbonate-rich materials. Carbonate species differing from those of the parent material, for example CO_2 derived from biogenic activity and characterized by a different and recognizable isotopic markers, can contribute to this precipitation (Magaritz et al., 1981; Cerling, 1984; Cerling et al., 1991).

Precipitation of carbonates is favored by either of two processes:

- i) movement of the soil solution toward an environment with a lower partial pressure of CO_2 ; or
- ii) evaporation of the soil solution.

The chemical reactions involved in the inorganic dissolution and precipitation of carbonates are (Salomon and Mook, 1976):



Furthermore, calcite may precipitate due to an increase in temperature of the solution because of an increase in ionic activity, or due to a change in the soil solution composition during freezing of the soil. Microbial action may well play an important role in pedogenic carbonate formation (Schlesinger, 1984; Cerling and Quade, 1993). It is recognized that precipitation of carbonates at depth is due to a lower CO₂ partial pressure below the zone of rooting and major biological activity, and to concentration effects resulting from leaching and water loss by evapotranspiration (Birkeland, 1974).

2.2.3 Carbonate Pendants and Pedogenic Carbonate

Calcium carbonate occurs in soils as particles, as coatings on mineral grains, or in the form of bridges between grains. Secondary carbonates on the lower surface of pebbles and cobbles form carbonate pendants. Pendants represent almost pure pedogenic carbonate formed in an environment that contains lithogenic carbonate minerals. A complex, layered structure has been observed in pendants, a probable result of sequential deposition and recrystallization (Rabenhorst et al., 1984b; Chadwick et al., 1988; Black and Fosberg, 1990).

The surface morphologies of carbonate pendants and lithogenic carbonate pebbles have different features. Pedogenic carbonates occur in the form of microscopic calcite crystals are strongly clustered, with individual crystal sizes ranging from about 0.1-mm to crystal clusters of 3-mm diameter. Depending on soil matrix composition microsparite, sparite and micritic fabric can form (Wieder and Yaalon, 1974; 1982). Polymorphic crystals are mostly displayed as layers that form a compact and layered structure.

As the pendants consist of almost pure pedogenic carbonate, their $\delta^{13}\text{C}$ values will reflect the long-term average $\delta^{13}\text{C}$ value of the soil CO_2 . The pure form of pedogenic carbonate (pendant) is commonly used to establish the C isotope fractionation factor between organic and inorganic form, important to the calculation of the pedogenic carbonate content in soils in Canadian prairies (Wang and Anderson, 1998).

Secondary carbonates contain relatively young C derived from the decomposition of organic matter in comparison to the ancient C of lithogenic carbonates. This is reflected in the average radiocarbon age of clay-sized carbonates ($1,595 \pm 115$ to $3,750 \pm 125$ yr) as compared to the age of primary carbonates that dominate the sand and coarse silt fractions ($> 31,690$ yr) (St. Arnaud, 1979). Carbon dating of pendant carbonates (3,500 yr) from Saskatchewan showed that they are clearly pedogenic due to their young age and $\delta^{13}\text{C}$ values, and that the C is derived from organic matter (Heck, 1989).

The $\delta^{13}\text{C}$ values of pendants decrease with depth in Calcareous Black soils (Oxbow Association) and Orthic Dark Brown soils (Biggar and Amulet Associations) (Wang and Anderson, 1998). The $\delta^{13}\text{C}$ of the pedogenic carbonate are (averaged for all pendants in the profile) -8.0‰, -5.60‰, and -5.80‰ for Oxbow (Black), Biggar (Dark Brown), and Amulet (Dark Brown) associations, respectively. Penetration of atmospheric CO_2 ($\delta^{13}\text{C}$ of -7.8‰) into the upper profile would result in heavier $\delta^{13}\text{C}$ values in the upper 25 to 30 cm, becoming progressively more negative with depth. The $\delta^{13}\text{C}$ values of pedogenic carbonate in pendants are controlled largely by the isotopic

composition of the soil organic matter (Kelly et al., 1991; Wang et al., 1993; Humphrey and Reid Ferring, 1994). The larger $\delta^{13}\text{C}$ values for Dark Brown than Black soils reported by Wang and Anderson (1998) are consistent with more C_4 vegetation in the former.

2.2.4 Magnesium-Bearing Calcite

The presence of Mg-bearing calcite in secondary carbonates is associated with soluble $\text{Mg}^{2+} / \text{Ca}^{2+}$ ratios of one or greater in the soil solution attendant or underlying layers. The dissolution of both calcite and dolomite within the solum and the precipitation of calcite in the carbonate accumulation zone (calcic horizon) leads to a build up of Mg^{2+} in the solution. If the depth of leaching is below the calcic horizon, secondary calcite is Mg-free. Where leaching is restricted to relatively shallow depths, the buildup of soluble salts and higher $\text{Mg}^{2+} / \text{Ca}^{2+}$ ratios create conditions for the precipitation of Mg-bearing calcite (St. Arnaud, 1979). Breazeale and Smith (1930) reported that the secondary carbonates in caliche or petrocalcic horizons have low magnesium contents even though the parent material may have contained dolomite or other Mg-bearing minerals.

2.3 ORGANIC MATTER

The term soil organic matter refers to the whole of the organic material in soils including litter, light fraction, microbial biomass, water-soluble organics, and stabilized organic matter or humus. Organic matter often has been partitioned into two major pools

active (labile) and stable. Included in the active pool is comminutive plant litter, the light fraction, the biomass, and non-humic substances not bound to mineral constituents. The stable fraction, which is more resistant to further decomposition, functions as a reservoir of plant nutrients and is important from the long-term balance of the soil (Stevenson, 1994).

The type, content, and extent of aggregation of clay is a major factor affecting SOM dynamics (Paul, 1984). Clay protection of humus may act to enhance storage of C, by slowing the decomposition of labile, energy and nutrient-rich substrate; and may slow down the processes that result in highly humified humic materials of limited biological importance (Anderson, 1995).

Organic matter associated with fine clay is of high molecular weight, largely aliphatic and rich in nutrients, whereas the material associated with coarse clay was much older and dominated by more strongly condensed, aromatic constituents (Anderson and Paul, 1984). The protection of these readily degradable substrates, including proteinacious materials and polysaccharides, makes clay-adsorbed materials an important contributor to the dynamics of material with an intermediate turnover time.

Changes in the soil environment influence both the quantity and qualitative characteristics of the soil organic matter. The organic matter of dry soils, where biological activity is repressed by drought, is characteristically made up humic materials with comparatively high proportions of fulvic acids, with minimal condensation of aromatic structures, and high contents of easily mineralized nutrient components (Volkovintser, 1969; Anderson et al., 1974). In more moist regimes, increasing moisture results in greater organic inputs, enhanced biological activity, and more organic matter. The proportion of weakly decomposed residues decreases, and the relative amount of organic matter with large and

complex molecules with strongly condensed aromatic structures (humic acids) increases in moving from Brown to Black soils (Anderson, 1987).

To understand ecosystem functioning, solid knowledge of the actual amount of C that circulates within the system is needed. It requires an estimate of C gain, distribution, and losses during a given period of time in order to calculate the net production and, therefore, the actual amount of material allocated at each trophic level (Warembourg and Kummerow, 1991).

It is beyond human capability to directly monitor the C pool of any soil during its development. There are two general methods to determine rates of soil C accumulation and cycling: i) the "chronosequence", which measures soil organic C (SOC) stores in soils of different ages but similar environment and parent material. With this method it is possible to calculate empirical rates of C sequestration after geological or anthropogenic disturbances ii) a "mass balance", in which C cycling rates are inferred for soils near or at steady state. This method provides data to help constrain soil responses to perturbations, such as climate change or cultivation. There are two approaches for the mass balance measurement. The first is a single-pool approach, in which measurements of total soil C storage and estimates of C loss and input rates are made via photosynthesis and respiration measurements. The second is a multiple-pool approach, in which C dating provides estimates of decomposition rates and C inputs (Amundson, 2001).

2.4 STABLE ISOTOPE GEOCHEMISTRY OF CARBONATE AND ORGANIC MATTER

The stable isotope method, used in many geological, biological and pedological studies, is based on the small difference in physico-chemical behavior between measurable isotopes of H, C, O, and S (Magaritz and Ameil, 1980). Stable isotope ratios of elements in both organic and inorganic components of nature record and integrate information relating to the kinds of processes that formed them, the rates of the processes, and the environmental conditions prevailing at the time. A wealth of environmental and ecological information can often be obtained from stable isotope analyses (Boutton, 1996). In this section the distribution and fractionation of C and O isotopes in organic matter and carbonate in natural environments and soil system will be reviewed. Carbon has two stable isotopes, ^{12}C and ^{13}C , with relative abundances of 98.89% and 1.11% (Boutton, 1991). Oxygen has three stable isotopes, ^{16}O , ^{17}O , and ^{18}O , with average abundances of 99.763%, 0.037%, and 0.199%, respectively (Hoefs, 1997).

2.4.1 Carbon Isotope of Soil Carbonate

The isotopic composition of pedogenic carbonates reflects the isotopic composition of the soil CO_2 , which is usually different from that of the existing vegetation and free atmosphere (Cerling, 1984). The main sources of soil CO_2 are root respiration and the decomposition of organic matter, with the relative importance of each source varying over the course of the season (Buyanovsky and Wagner, 1983). In humid and sub-humid regions, where soils are covered by relatively dense vegetation,

little atmospheric CO_2 enters the soil, and the carbonate that may form reflects the relative abundance of C_3 and C_4 plants (Cerling, 1984; Cerling and Hay, 1986). In more arid regions with sparse, discontinuous vegetative cover, the $\delta^{13}\text{C}$ values of the soil may be influenced by the atmosphere above the soil, resulting in higher $\delta^{13}\text{C}$ values for pedogenic carbonates particularly near the soil surface. When plant density increases, the $\delta^{13}\text{C}$ value of pedogenic carbonate becomes smaller and less affected by atmospheric CO_2 and vice versa (Amundson et al., 1988).

In humid regions, assuming half of the CO_2 comes from parent carbonate with $\delta^{13}\text{C}$ of about 0‰ (marine limestone), reacting with soil CO_2 with $\delta^{13}\text{C}$ of -24‰ will yield bicarbonate with $\delta^{13}\text{C}$ of -12‰. In an open system, continuous exchange occurs between the dissolved bicarbonate and CO_2 which causes the $\delta^{13}\text{C}$ (HCO_3^-) values to become more negative ($\delta^{13}\text{C}$ value reaches to -16‰ at 25 °C) (Magaritz and Amiel, 1980).

The soil atmosphere commonly has a much higher CO_2 contribution than the bulk atmosphere (Amundson, 1989). Cerling (1984) postulated that the isotopic composition of pedogenic carbonate will be controlled by the isotopic composition of the soil CO_2 . The inheritance of parent material $\delta^{13}\text{C}$ values through dissolution of carbonates is insignificant because the rate of new soil carbonate (pedogenic carbonate) accumulation is small (10^{-7} to 10^{-6} moles $\text{m}^{-2} \text{hr}^{-1}$) compared to the CO_2 respired from biogenic sources (10^{-3} to 10^{-5} moles $\text{m}^{-2} \text{hr}^{-1}$). Soil respiration rates for grassland soils during the growing season are typically 6×10^{-3} to 9×10^{-3} moles $\text{m}^{-2} \text{hr}^{-1}$, decreasing to

about $1 \times 10^{-3} \text{ moles m}^{-2} \text{ hr}^{-1}$ during the dry or cool non-growing season (Singh and Gupta, 1977; Schlesinger, 1977; Parker et al., 1983). The respiration rate may drop to almost zero during periods of soil freezing (Kucera et al., 1971).

The CO_2 produced in the soil by respiration is transported, primarily by diffusion, to the overlying atmosphere. The combination of the processes of respiration and diffusion determines the shape of the CO_2 profile in the soil (de Jong and Schappert, 1972). The C isotopic composition of soil CO_2 is a function of the soil respiration rate and soil depth (Mermut et al., 2000). The changes in $\delta^{13}\text{C}$ values of CO_2 are more rapid near the soil surface, and at depth tend to reach a constant level, especially with higher respiration rates (Fig. 2.3).

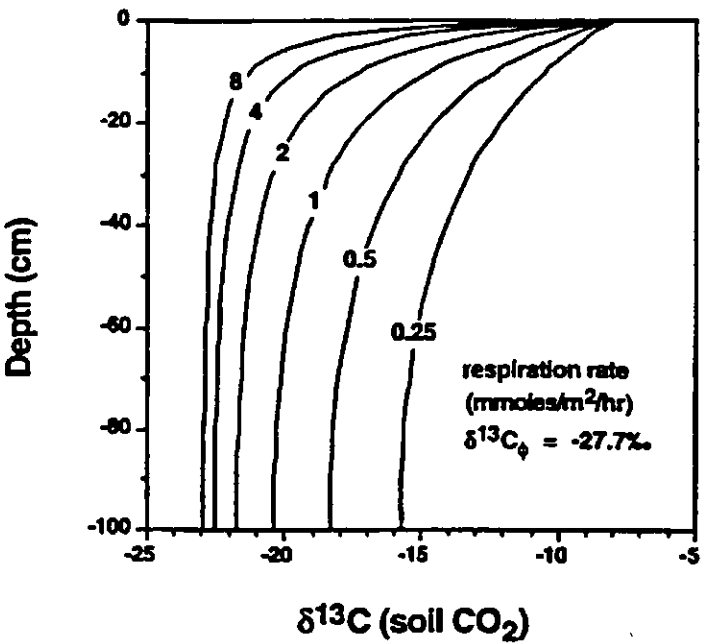


Figure 2.3 Carbon isotope composition of soil CO_2 and soil respired CO_2 for soils in North America (Cerling and Quade, 1993).

Values for respiration between $5 \text{ to } 10 \text{ mmol m}^{-2} \text{ y}^{-1}$ are typical for temperate and montane regions and values between $0.5 \text{ and } 2 \text{ mmol m}^{-2} \text{ y}^{-1}$ were measured in desert

regions (Solomon and Cerling, 1987; Quade et al., 1989a). The steady state condition for CO_2 in soil can be calculated assuming that the net soil respiration (Q) be distributed equally over some distance (L), so that the rate of CO_2 production is $\Phi = Q/L$ (Cerling, 1984).

2.4.2 Oxygen Isotope of Soil Carbonate

The H_2O of the soil solution is an infinitely large O reservoir relative to the O bound in dissolved C species. For example, the flux of water in a soil receiving 50 cm of rain per year is $2.8 \text{ moles cm}^{-2} \text{ y}^{-1}$, however typical biogenic CO_2 from grassland soils are on the order of $5 \times 10^{-3} \text{ moles cm}^{-2} \text{ y}^{-1}$ (Schlesinger, 1977; Singh and Gupta 1997). As a result of hydration-dehydration reactions, H_2O controls the O isotope composition of the O in CO_3^{2-} and the CaCO_3 that precipitates (Amundson, 1989). Cerling (1984) found a good correlation between the O isotopic composition of meteoric water and that of modern soil carbonate (Fig. 2.4). The $\delta^{18}\text{O}$ of soil carbonate, when preserved without diagenetic modification in the geologic record, should be a good indicator of the composition and source of past meteoric water.

The $\delta^{18}\text{O}$ of pedogenic CaCO_3 reflects that of the soil which, in the absence of ground water, is derived from atmospheric water (Cerling, 1984; Amundson and Lund, 1987). The isotopic composition of soil water can be significantly different than average local meteoric water (Mermut et al., 2000). In arid and semi-arid regions, however, the $\delta^{18}\text{O}$ value of soil water may be greater than those of precipitation due to evaporation, which preferentially enriches the remaining soil water in ^{18}O (Alison and Hughes, 1983).

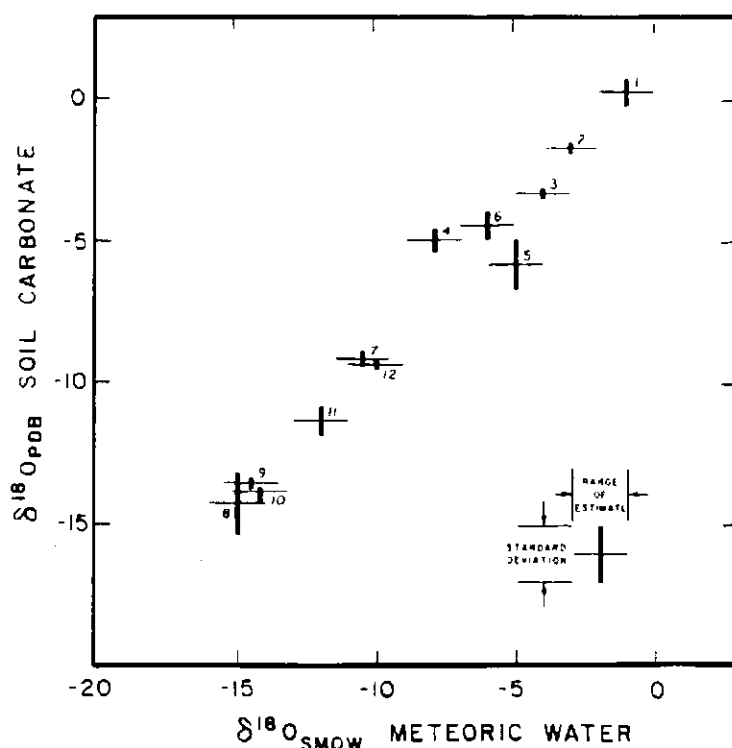


Figure 2.4 Oxygen isotopic composition of modern soil carbonates from Africa (1, 2, 3), North America (6, 7, 8, 9, 10, 11, 12) and Europe (4, 5) plotted against the estimated isotopic composition of meteoric water (Cerling, 1984).

The $\delta^{18}\text{O}$ values of carbonates in minerals of Cca and Ck horizons from Alberta soils were -13.1 and -12.0‰, respectively (Miller et al., 1987). This observation is consistent with the findings of Salomons and Mook (1976), who reported that soil carbonate minerals generally have more negative $\delta^{18}\text{O}$ values than lithogenic carbonate minerals. The formation of soil carbonates enriched in ^{18}O will occur mainly during periods of reduced rainfall when mineral precipitation is driven by evaporation and evapotranspiration, and by CO_2 losses from the soil solution. Hendy (1971), in a study of calcium carbonate precipitation from solutions seeping into limestone caves, mentioned that when loss of CO_2 is rapid, a kinetic fractionation will occur between

HCO_3^- and $\text{CO}_2(\text{aq})$ and the calcite precipitated will show a simultaneous enrichment in ^{13}C and ^{18}O .

Schlesinger (1985) found a significant positive correlation between the $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios from the calcic horizons in Eagle Mountain of the USA (Fig. 2.5). The correlation may result from a seasonal climatic pattern that affects both soil $P(\text{CO}_2)$ and soil water in a open system that allows isotopic fractionations while water HCO_3^- remains in equilibrium with soil CO_2 during the precipitation of CaCO_3 (Rabenhorst et al., 1984b).

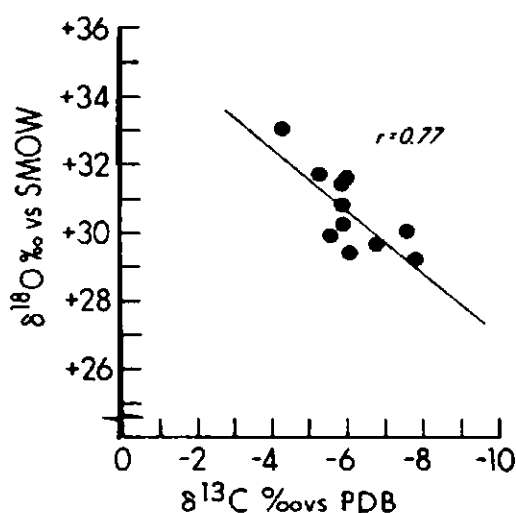


Figure 2.5 Relationship between $\delta^{18}\text{O}$ (‰ vs. SMOW) and $\delta^{13}\text{C}$ (‰ vs. PDB) for calcic horizons of the Eagle Mountain soils (Schlesinger, 1985).

The most active root growth and soil respiration are expected following seasonal rains that occur during winter in the present climate of the Mojave Desert (Schlesinger, 1985). Pedogenic carbonate may precipitate as water evaporates from the soil during a subsequent period of drought, enriching the remaining soil water in ^{18}O as soil $P(\text{CO}_2)$

decreases because of plant dormancy. As the supply of CO₂ from root respiration and organic matter decomposition decreases, there is an increase in the relative influence of the atmosphere, which has lower concentration of CO₂ and a higher $\delta^{13}\text{C}$ value.

2.4.3 Carbon and Oxygen Isotopic Fractionation in Carbonates

The alteration in isotope abundances is termed “stable isotope fractionation”. The main phenomena producing isotope fractionation are: 1) isotope exchange reactions, which there is no net reaction, but in which the isotope distribution changes between different substances, between different phases, or between individual molecules, 2) kinetic process, which are associated with incomplete and unidirectional processes such as evaporation, dissociation reactions, biologically mediated reactions, and diffusion (Hoefs, 1997). The fractionation factor (α) is defined as the ratio of the numbers of any two isotopes in one chemical compound A divided by the corresponding ratio for another chemical compound B:

$$\alpha_{A-B} = R_A/R_B \quad [2.1]$$

For the two compounds A and B, the δ -values and fraction factor α are related by:

$$\delta_A - \delta_B = \Delta_{A-B} \sim 10^3 \ln \alpha_{A-B} \quad [2.2]$$

The isotopic fractionation between the carbonate minerals and the main reservoirs of O and C are important factors that determine the isotopic composition of pedogenic carbonate (Salomons and Mook, 1976). Under equilibrium conditions, the degree of isotope fractionation depends on the temperature only. The fractionation of O and C decreases with increase in temperature (Table 2.2, Table 2.3) (Salomons and Mook, 1986).

Knowledge of the magnitude of isotope fractionation is essential for the interpretation of isotopic variations of C and O in natural calcium carbonate (Emrich et al., 1970). At equilibrium, the isotopic equilibrium factor $10^3 \ln \alpha_{\text{CO}_2\text{-calcite}}$ varies between -12.4‰ to -9.8‰ for the temperature range between 0 and 25°C (Denis et al., 1974). The ^{13}C enrichment between CaCO_3 and $\text{CO}_2(\text{g})$ at 0°C, 10°C, and 25°C are reflected in $\delta^{13}\text{C}$ values of 11.4‰, 10.8‰, and 9.9‰, respectively.

Table 2.2 Isotope fractionation (in ‰) for carbon in the system $\text{CO}_{2\text{g}}$, $\text{CO}_{2\text{aq}}$, HCO_3^- , CO_3^{2-} , CaCO_3 (Salomons and Mook, 1986).

t (°C)	$\epsilon^{13}\text{HCO}_3^-$ ($\text{CO}_{2\text{g}}$) ^a	$\epsilon^{13}\text{CO}_{2\text{g}}$ ($\text{CO}_{2\text{aq}}$) ^b	$\epsilon^{13}\text{HCO}_3^-$ ($\text{CO}_{2\text{aq}}$) ^c	$\epsilon^{13}\text{HCO}_3^-(\text{CaCO}_3)$ ^d
5	-10.20	-1.15	-11.35	-0.11
15	-9.02	-1.15	-10.12	+0.41
25	-7.92	-1.08	-8.97	+0.91
35	-6.88	-1.02	-7.90	+1.37

^a Mook et al. (1974).

^b Vogel et al. (1970).

^c From Mook et al. (1974); Vogel et al. (1970).

^d According to Salomons et al., (1976). Evaluation of the original data by Emrich et al. (1970); Robinson and Clayton (1969).

Table 2.3 Oxygen isotope fractionation (in ‰) in the system H_2O - CaCO_3 (Salomons and Mook, 1986).

t (°C)	$\epsilon^{18}\text{H}_2\text{O}_{\text{liq}}$ ($\text{H}_2\text{O}_{\text{vap}}$) ^a	$\epsilon^{18}\text{H}_2\text{O}$ (CaCO_3) ^b
5	-11.09	+2.67
15	-10.17	+0.33
25	-9.32	-1.85
35	-8.51	-3.89

^a Majoube (1971)

^b Epstein (1976) (equilibrium refers to CO_2 from CaCO_3 by H_3PO_4 and CO_2 in equilibrium with H_2O at 25 °C).

The isotope fractionation occurs between $\text{CO}_2(g)$ and the inorganic species in the soil solution. According to Romanek et al. (1992), isotopic fractionation between soil CO_2 and pedogenic carbonate results in a temperature-dependent enrichment of ^{13}C in the carbonate phase of about 12‰ at 0°C , and 9‰ at 25°C .

The $\delta^{18}\text{O}$ value of water can not be affected by diffusion fractionation. A large fractionation for ^{18}O is to be expected, however, if the surface water or water near the soil surface is subject to evaporation (Salomons and Mook, 1986). The formation of carbonates enriched in $\delta^{18}\text{O}$ occurs mainly during dry periods when mineral precipitation is driven by evaporation, evapotranspiration, and by CO_2 losses from the soil solution, for example through plant uptake (Bellance and Neri, 1993).

2.4.4 Stable Isotopes of Organic Carbon

The natural stable C isotope ratio ($^{13}\text{C}/^{12}\text{C}$) of soil organic matter contains information regarding the relative proportion of plant species with the C_3 (low $^{13}\text{C}/^{12}\text{C}$ ratios) and C_4 (high $^{13}\text{C}/^{12}\text{C}$ ratios) pathways of photosynthesis in plant communities, and their relative contribution to net primary productivity through time (Boutton, 1996). Organic matter at any depth should closely reflect the relative contribution of organic matter from C_3 and C_4 plants. Where vegetation has been comparatively uniform over time, the $\delta^{13}\text{C}$ values of the organic matter may be consistent with the proportion of C_3 and C_4 plants in the present vegetation (Kelly et al., 1991).

Plants with a C_3 pathway of photosynthesis reduce CO_2 to phosphoglycerate, a 3-C compound, via the enzyme RuBP carboxylase. This enzyme discriminates against $^{13}CO_2$, resulting in relatively low $\delta^{13}C$ values for C_3 plants. Plants with C_3 pathway (most temperate region terrestrial plants) have $\delta^{13}C$ values in the range of -21 to -32‰ with a mean value of -27‰ (Fig. 2.6).

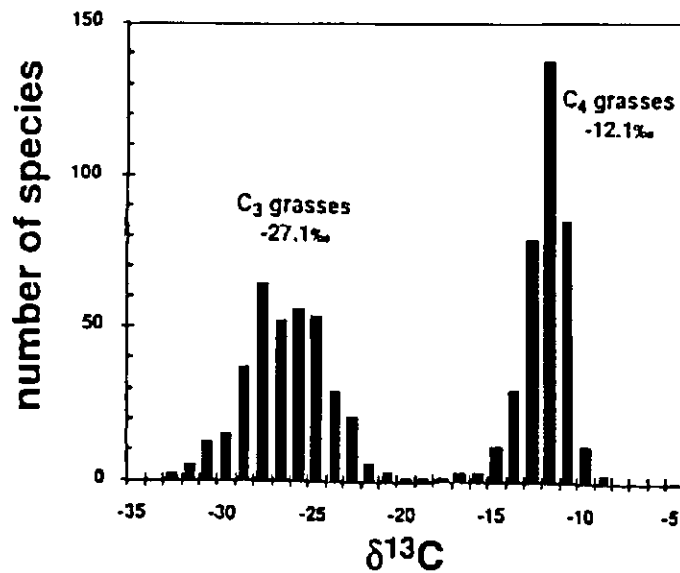


Figure 2.6 $\delta^{13}C$ Values for C_3 and C_4 grasses (Cerling and Quade, 1993).

C_4 plants reduce CO_2 to aspartic or malic acid, both 4-C compounds, via the enzyme PEP carboxylase. This enzyme does not discriminate ^{13}C as strongly as RuBP carboxylase does, so that C_4 plants (many arid plants, salt marsh species, and some tropical grasses) have comparatively high $\delta^{13}C$ values. Values for C_4 plants range from of -9 to -17‰, with a mean of about -13‰. Plants with the Crassulacean acid

metabolism (CAM) pathway are intermediate with $\delta^{13}\text{C}$ values, ranging from -9‰ to -19‰ with a mean value of -17‰ (Hoefs, 1980; Cerling, 1984).

The isotopic composition of soil organic matter determines the isotopic composition of pedogenic carbonate in soils where rates of decomposition are rapid, and where diffusion dominates mass transport (Cerling, 1984; Cerling et al., 1989; Quad et al., 1989; Cerling and Quad 1993). The diffusion gradient of soil CO_2 is on the order of $10^{-2} \text{ cm}^{-2} \text{ s}^{-1}$, whereas biodiffusion coefficient are on the order of $10^{-7} \text{ cm}^{-2} \text{ s}^{-1}$ (Tsai, 1989). The influence of organic matter on the ^{13}C content of the soil atmosphere is strongest at depth, whereas surface horizons may be affected by the diffusion of atmospheric CO_2 into the soil (Cerling and Wang, 1996).

The limited number of $\delta^{13}\text{C}$ values for organic matter in the Canadian prairies range from -25.5‰ to -21.3‰, with the more positive values typical of soils in southern regions, or on warmer slopes where C_4 plants have been represented more fully in the ecosystem (Anderson and Paul, 1984; Wang and Anderson, 1998).

2.4.5 Using Stable Isotopes to Calculate Pedogenic Carbonate in Soil

The C isotope geochemistry technique is used to distinguish between pedogenic and inherited carbonate (Magaritz and Amiel, 1980). The basis of this technique is that C in the lithogenic carbonate has significantly different isotopic composition than carbonates formed by pedogenesis.

Carbon isotopic ratios are given as relative deviation in per mil from the isotope ratio in the PDB (Specimen of *Belemnite americana* found in the Pee Dee formation of South Carolina) standard (Craig, 1957; Salomons and Mook, 1976). Since PDB has been exhausted, most of the researchers now report $\delta^{13}\text{C}$ values relative to Vienna Pee Dee Belemnite (VPDB).

$$\delta \text{‰} = [(R_s - R_{\text{std}})/R_{\text{std}}] \times 1000 \quad [2.3]$$

where R_s is the isotopic ratio for an element in a compound and R_{std} is the corresponding isotope ratio in a standard.

The difference between $\delta^{13}\text{C}$ values of parent material carbonate and pedogenic carbonate can be used as an indicator of dissolution-precipitation process taking place in soil horizons (Magaritz and Aneil, 1980). The amount of newly formed carbonates can be calculated from the C isotopic composition (Salomons and Mook, 1976):

$$\% \text{ Pedogenic carbonate} = \frac{\delta^{13}\text{C}(\text{soil}) - \delta^{13}\text{C}(\text{pm})}{\delta^{13}\text{C}(\text{new}) - \delta^{13}\text{C}(\text{pm})} \times 100 \quad [2.4]$$

where $\delta^{13}\text{C}(\text{soil})$, $\delta^{13}\text{C}(\text{pm})$, $\delta^{13}\text{C}(\text{new})$ represent the stable C isotopic composition of the carbonate in the bulk soil, parent material, and the pure pedogenic carbonate.

Stable isotope ratios of $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ are used to study carbonate dissolution, transportation and precipitation processes and rates (Amundson and Lund, 1987). Stable C and O isotopes in soil carbonate provide an additional record of past environments that include shifts in vegetation, climate, and atmospheric circulation (Cerling, 1984; Quade et al. 1989; Amundson et al. 1996). As a result, studies of

carbonate isotope chemistry have become an important component of paleoecology and global change research (Cerling and Quade, 1993). A summary of natural distribution of stable C isotopes ($^{13}\text{C}/^{12}\text{C}$) in major components of terrestrial environment (Fig. 2.7) shows substantial variation in the ratio of these two isotopes, which is important to trace and to quantify sources, sinks, and flux rates within the C cycle (Boutton, 1991; 1996).

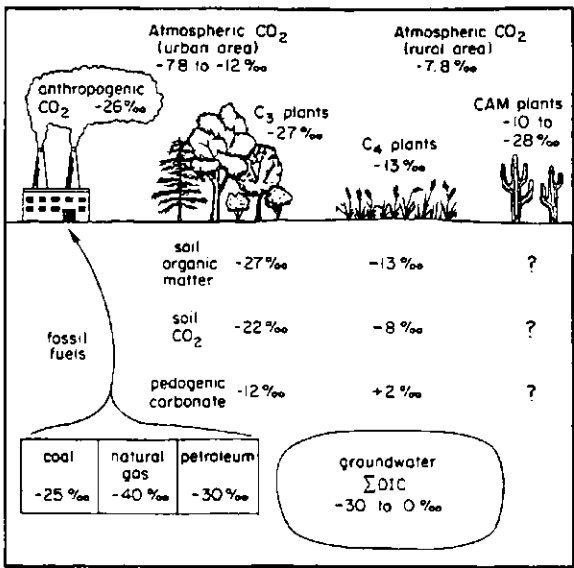


Figure 2.7 Stable C isotope ratios of major components of the terrestrial environment (Boutton, 1991).

2.5 REGO BLACK CHERNOZEM SOILS

In modern soil surveys, most “Wooded Calcareous” soils are classified as Rego Dark Gray or Calcareous Dark Gray Chernozems, sometimes as Rego Black soils (Soil Classification Working Group, 1998). Wooded Calcareous soils occur mainly on

extensive lowlands such as the Debden, Shellbrook and the Saskatchewan lowlands. A typical area is the Weirdale Plain, just to the northeast of Prince Albert (Mitchell et al., 1950).

Rego Black Chernozem soils may occur adjacent to Orthic Black soils under grassland, but they are typically under poplar forest (Fuller et al., 1999). These soils were first described by Mitchell et al. (1950) as having formed on calcareous deposits under a wooded to peat land vegetation. The Rego Black Chernozem soils have only limited indication of typical Chernozomic soil development. Their profile usually consists of Ahk, AC, Csca, and Ck horizons. In general they are somewhat lower in organic matter than comparable Black soils; they are only slightly leached as compared to Degraded Black soils (Dark Gray Chernozomic).

CHAPTER 3

3. SOIL DEVELOPMENT, ORGANIC C STORAGE AND STABLE ISOTOPE COMPOSITION ALONG A GRASSLAND TO FOREST ENVIRONMENTAL GRADIENT IN SASKATCHEWAN

3.1 INTRODUCTION

In arid and semiarid regions, soil development is best characterized by several pronounced time-dependent changes, including a decrease in particle size toward silt and clay texture; translocation and accumulation of precipitates, replacement of silicate fabric by carbonate, color changes, increases in plasticity, and the formation of clays enriched in Ca and Mg (Nettleton, 1991). The degree of soil development is dependent on many factors and processes, both internal and external to the soil (Jenny, 1941). The parameter or property in question might be highly sensitive to factors such as climate (and its many characteristics), vegetation, fauna, slope position, input of dust, and coarseness and mineralogy of the parent material. Time or duration of soil development integrates the many processes (Nettleton, 1991).

Nine phases of glacial retreat dominate the history of deglaciation of southern Saskatchewan (Fig. 3.1). As the continental glacier retreated downslope to the northeast, the North and South Saskatchewan rivers built successively lower deltas. Iceward, between the sand and gravel deltas and the retreating glacier, finer grained lacustrine silts and clays were deposited in glacial Lake Saskatchewan. As the lake level

dropped and the shoreline retreated, newer deltas were built on the older offshore lacustrine deposits (Christiansen, 1978).

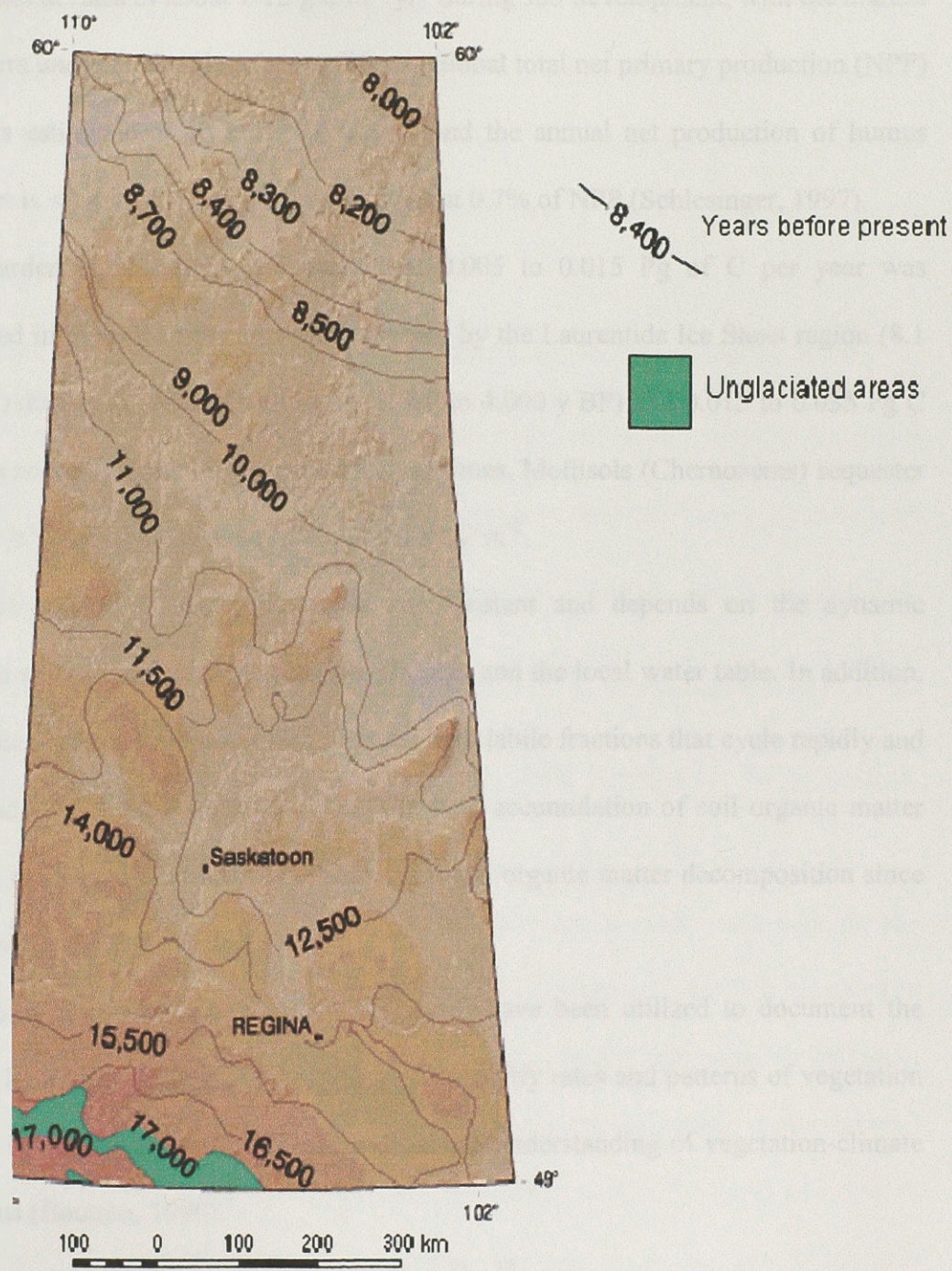


Figure 3.1 Ice margin positions during the deglaciation of Saskatchewan (Fung, 1999).

Storage of soil organic matter is related to the net ecosystem production (NEP) in the terrestrial environment. Studies of soil chronosequences suggest that humus accumulates at rates of about $1\text{--}12 \text{ g C m}^{-2} \text{ yr}^{-1}$ during soil development, with the highest rates occurs under cool and moist conditions. Global total net primary production (NPP) on land is estimated at $60 \times 10^{15} \text{ g C yr}^{-1}$, and the annual net production of humus substances is $<0.4 \times 10^{15} \text{ g C yr}^{-1}$, which is about 0.7% of NPP (Schlesinger, 1997).

Harden et al. (1992) estimated that 0.005 to 0.015 Pg of C per year was sequestered in the soil of the area once covered by the Laurentide Ice Sheet region ($8.1 \times 10^{12} \text{ m}^2$) during the Middle Holocene (8,000 to 4,000 y BP) and 0.015 to 0.035 Pg C per year was sequestered during pre-industrial times. Mollisols (Chernozems) sequester $2 \text{ g C m}^{-2} \text{ yr}^{-1}$, with a mean store of about 9.1 kg C m^{-2} .

The rate of C accumulation is not constant and depends on the dynamic interaction among landscape, vegetation, climate, and the local water table. In addition, soil organic C is heterogeneous, and includes both labile fractions that cycle rapidly and clay bound C with slow turnover rates. The total accumulation of soil organic matter represents the long-term balance between NEP and organic matter decomposition since the beginning of soil formation.

Isotopic measurements of soil organic C have been utilized to document the effects of land use practices on ecosystems, to quantify rates and patterns of vegetation dynamics in natural ecosystems, and to refine our understanding of vegetation-climate interactions (Boutton, 1996).

The natural stable C isotope ratio ($^{13}\text{C}/^{12}\text{C}$) of soil organic C possesses information regarding the relative proportion of plant species with the C_3 (low $^{13}\text{C}/^{12}\text{C}$)

3.2.1.3 Bulk Density

Two to four core samples (5.3 cm in diameter, 6 cm in height) were taken from each horizon for bulk density measurement. Total initial and oven dried (105-110°C) weights were recorded. Bulk density was calculated by dividing the dry weight by the sample volume, with the mean bulk density for each horizon reported (Culley, 1993).

3.2.3.3 Particle Size Analysis

Particle size analysis of the < 2 mm soil was conducted using the pipette method after removal of carbonates and organic matter (Sheldrick and Wang, 1993).

3.2.3.4 Cation Exchange Capacity and Exchangeable Cations

The cation exchange capacity (CEC) and exchangeable cations were determined using 0.25 M BaCl₂-triethanolamine buffered at pH 8 as a saturation solution. Five g soil samples were saturated using 100 mL of solution, and left to stand overnight. The next day, the initial solution was separated from the soil by filtration, followed by two more extractions. The “filtrate” was collected and total extractable major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺) were determined. The Ba²⁺ was replaced from the exchange site using 0.1 M ammonium acetate buffered at pH 7. Calcium, Mg²⁺, and Ba²⁺ were determined using atomic absorption spectrometry, and K⁺ and Na⁺ were determined by atomic emission spectrometry. Exchangeable cations were calculated by subtracting major soluble cations from total extractable major cations (Hendershot and Lalande, 1993).

3.2.1.5 Organic Carbon

Soils for organic measurement were ground to pass a 60-mesh sieve ($< 250\ \mu\text{m}$) and contents were measured using a Leco CR-12 C system furnace (Wang and Anderson, 1998a). In this method samples were combusted at $840\ ^\circ\text{C}$ and the CO_2 released is measured by an infrared cell. The C content (%) is determined by integrating the CO_2 that released during the combustion process. The method was tested for dolomite from the soil and synthetic calcite samples. This method is quick and very practical and possibility of error for the determination of organic and inorganic C is thought to be negligible for our materials.

3.2.1.6 Sample Preparation and Measurement of $\delta^{13}\text{C}$ of Organic C

The $\delta^{13}\text{C}$ value of organic C was measured for all horizons with $> 0.2\%$ organic C. Horizons containing both organic C and carbonates were treated with 3 M HCl to remove carbonates, then washed with deionized water using $0.22\ \mu\text{m}$ Millipore filters to remove excess HCl, until a negative test was obtained for chloride in the filtrate using AgNO_3 . Samples were dried and then ground to a fine powder by using a ball mill.

The isotopic composition ($\delta^{13}\text{C}$ value) of soil organic matter was determined using an Europa Scientific Instruments elemental analyzer coupled to a Europa Instruments 20/20 mass spectrometer in continuous-flow mode. In this method, samples are loaded into tin capsules and combusted in a furnace at $1000\ ^\circ\text{C}$. The gas is passed through traps to trap water and other unwanted gases. The gas stream passes into a gas chromatograph where components of interest are separated and is then bled into a mass-

spectrometer where the carbon isotopes are ionized and then separated in a magnetic field. The isotopic species are detected separately and from their ratios.

The results of the isotope analyses are expressed in term of δ notation units of per mil (‰):

$$\delta^{13}\text{C} = \left(\frac{R_s}{R_{st}} - 1 \right) \times 1000 \quad [3.1]$$

where $R_s = {}^{13}\text{C}/{}^{12}\text{C}$ in sample, and $R_{st} = {}^{13}\text{C}/{}^{12}\text{C}$ in the reference standard. The δ values for the $\delta^{13}\text{C}$ are reported relative to Vienna Pee Dee Belemnite (VPDB). The reproducibility of this method for C isotope ratios is $\pm 0.2\text{‰}$.

To calculate the proportion of C_3 and C_4 plants in the organic matter, the following equation was used:

$$\text{Percentage of } \text{C}_3 \text{ plants} = \frac{\delta^{13}\text{C}(\text{C}_3 + \text{C}_4) - \delta^{13}\text{C}(\text{C}_4)}{\delta^{13}\text{C}(\text{C}_3) - \delta^{13}\text{C}(\text{C}_4)} \times 100 \quad [3.2]$$

where $\delta^{13}\text{C}(\text{C}_3 + \text{C}_4)$ is from the bulk organic matter, $\delta^{13}\text{C}(\text{C}_3)$ is an average for C_3 plants (-27‰), and $\delta^{13}\text{C}(\text{C}_4)$ is an average of C_4 plants (-13‰) (Boutton, 1991).

3.3 RESULTS AND DISCUSSIONS

3.3.1 Soil Characteristics

Soils from the 18 sites are classified as Chernozomic or Luvisolic soils (Soil Classification Working Group, 1998) (Table 3.1). The equivalent of these soils in US Taxonomy is given in Appendix D. The Chernozemic soils, with one exception, are

Orthic subgroups of the Brown, Dark Brown, and Black great groups. The criterion of ≥ 10 cm Ah was not applied to some Brown (B1, B2, B3, B5) and Dark Brown (DB.3) soils in that it seemed that the Chernozemic order was the most suitable order despite Ah horizon < 10 cm thickness. Elevation decreases from 781.4 m in the southwest to 518.3 m in the northeast.

Table 3.1 Location, soil zone, and taxonomic classification of the soils.

Climatic Soil Zone ^a	Association ^b	Classification (Subgroup) ^c	Longitude West	Latitude North	Elevation (m)
Dry Brown (B.5) ^d	Haverhill	Orthic Brown Chernozem	107° 53'	49° 13'	781.4
Dry Brown (B.6)	Haverhill	Rego Brown Chernozem	108° 02'	49° 18'	869.1
Brown (B.1)	Ardill	Orthic Brown Chernozem	106° 23'	49° 68'	731.1
Brown (B.2)	Haverhill	Orthic Brown Chernozem	107° 02'	50° 92'	634.7
Brown (B.3)	Haverhill	Orthic Brown Chernozem	106° 82'	50° 74'	696.5
Brown (B.4)	Haverhill	Orthic Brown Chernozem	107° 01'	49° 61'	725.2
Dark Brown (DB.1)	Weyburn	Orthic Dark Brown Chernozem	106° 37'	52° 20'	555.7
Dark Brown (DB.2)	Weyburn	Orthic Dark Brown Chernozem	106° 17'	52° 17'	524.6
Dark Brown (DB.3)	Weyburn	Orthic Dark Brown Chernozem	107° 71'	52° 05'	591.3
Black (Bl.1)	Oxbow	Orthic Black Chernozem	104° 92'	51° 84'	516.0
Black (Bl.2)	Oxbow	Orthic Black Chernozem	106° 67'	52° 53'	514.8
Black (Bl.3)	Oxbow	Orthic Black Chernozem	107° 66'	52° 73'	566.4
Gray (G.1)	Waitville	Orthic Gray Luvisol	105° 88'	53° 56'	524.15
Gray (G.2)	Waitville	Orthic Gray Luvisol	105° 29'	53° 56'	524.6
Gray (G.3)	Waitville	Orthic Gray Luvisol	105° 27'	52° 87'	518.2
Gray (W1)	Weirdale	Rego Black Chernozem	105° 26'	53° 45'	480.4
Gray (W2)	Weirdale	Rego Black Chernozem	105° 26'	53° 45'	480.4
Gray (W3)	Weirdale	Rego Black Chernozem	105° 26'	53° 45'	480.4

^a As delineated by Henry and Harder (1991).

^b Soil associations as described in the Saskatchewan Soils Name Files, and various soil survey reports.

^c Based on the Canadian System for Soil Classification (Soil Classification Working Group, 1998).

^d () shows the profile No. in each soil zone.

Soils from southeast to northwest become more developed and thickness of horizons increase. The Ah horizons were as thin as 4 cm for Brown soils (B.3), increasing to 10 cm for Dark Brown, and 14 cm for Black soils. The depth of solum is an expression of the duration and intensity of downward moisture flux and intensity of weathering. The Orthic Gray Luvisols had thick LFH horizons, no Ah horizons and much deeper sola than the Chernozemic soils (Fig. 3.3). Organic C in the Ah horizon increases from 1.65% in Brown soils to 5.65% in Black soils. The major soluble cations are Ca^{2+} and Mg^{2+} , and Mg^{2+} increases with depth. Major soluble anions are SO_4^{2-} and HCO_3^- . Major exchangeable cations are Ca^{2+} and Mg^{2+} (Appendix A, B).

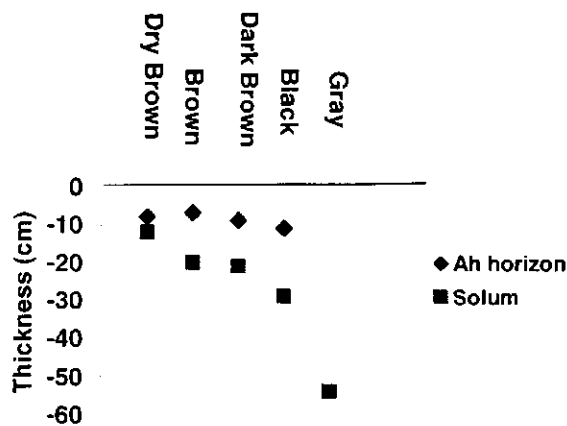


Figure 3.3 Ah horizons and solum thickness for soils of the study area. There were three or more replicates of each soil group.

The pH values for the Ah horizons of the Chernozemic soils are neutral to mildly acidic, more alkaline in the calcareous Rego Black Chernozems (Appendix A). The Orthic Gray Luvisols have well-developed Ae and Bt horizons that are more strongly acidic than the Chernozems. In general, electrical conductivity (EC) values increase with depth for Brown, Dark Brown, and Black soils, indicating high contents of soluble salts in subsoils, which are characteristic of upper slope soils of semiarid to

subhumid regions. The Gray Luvisols had low EC values to 1.2 m depth, indicative of stronger and more frequent downwards flux of soil water. The Rego Black Chernozems had comparatively low salt contents, but EC values increased towards the surface of the mineral soil, which is considered indicative of a net upwards flux of soil water in a ground water discharge area (Appendix B).

3.3.2 Organic Carbon Storage

Organic C stores in the soil change regularly with changes in climatic conditions, which is consistent with the idea that each soil zone has a different inherent capability for biomass production. In the Dry Brown zone, short and sparse grasses are the dominant vegetation. In the Dark Brown to the Black zones, grasses become taller and more dense, producing more biomass and hence more organic matter accumulates. In the forest, a greater proportion of the plant litter accumulates on the soil surface, with less production below ground. Lower temperature causes a slower decomposition of residue, and there is a possibility of leaching of organic matter from the soil system (Lichter et al., 2001). Therefore, organic matter accumulation is less in the Gray than in the Dark Brown and Black soils, and slightly higher than the Brown soils of the dry grasslands.

The Rego Black Chernozem soils contains large amounts of organic matter and CaCO_3 , especially in the surface horizons. This may be due to the association of organic matter with carbonates. Duchaufour (1976) suggested that carbonates are able to sequester organic matter, and humified compounds are precipitated without transformation and polymerization.

The amount of organic C to 1.2 m depth increases from an average of 9.1, 11.7, 14.9, 9.6, and 21.0 kg m⁻² (90.8, 117.2, 148.8, 96.3, and 210.2 Mg C ha⁻¹) for Brown, Dark Brown, Black, Gray, and Rego Black Chernozem soils (LFH horizons are included for Gray and Rego Black Chernozem soils), respectively (Fig. 3.4). These results are similar to the data reported by McGill et al. (1988) for similar soil zones in Alberta. Huang and Schoenau (1996) measured 95.4 Mg C ha⁻¹ to 103.4 Mg C ha⁻¹ with the average of 99.2 Mg C ha⁻¹ in Orthic Gray Luvisol soils under aspen forest, with 47% of the C in the LFH layer.

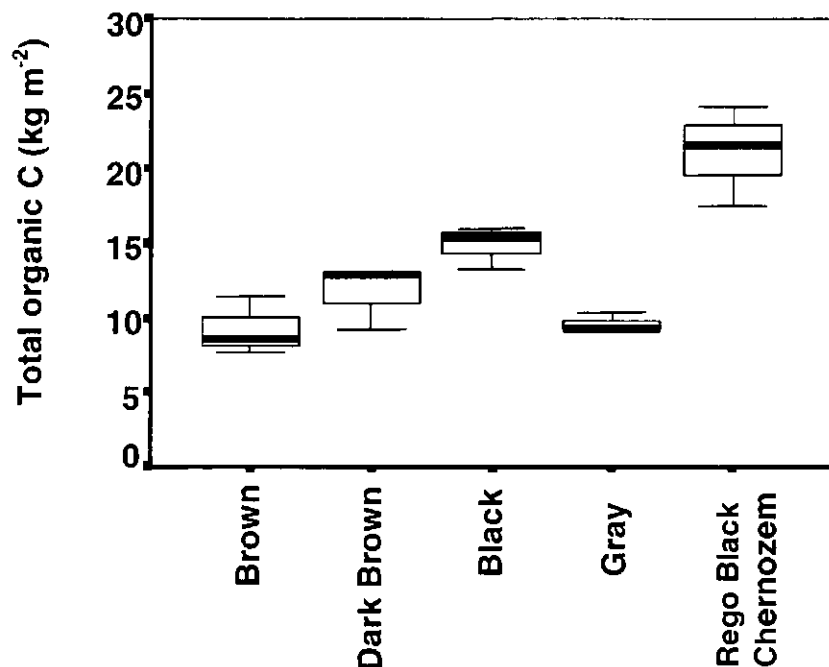


Figure 3.4 Total organic carbon storage in a sequence of Brown to Gray soils to a 1.2 m depth. The boxes show the central 50% of the values with the median. Whiskers show 25th and 75th centiles. There were three or more replicates of each soil group.

The time for soil formation since deglaciation, ranges from 17,000 yr in the southwest (Dry Brown soils) to 11,500 yr in the east-central area with Gray soils.

Average annual C accumulation rates in the soils studied are 0.57, 0.90, 1.18, 0.84, and 1.83 $\text{g m}^{-2} \text{yr}^{-1}$ for Brown, Dark Brown, Black, Gray, and Rego Black Chernozem soils, respectively (Fig. 3.5). Rates of accumulation for Gray and Brown soils are higher, and for Black and Dark Brown soils are lower than those calculated by Harden et al. (1992). For the glaciated area of North America their calculation shows that Mollisols (similar to Black and Dark Brown Chernozems) store $2 \text{ g C m}^{-2} \text{yr}^{-1}$, Alfisols and Inceptisols, similar to Gray and Brown soils, sequester $0.27 \text{ g C m}^{-2} \text{yr}^{-1}$.

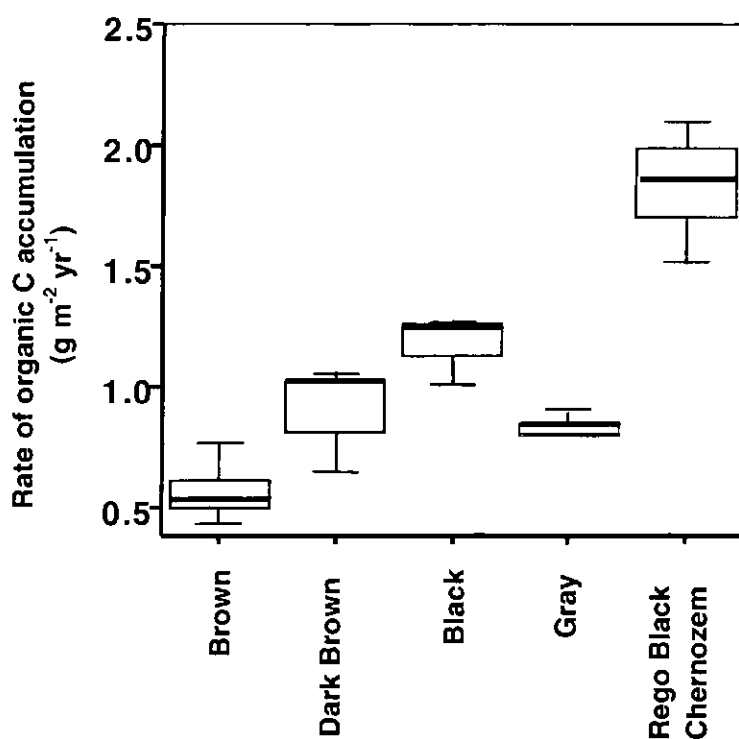


Figure 3.5 Organic carbon accumulation rate in a sequence of Brown to Gray soils. The boxes show the central 50% of the values with the median. Whiskers show 25th and 75th centiles. There were three or more replicates of each soil group.

The rate of organic C accumulation is high in the early stages of soil development, and gradually levels off to a near steady state after several thousand years. Harden et al. (1992) confirm that for most soils, the rate of net C accumulation is greatest during early stages of soil development. Anderson (1977) has reported 29 g C

$\text{m}^{-2} \text{yr}^{-1}$ for glacial till mine spoils after 28-40 yr in the Dark Brown soil zone of Saskatchewan. In temperate grassland the rate decreases to about $0.5 \text{ g m}^{-2} \text{yr}^{-1}$ after 25,000 yr (Chadwick et al., 1994).

The NPP of seeded forage grasses (based on dry matter) for the different soil zones are estimated to be 323.8, 464.7, 490.1 $\text{g m}^{-2} \text{yr}^{-1}$ for Brown, Dark Brown, and Black soils, respectively (Saskatchewan Agriculture and Food, 2001). Using the following equation we can calculate the total annual mineralization of NPP.

$$\text{Dm} = 100 - \left(\frac{R}{\text{NPP} \times 0.45} \times 100 \right) \qquad [3.3]$$

where Dm is NPP mineralization in percent, R is the annual accumulation rate ($\text{g C m}^{-2} \text{yr}^{-1}$) of organic C, NPP ($\text{g C m}^{-2} \text{yr}^{-1}$), and 0.45 is the C content of plant residue to convert dry matter to organic C. The results are given in Table 3.2.

Table 3.2 Relationship between net primary production and organic carbon accumulation.

Soil Zone	Above-ground ^a NPP ($\text{g m}^{-2} \text{yr}^{-1}$)	Below-ground ^b NPP ($\text{g m}^{-2} \text{yr}^{-1}$)	Rate of organic C accumulation ($\text{g m}^{-2} \text{yr}^{-1}$)	NPP accumulation as organic C (%)	Converted to CO ₂ (%)
Brown	323.8	136.0	0.57	0.28	99.72
Dark Brown	464.7	195.2	0.90	0.30	99.70
Black	490.1	205.9	1.18	0.38	99.62

^a Based on Saskatchewan Agriculture and Food (2001) report.

^b Calculated based on 42.6% belowground reported by Slobodian (2001) for Dark Brown soils.

It should be remembered that a part of the CO₂ produced in the soil is converted to secondary carbonates and should be deducted from the percentage of NPP that is released back to atmosphere. Chadwick et al. (1994) suggest that in temperate grasslands more than 98 % of NPP returns to the atmosphere through soil respiration. The estimated average C sequestration worldwide is about 0.7 % of NPP (Schlesinger, 1997). The calculated average value of 0.32 % of NPP (Table 3.2) appears to be less than the world average. Considering the long-term average rate for other soils such as Spodosols and peat soils, which are between 10 to more than 50 g m⁻² yr⁻¹, our estimate seems to be quite reasonable. It must be noted that the annual C accumulation rates calculated are an average for soils that may have well been more or less at equilibrium for thousands of years.

3.3.3: Stable Isotopes of Soil Organic Carbon

The $\delta^{13}\text{C}$ values of organic C (an average of all profiles in each climatic soil zone) are given in Table 3.3.

Table 3.3 The average $\delta^{13}\text{C}$ values of organic C and the calculated proportion of C₃ and C₄ plants in a sequence of Brown to Gray soils in Saskatchewan.

Soil Zone .	$\delta^{13}\text{C}$ (‰)	C ₃ (%)	C ₄ (%)
Dry Brown (grassland)	-22.9	70	30
Brown (grassland)	-24.3	80	20
Dark Brown (grassland)	-24.8	85	15
Black (grassland)	-25.3	90	10
Gray (forest)	-26.8	100	0

The gradual decrease in $\delta^{13}\text{C}$ values from the Dry Brown to the Gray soils is evident. The relative percentage of soil organic matter derived from C_3 plants such as *Stipa comata* ($\delta^{13}\text{C}$ of -25‰), *Agropyron smithii* ($\delta^{13}\text{C}$ of -28‰), *Agropyron trachycaulum* ($\delta^{13}\text{C}$ of -28‰), *Stipa viridula* ($\delta^{13}\text{C}$ of -27‰) (Waller and Lewis, 1978), *Artemisia sp.* ($\delta^{13}\text{C}$ of -28‰) (Bender, 1971), *Populus tremuloides* ($\delta^{13}\text{C}$ of -27.2‰), *Pinus banksiana* ($\delta^{13}\text{C}$ of -26.6‰), *Rosa acicularis* ($\delta^{13}\text{C}$ of -27.9‰), *Fragaria virginiana* ($\delta^{13}\text{C}$ of -31.7‰) (Brooks et al., 1997), and C_4 plants such as *Bouteloua gracilis* ($\delta^{13}\text{C}$ of -13‰) (Waller and Lewis, 1978) was calculated using equation [3.2].

The gradual decrease in $\delta^{13}\text{C}$ values from the Dry Brown to Gray zones reflects the long-term effects of vegetation composition (Fig. 3.6).

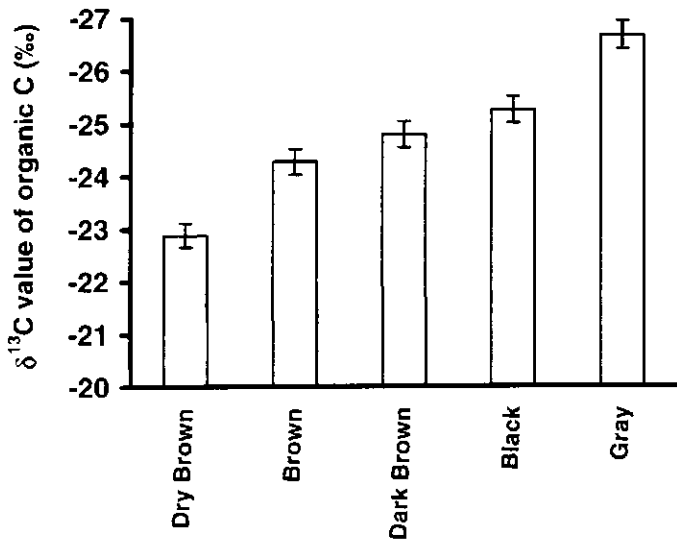


Figure 3.6 Average $\delta^{13}\text{C}$ value of organic carbon in each climatic soil zone. There were three or more replicates of each soil group.

The $\delta^{13}\text{C}$ values of organic C in Dark Brown and Black Chernozomic soils are -24.8‰ and -25.3‰ , which are similar to the values of -24.5‰ for Dark Brown and -25.5‰ for Black (Anderson, 1995; Wang and Anderson, 1998b), and less than the -23.2‰ for Dark Brown and -21.8‰ for Brown soils reported by Anderson and Paul (1984). The $\delta^{13}\text{C}$ values of organic C from Ah horizons indicate that the soil organic matter was derived from a vegetation association that is quite similar to the current cover.

Stable carbon isotope analyses of organic C with the depth of a soil profile reflects the past history of vegetation. The $\delta^{13}\text{C}$ values of organic C in Brown soils decrease with depth (Fig. 3.7). Kelly et al. (1991) also reported a trend of smaller $\delta^{13}\text{C}$ values with depth for soils of the semi-arid grasslands of South Dakota, contrary to the general belief that the $\delta^{13}\text{C}$ values of organic C increase with depth. Volkoff and Cerri (1987); Natelhoffer and Fry (1988); Balesdent et al. (1993); Skjemstad et al. (1990); and Khademi and Mermut (1999) reported the enrichment of ^{13}C in organic matter with depth, and have suggested that greater $\delta^{13}\text{C}$ values are related to organic matter that is derived from root decomposition (Boutton, 1996). Other factors include, discrimination against ^{13}C during organic matter decomposition, differential preservation of organic matter or plant litter components enriched in ^{13}C , and changes through time from litter inputs with high $\delta^{13}\text{C}$ values (due to more positive value of atmospheric CO_2 in the past) to litter inputs with lower values (Natehoffer and Fry, 1988).

Organic C in subsoils is older than the SOC in A horizons and, therefore, can represent vegetation composition different than today (Mermut and Acton, 1984). The

organic C in the Ah of a Black soil had an equivalent age of 385 ± 110 yr, compared to 2420 ± 110 yr in the B horizon (Anderson, 1995).

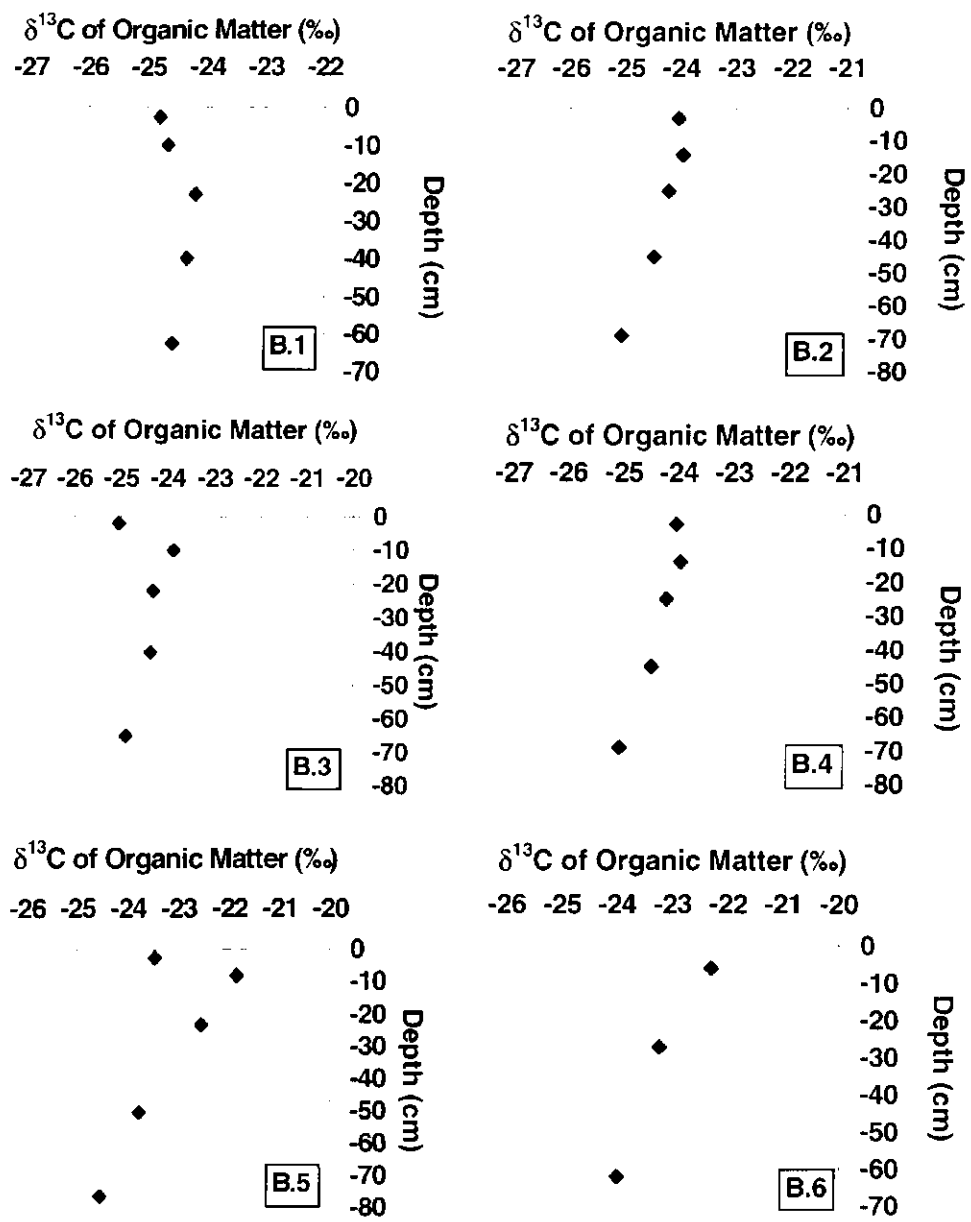


Figure 3.7 $\delta^{13}\text{C}$ values of organic carbon with depth in Brown soils. Each point is the mean of at least two replicates that are within $\pm 0.15\text{‰}$ of the mean.

The smaller $\delta^{13}\text{C}$ values with depth are consistent with the findings of Ritchie (1987), and Yansa and Basinger (1999), who postulated, based on the pollen records,

that the grasslands region was covered by an open spruce woodland for a period of at least several thousand years following deglaciation. The spruce woodland was replaced by deciduous parkland vegetation that persisted until about 8,800 BP. A warm and dry climate then resulted in a transition to grassland that was completed by about 5,800 BP.

The $\delta^{13}\text{C}$ values of organic C of Dark Brown soils are consistently about -25‰ , with enrichment in $\delta^{13}\text{C}$ values in subsurface horizons (Fig. 3.8).

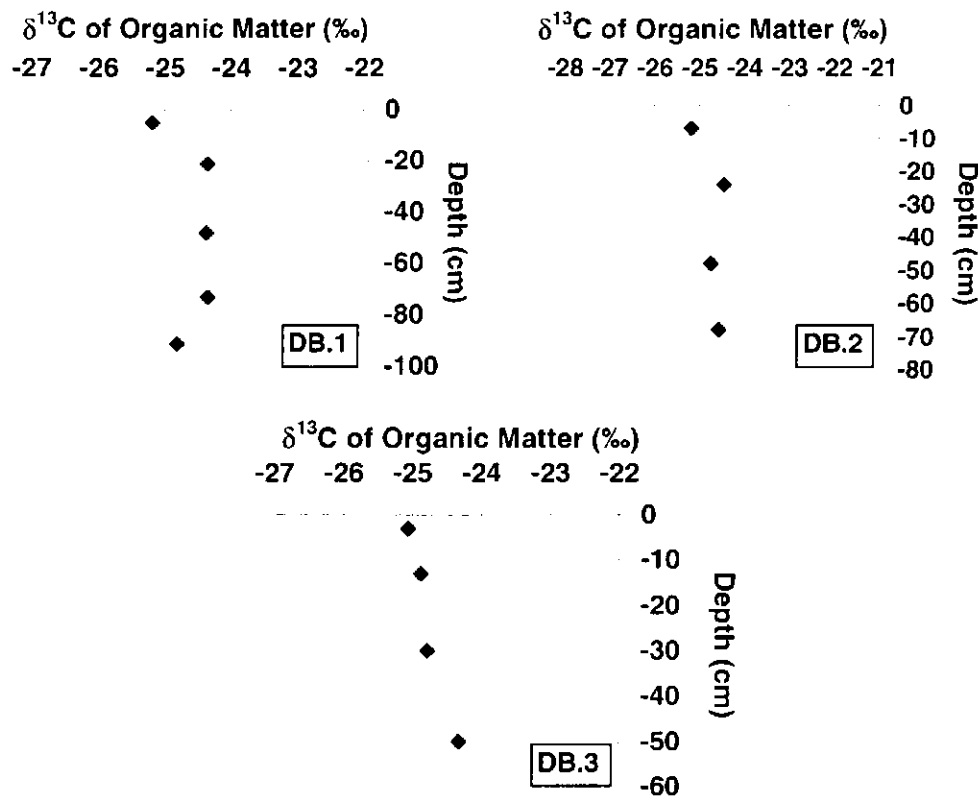


Figure 3.8 $\delta^{13}\text{C}$ values of organic carbon with depth in Dark Brown soil zone. Each point is the mean of at least two replicates that are within $\pm 0.15\text{‰}$ of the mean.

The larger values at depth may be related to larger additions of roots, which through decomposition could produce a more positive value. In the C horizon, the $\delta^{13}\text{C}$ values of organic C become smaller than in the B horizon except for profile 3 (DB.3) in which

$\delta^{13}\text{C}$ values of organic C increase with depth. Slight differences in $\delta^{13}\text{C}$ values between the surface and subsurface horizons are likely due to the differences between present and past vegetation. The DB.3 soil is located in the drier part of the Dark Brown zone and has a sandy texture at depth. It is therefore possible that the remains of the previous vegetation did not survive and consequently could not change the isotopic signal of organic matter in this particular profile (Fig. 3.8).

The slight trend to greater $\delta^{13}\text{C}$ values with depth is consistent with findings that suggest a greater degree of humification in subsoil organic matter, but may also represent slightly more C_4 plants in the more recent past. Studies have shown that climate fluctuations in the Holocene have indeed influenced the trend of soil formation and, consequently, the vegetation pattern in central Saskatchewan (Mermut and Acton, 1984).

In the first two soils from west and east parts of the Black soil zone (Bl.1, Bl.2), $\delta^{13}\text{C}$ values of organic C in the profile shows the same trend as in the Dark Brown zone, supporting the idea that there may have been more C_3 plants in these regions in the past, although differences are slight (Fig. 3.9). In soils from the north (Bl.3, Fig.3.9), the $\delta^{13}\text{C}$ values of organic C slightly increase with depth, suggesting that the vegetation on this soil has not changed (Fig. 3.9).

The $\delta^{13}\text{C}$ values of organic C for Gray soils increase slightly with depth. In this region, the past vegetation appears to have been similar to the present and differences in $\delta^{13}\text{C}$ values of organic C in upper and lower horizons may well be related to a greater values for roots and more humified organic matter (Fig. 3.10).

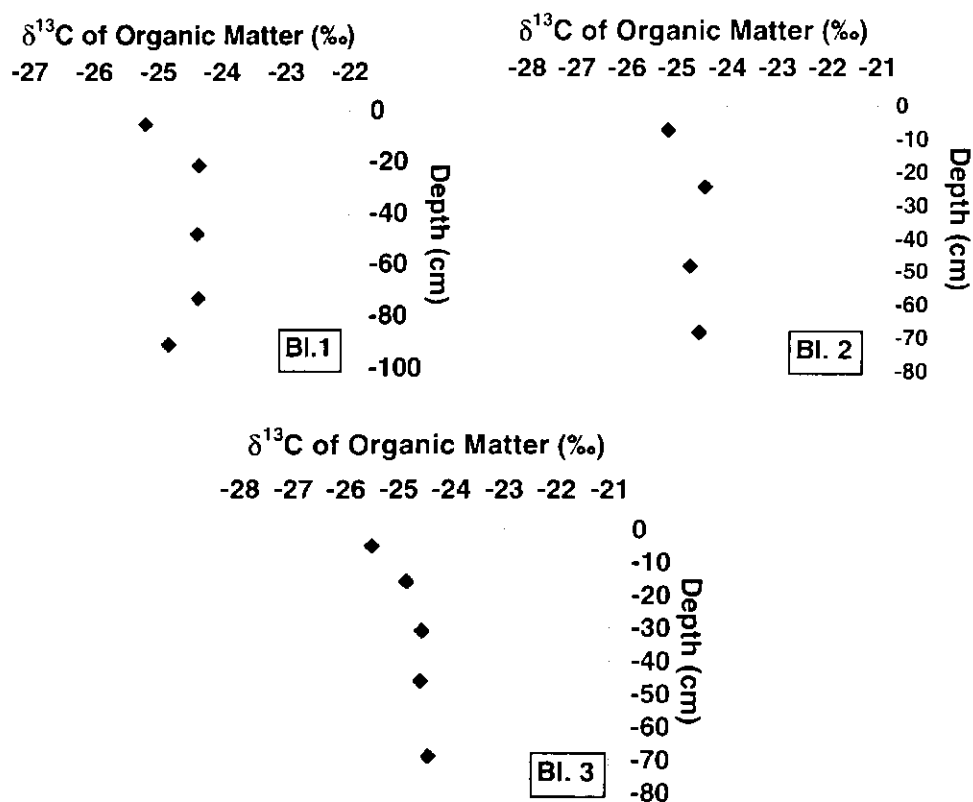


Figure 3.9 $\delta^{13}\text{C}$ values of organic carbon with depth in Black soil zone. Each point is the mean of at least two replicates that are within $\pm 0.15\text{‰}$ of the mean.

3.4 CONCLUSIONS

The thickness of Ah horizons, depth of solum, organic matter contents and rates of organic C accumulation increase from the Dry Brown zone to the Black zone, despite the fact that the actual time for soil formation decreases. The amount of organic C to 120 cm depth for Brown, Dark Brown, Black, and Gray soils are 9.08, 11.72, 14.88, 9.63 g m^{-2} , respectively. Calculated annual average accumulation rates in the soil are about 0.57, 0.90, 1.18, and 0.84 $\text{g m}^{-2} \text{yr}^{-1}$ for Brown, Dark Brown, Black, and Gray soils, respectively. The Rego Black Chernozem soils contains 21.02 kg m^{-2} (210.2 Mg

ha⁻¹) with an accumulation rate of 1.83 g m⁻² yr⁻¹, which is the highest among the soil groups in Saskatchewan. Based on the rate of organic C accumulation calculated, more than 99% of NPP is converted to CO₂ through soil respiration and returned to the atmosphere.

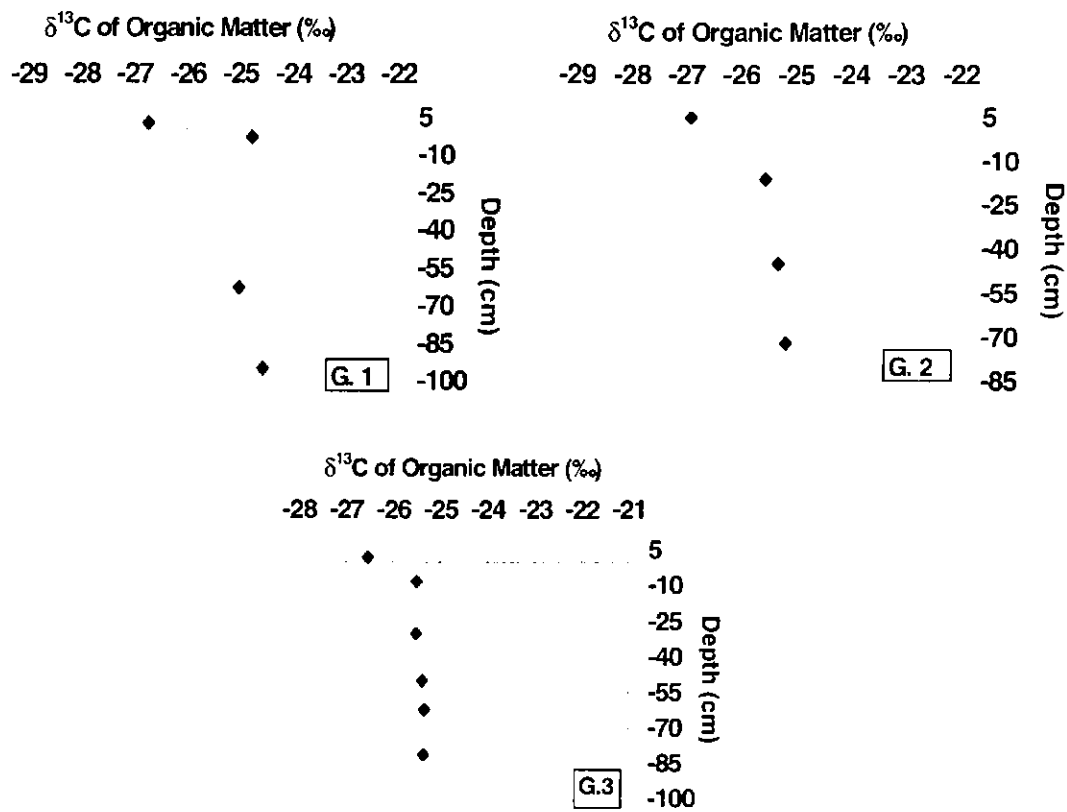


Figure 3.10 $\delta^{13}\text{C}$ values of organic carbon with depth in Gray soils. Each point is the mean of at least two replicates that are within $\pm 0.15\text{‰}$ of the mean.

The mean $\delta^{13}\text{C}$ value of organic C for all samples within a zone ranges from -22.9‰ in the Dry Brown, -24.3‰ in the Brown, -24.8‰ in the Dark Brown, -25.3‰ in the Black, and -26.8‰ in the Gray soil zones. The regular differences are considered to be a consequence of increasing input to organic matter of C₄ plants in drier and warmer regions, with an estimated 30% C₄ plants in the Dry Brown, and none in the Gray soils.

Dry Brown and Brown soils have more depleted organic C with depth, suggesting a greater proportion of C₃ plants in the past.

Certainly, the grasslands and southern forested areas are a sink for C, although our calculations suggest that input of C from biomass is about 0.32% of NPP in native prairie. There is, however, the possibility of storage of biogenic C as pedogenic carbonate.

CHAPTER 4

ORIGIN AND RATE OF PEDOGENIC CARBONATE ACCUMULATION IN SASKATCHEWAN SOILS, CANADA

4.1 INTRODUCTION

Information about the amount and rate of pedogenic carbonate accumulation in soils is important for the estimation of C pools and fluxes in the terrestrial environment as well as an understanding of past climatic conditions. Because of the complexity of processes involved in atmosphere-vegetation-soil-landscape relationships, there are few estimates for secondary carbonates in the world's soils. Carbonates form in soils under arid to sub-humid climates with annual precipitation < 700 mm depending on temperature (Jenny, 1941; Birkeland, 1999). When the soil parent materials are calcareous, massive deposits of secondary or pedogenic carbonates occur in subsoils (Schlesinger et al., 1989). Secondary carbonate occurs in a variety of forms in soils, ranging from precipitates in the interstitial spaces of parent material to almost pure, laminated layers of carbonate coating on the underside of cobbles that are known as carbonate pendants (Gile, 1961; Gile et al., 1966; Flach et al., 1969; Mermut and St. Arnaud, 1981a, b).

Several attempts have been made to calculate the rate of pedogenic carbonate accumulation in soils. A simulation model, CALDEP, was developed by Marion and Schlesinger (1994) to predict the amount of pedogenic carbonate deposition in soils

(caliche) of the deserts of the southwestern U.S.A. The model assumed that most pedogenic carbonate formed under climates with cool and wet winters during the Pleistocene. The predicted CaCO_3 deposition rate was 1 to 5 $\text{g m}^{-2} \text{yr}^{-1}$ ($0.12\text{-}0.6 \text{ g C m}^{-2} \text{yr}^{-1}$) with an input of CaCO_3 as atmospheric dust of $0.51 \text{ g m}^{-2} \text{yr}^{-1}$. The model also predicted that an increase in rainfall resulted in an increase in CaCO_3 precipitation.

The rate of pedogenic carbonate accumulation calculated by Machette (1985) for non-calcareous parent materials ranges from 1.4 to 5.1 $\text{g m}^{-2} \text{yr}^{-1}$ ($0.17\text{-}0.61 \text{ g C m}^{-2} \text{yr}^{-1}$) for three areas in New Mexico and Utah. Using ^{14}C , ^{230}Th , and ^{234}U dates of calcic horizons of Aridisols in the Mojave Desert, Schlesinger (1985) has calculated the rate of deposition of pedogenic carbonate to be between 1.0 and 3.5 $\text{g CaCO}_3 \text{ m}^{-2} \text{yr}^{-1}$ ($0.12\text{-}0.42 \text{ g C m}^{-2} \text{yr}^{-1}$). These are similar to the rates calculated using a variety of approaches for soils of the southwestern deserts of the United States (Eghbal and Southard, 1993). No data are available currently about the rate of formation of pedogenic carbonate in the Canadian prairies. Yet this is important to realistically estimate inorganic C sequestration at global levels.

The isotopic composition of C in pedogenic carbonate reflects the $\delta^{13}\text{C}$ value of the soil CO_2 , which is a function of the mixing of atmospheric and biologically respired CO_2 . The oxygen isotopic composition ($\delta^{18}\text{O}$) is dependent on the isotopic composition of soil water which is related to local meteoric water (Cerling, 1984; Quade et al., 1989a; Amundson et al., 1989; Mermut et al., 2000). Even in desert soils with low respiration rates, soil CO_2 is the primary contributor to pedogenic carbonate (Pendall and Harden, 1994). Only a small portion of the CO_2 produced through biological activity is utilized to

form inorganic C (Nordt et al., 2000). Stable isotope ratios of elements in both organic and inorganic components often record and integrate information related to the kind of processes that were involved in the formation of the components, and the environmental conditions under which they were formed.

A wealth of environmental and ecological information often can be obtained from stable isotope analyses (Boutton, 1996). A high correlation was established between the C and O isotopes of pedogenic carbonate (Cerling and Quade, 1993; Khademi and Mermut 1999). These correlation were used to describe the paleoenvironments (Cerling and Hay, 1986; Cerling et al., 1989; Quade et al., 1989b). The $\delta^{18}\text{O}$ of soil carbonate is controlled by a number of factors and processes, including the $\delta^{18}\text{O}$ of meteoric water, soil temperature, evaporation, and differential infiltration in successive seasons (Zimmerman et al., 1967; Salomons and Mook, 1986; Cerling and Wang, 1996).

The objectives of this work were to determine the amounts and accumulation rates of pedogenic carbonate in a series of zonal soils representing gradients of environment and time in Saskatchewan. Using available data on soil orders, I also attempted to calculate the total amount of organic C that is converted to pedogenic carbonate during soil formation.

4.2 MATERIALS AND METHODS

4.2.1 Soil and Carbonate Pendant Sampling

A southwest to northeast transect of about 500 km length was used in this study. The transect crossed five different soil-climatic zones (Dry Brown, Brown, Dark Brown,

Black, and Gray) in Saskatchewan, between 49° 13' and 53 ° 63' N latitude and 104° 92' and 107° 66' W longitude. Soil sampling is described in the section 3.2 chapter 3. Pebbles with pedogenic carbonate (pendants) were collected when they were present.

4.2.2 Analytical Methods

4.2.2.1 Sample Preparation

Bulk soils were ground and passed through a 60-mesh (250 μm) sieve. Samples with $> 0.1\%$ organic C, which is 10 times less than the value suggested by Lerman (1975) and Smith and Turner (1975), were treated with sodium hypochlorite 5.25% (commercial bleach) for 15 days to remove organic matter. For biological material the best resolution of $\delta^{13}\text{C}$ is about 0.2‰, which is equivalent to 1 to 2% organic matter (Lerman, 1975; Smith and Turner, 1975). The $\delta^{13}\text{C}$ determined for pedogenic carbonate will not be affected by the $\delta^{13}\text{C}$ of organic C when the content of organic C is $< 0.1\%$. Bleach is the most effective reagent to remove organic materials (Gaffey and Bronnimann, 1993), and far less reactive with calcium carbonate in comparison to deionized water, sodium hydroxide, Alconox, and hydrogen peroxide (Pangitore et al., 1993). Once a day and for 15 days, samples were shaken and bleach was added. The samples were washed with deionized water and centrifuged to remove extra bleach. Treated samples were powdered and analyzed for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. None carbonatic pebbles with pedogenic carbonates (pendants) were washed with deionized water and then ultrasound was used to remove loose material. After drying, a sample was scraped from each pendant, ground to a fine powder and analyzed for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.

4.2.2.2 Carbon Content

Samples passed through a 250 μm sieve were used to measure the amount of organic and inorganic C. The organic C content was determined by heating the samples to 840 $^{\circ}\text{C}$, and total C was measured at 1140 $^{\circ}\text{C}$ by using a Leco CR-12 carbon system furnace (Wang and Anderson, 1998a). Inorganic C was estimated by subtracting organic C from total C, and expressed as CaCO_3 equivalent.

4.2.2.3 Mass Spectrometer Analyses

About 15 mg of powdered-soil (400-500 μg for pendants) samples were placed in Exotainer tubes (Pyrex). The tubes were pre-heated to 72 $^{\circ}\text{C}$ (suggested by manufacturer). A Thermo-Quest-Finnigan-GasBench-II mass spectrometer with continuous flow technology was used to measure $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ isotopes. Helium gas is used instead of a vacuum to clean the tubes of other gases in this method. Then phosphoric acid (99%) is injected into the samples and after a 15 minute CO_2 headspace samples from the tubes were taken to analyze for stable C and O isotopes. Two International Atomic Energy Agency (IAEA) standards (NBS18 and NBS19) were used to adjust the data for temperature and machine accuracy, at the beginning and after each seven samples. The reproducibility of this method for C and O isotope ratios is ± 0.1 and $\pm 0.2\text{‰}$, respectively.

The results of the isotope analyses are expressed in δ notation in units of per mil (‰):

$$\delta^{13}\text{C} \text{ or } \delta^{18}\text{O} = \left(\frac{R_s}{R_{st}} - 1 \right) \times 1000 \quad [4.1]$$

where $R_s = {}^{13}\text{C}/{}^{12}\text{C}$ or ${}^{18}\text{O}/{}^{16}\text{O}$ ratio in sample, and R_{st} corresponding stable isotope ratio in the reference standard (Friedman and O'Neil, 1977). The δ values for the $\delta^{13}\text{C}$ is reported relative to Vienna Pee Dee Belemnite (VPDB), and for $\delta^{18}\text{O}$ it is relative to Vienna Standard Mean Ocean Water (VSMOW).

The Dry Brown and Brown soils were combined to calculate the amount of pedogenic carbonate for the Brown soil zone. The percentage of newly formed carbonates within a 120 cm depth of soil is calculated from the C isotopic composition by using equation [2.3] in section 2.4.5. In the equation $\delta^{13}\text{C}$ (soil), $\delta^{13}\text{C}$ (pm), and $\delta^{13}\text{C}$ (new) represent the stable C isotopic composition of the carbonate in the bulk soil, lithogenic (original carbonate rocks with $\delta^{13}\text{C}$ of -0.8‰), and the pure pedogenic carbonates (collected from pendants). Where there were no pendants in soil profiles such as the Rego Black Chernozem soils, the fractionation value between organic C and pedogenic carbonate for each soil zone was used to calculate the percentage of pedogenic carbonate.

4.2.4 Mineralogical Analyses

4.2.4.1 XRD Pattern

The mineralogy of parent materials (original carbonate pebbles) and pedogenic carbonate (from pendants) were determined by the X-ray diffraction (XRD) technique. Pendant samples from Cca horizons were selected and carbonates were removed physically (using sharp sculpture) then ground and mounted on glass slides by adding a few drops of acetone. The XRD analysis was carried out using Rigaku X-ray diffractometer with $\text{Fe K}\alpha$ radiation, and a graphite crystal monochromator.

4.2.4.2 Scanning Electron Microscopy

Pendants were crushed to separate the carbonate from rocks for study using scanning electron microscope (SEM). Carbonate pieces from outside and inside faces of pendants were mounted on Al stubs using double-sided tape, then coated with gold and examined with a Philips 505 SEM.

4.3 RESULTS AND DISCUSSIONS

4.3.1 Mineralogical Identification

X-ray diffraction analysis indicated that randomly selected carbonate pebbles from parent materials were entirely dolomite (Fig 4.1). The $\delta^{13}\text{C}$ values of these pebbles were considered as lithogenic carbonate in calculations.

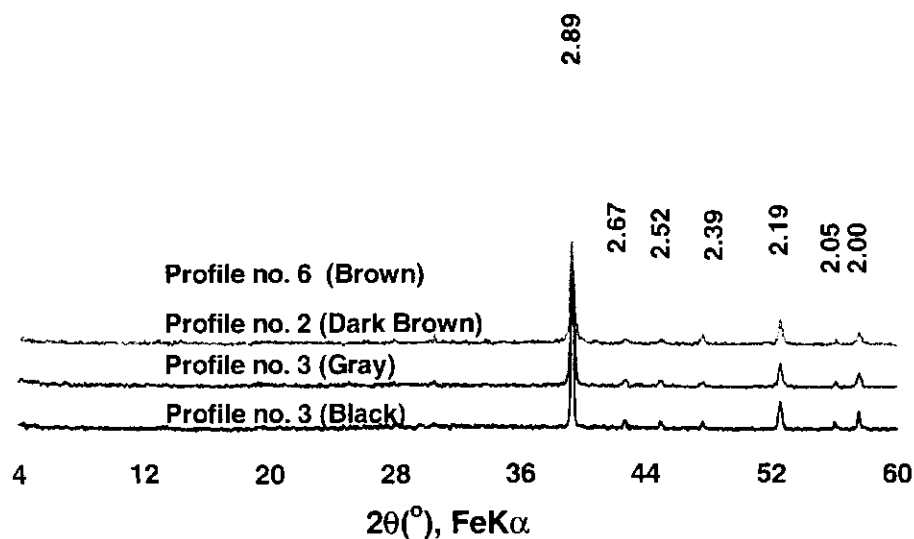


Figure 4.1 X-ray diffractograms of finely ground carbonate pebbles from the soil parent materials (rocks).

Calcite with a d-spacing of 3.01 Å was the dominant mineral in pendants from carbonate accumulation zones in all except Dark Brown soils (Fig. 4.2). A shift in the calcite peak from 3.03 Å to 3.01 Å is an indication of the presence of Mg-bearing calcite as reported by St. Arnaud and Herbillon (1973) for Saskatchewan soils. The Mg/Ca ratios in the soil solution and from pendants dissolved with HCl show that the ratio increases with increased electrical conductivity, as does the possibility of carbonate precipitation as Mg-bearing calcite (Appendix A).

Some pendants contained minor amounts of quartz and dolomite. Because only pendants on non-carbonate pebbles were selected, the peak for dolomite could be due to small dolomite particles entrapped during the formation of the pendant. Wang and Anderson (1998b) also reported trace amounts of dolomite and silicate minerals in pendants on non-calcareous clasts.

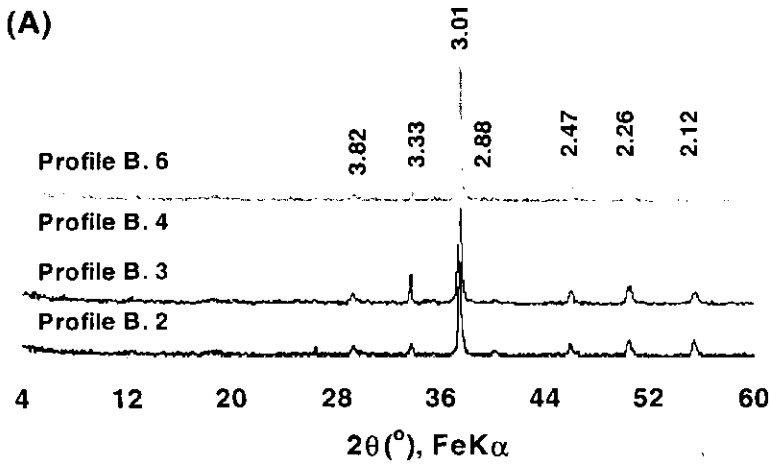
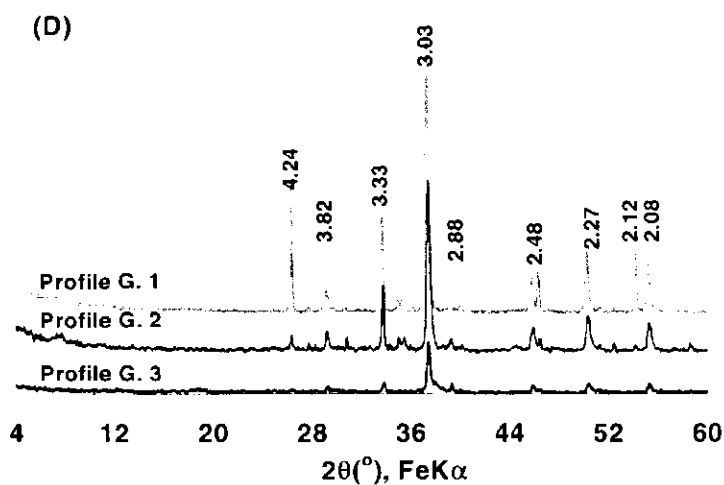
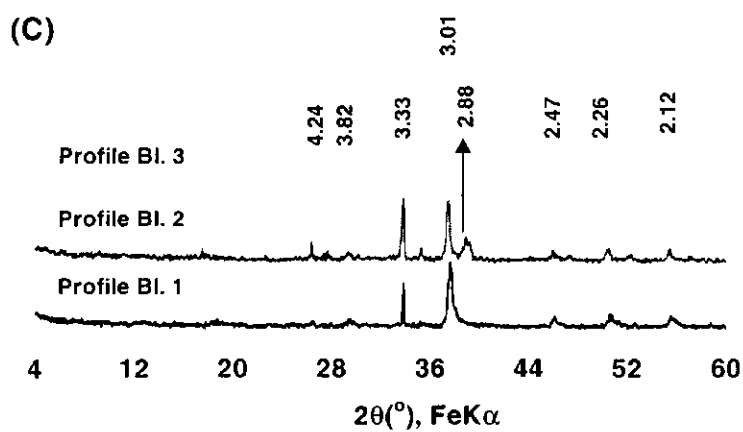
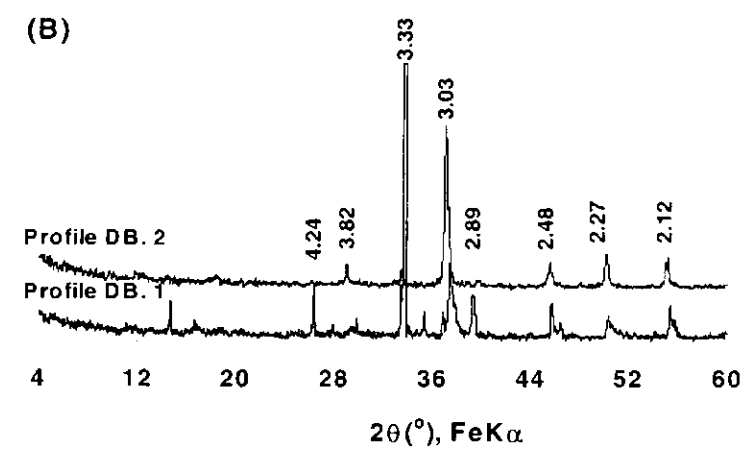


Figure 4.2 X-ray diffractograms of pendants from Brown (A), Dark Brown (B), Black(C), and Gray (D) soils.



Cont. Figure 4.2 X-ray diffractograms of pendants from Brown (A), Dark Brown (B), Black(C), and Gray (D) soils.

The internal part of the pendant was much more crystalline than the surface layers as observed by SEM (Fig.4.3). The outer layers are more recently deposited (Amundson et al., 1989), were soft and porous, and consisted of calcite with minor amount of quartz and dolomite. The inner laminae were denser and more crystalline than the outer layer. Different morphological forms of pedogenic carbonate (calcite) are typical of Saskatchewan soils (Mermut and St. Arnaud, 1981a,b; Wang and Anderson, 2000).

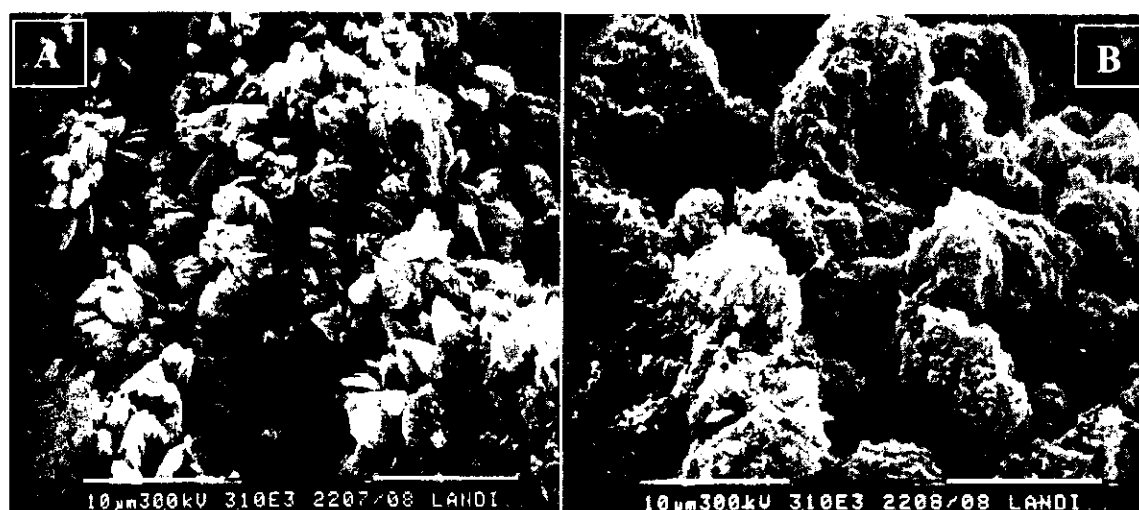


Figure 4.3 Scanning electron micrographs of pedogenic carbonate from the inner (A) and outer (B) layers of a carbonate pendant.

4.3.2 Stable Isotope Composition of Pedogenic Carbonate

There is a positive correlation between the $\delta^{13}\text{C}$ values of pedogenic carbonate and organic C in the soils studied (Fig. 4.4), indicating that the $\delta^{13}\text{C}$ value of pedogenic carbonates reflect the relative contribution of C_3 and C_4 in vegetation to the organic matter. The $\delta^{13}\text{C}$ value of pedogenic carbonate decreases to a 50 cm depth, below which the values are almost constant (Fig. 4.5).

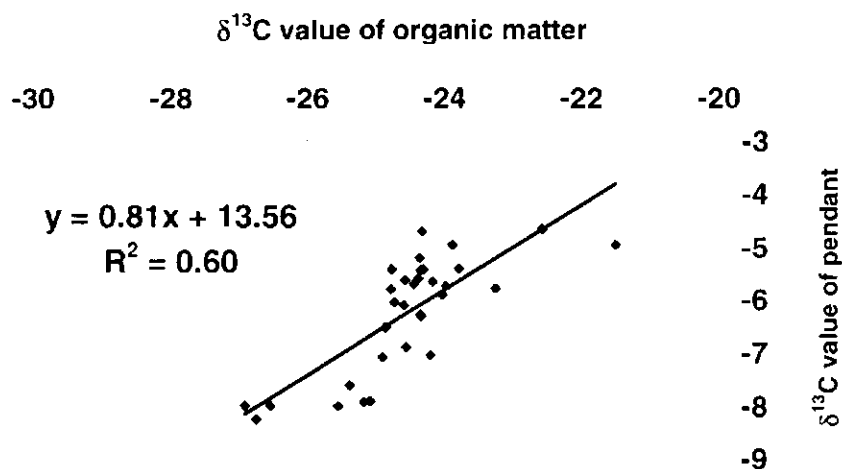


Figure 4.4 Relationship between $\delta^{13}\text{C}$ values (‰ vs. VPDB) of organic carbon and the pedogenic carbonate of carbonate pendants from the same depth.

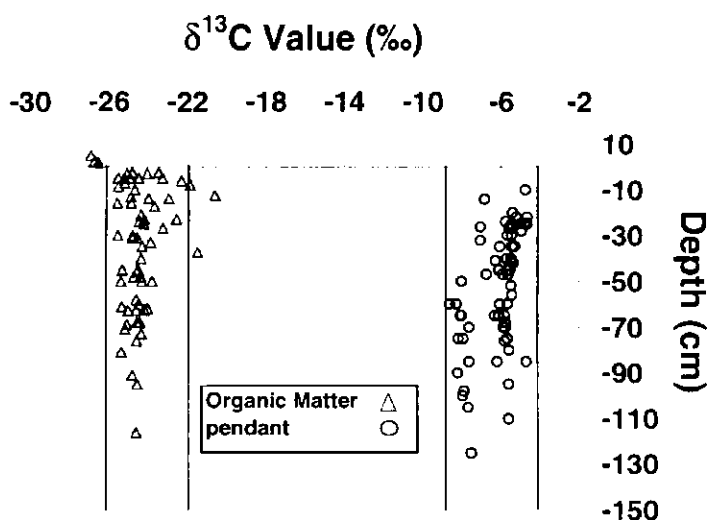


Figure 4.5 Relationship between $\delta^{13}\text{C}$ values of organic carbon and the $\delta^{13}\text{C}$ value of pedogenic carbonate with depth.

This depletion in ^{13}C may well be due to different climate and vegetation in the past, during the time of pedogenic carbonate formation. Studies by Ritchie (1987) and Yansa and Basinger (1999) based on using pollen records postulated, that the grasslands

region was covered by an open spruce woodland for a period of at least several thousand years following deglaciation. The spruce woodland was replaced by deciduous parkland vegetation that persisted until about 8,800 BP. A warm and dry climate resulted in a transition to grassland about 5,800 BP.

The contribution of atmospheric CO₂ to the formation of pedogenic carbonate is considered insignificant (Cerling, 1984). Changes in $\delta^{13}\text{C}$ values mainly reflect the changes in the vegetation. Kelly et al. (1991) reported that at Cheyenne Wells in Colorado the $\delta^{13}\text{C}$ values of pedogenic carbonate at depth is 3‰ less than expected from current vegetation, and concluded that the pedogenic carbonate formed under different vegetation with more C₃ plants than those of present day.

In the six Brown soils, the average $\delta^{13}\text{C}$ value of pedogenic carbonate in carbonate pendants is -6.0‰ with a high value of -4.6‰ at 25cm depth for B.5 and a low value of -7.9‰ at 25cm depth for B.2 (Fig. 4.6). There is a slight trend to depletion in ^{13}C with depth for all the profiles except for B.1 and B.6, in which there is an increase of about 0.8‰ at the 45-cm depth. The same trend is found for oxygen isotopic values of pedogenic carbonate (Fig. 4.6). The decrease with depth supports the idea that climate and vegetation were different at the time when most of the pedogenic carbonates were forming.

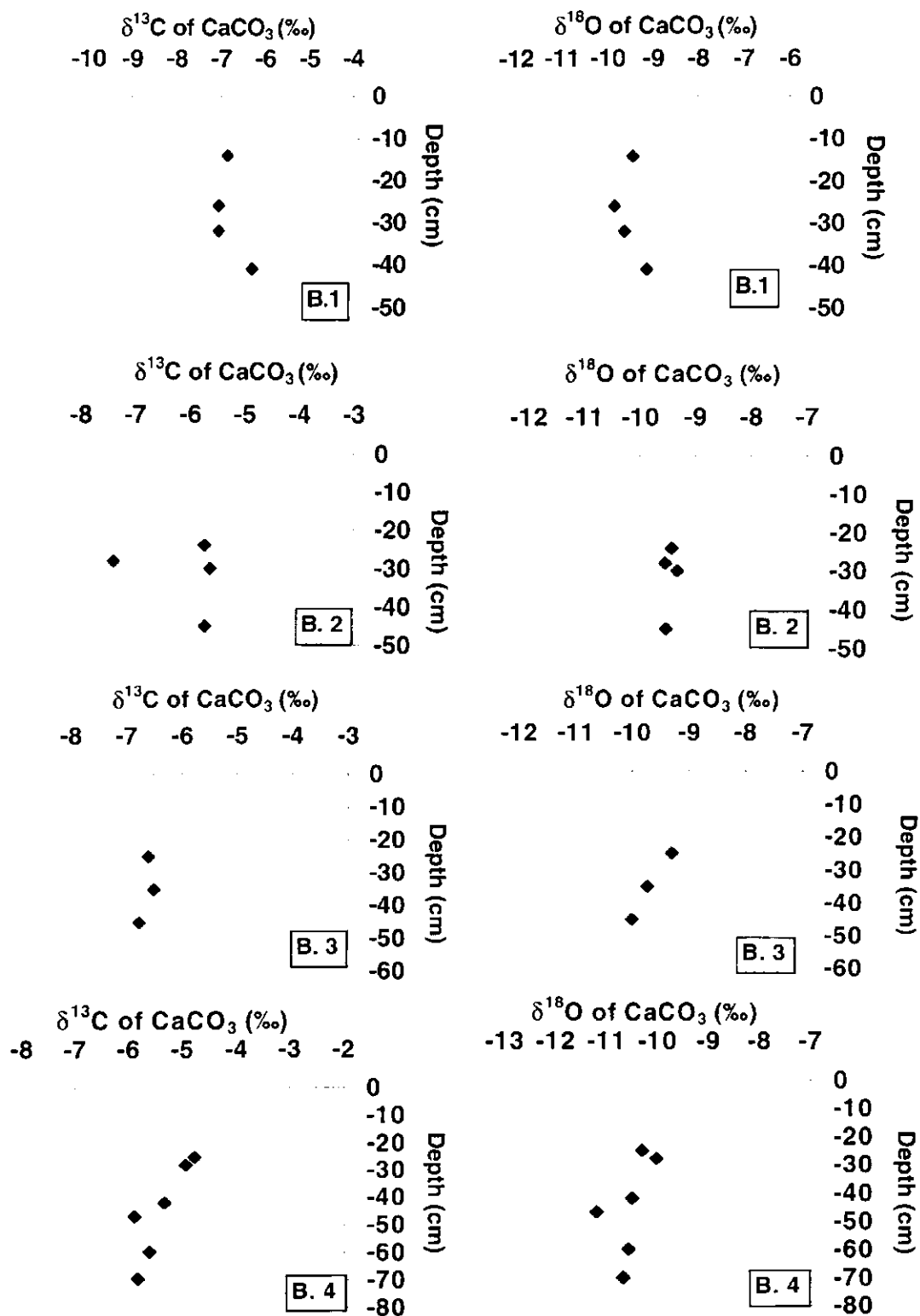
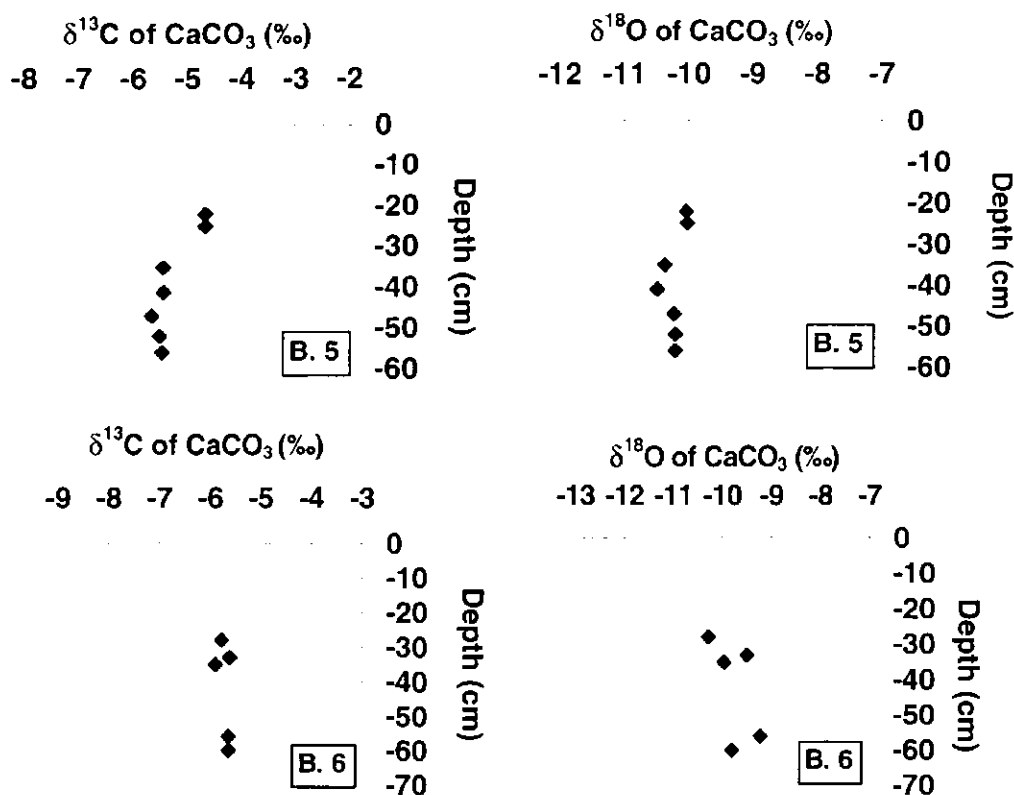


Figure 4.6 Relationship between carbon and oxygen isotopes of pedogenic carbonates with depth in Brown soils. Each point is the mean of at least two replicates that are within $\pm 0.15\text{‰}$ of the mean.



Cont. Figure 4.6 Relationship between carbon and oxygen isotopes of pedogenic carbonates with depth in Brown soils. Each point is the mean of at least two replicates that are within $\pm 0.15\%$ of the mean.

In Dark Brown soils, the mean $\delta^{13}\text{C}$ value for pendants is about -5.5% with a high value of -4.7% at 10cm depth and a low value of -6.1% at 45cm depth for DB.2 (Fig. 4.7). The $\delta^{13}\text{C}$ values for pendants in Dark Brown soils are consistent with values (-4 to -6%) reported by Wang and Anderson (1998b) for Dark Brown soils in southeastern Saskatchewan. Considering average $\delta^{13}\text{C}$ values of organic matter (-24.5%) for the whole profile and the average $\delta^{13}\text{C}$ value of pendants (-5.5%), the fractionation between organic and pedogenic carbonate for Dark Brown soils is 19.0% . This value is higher than the theoretical values of 14% to 17% (Cerling and Quade, 1993).

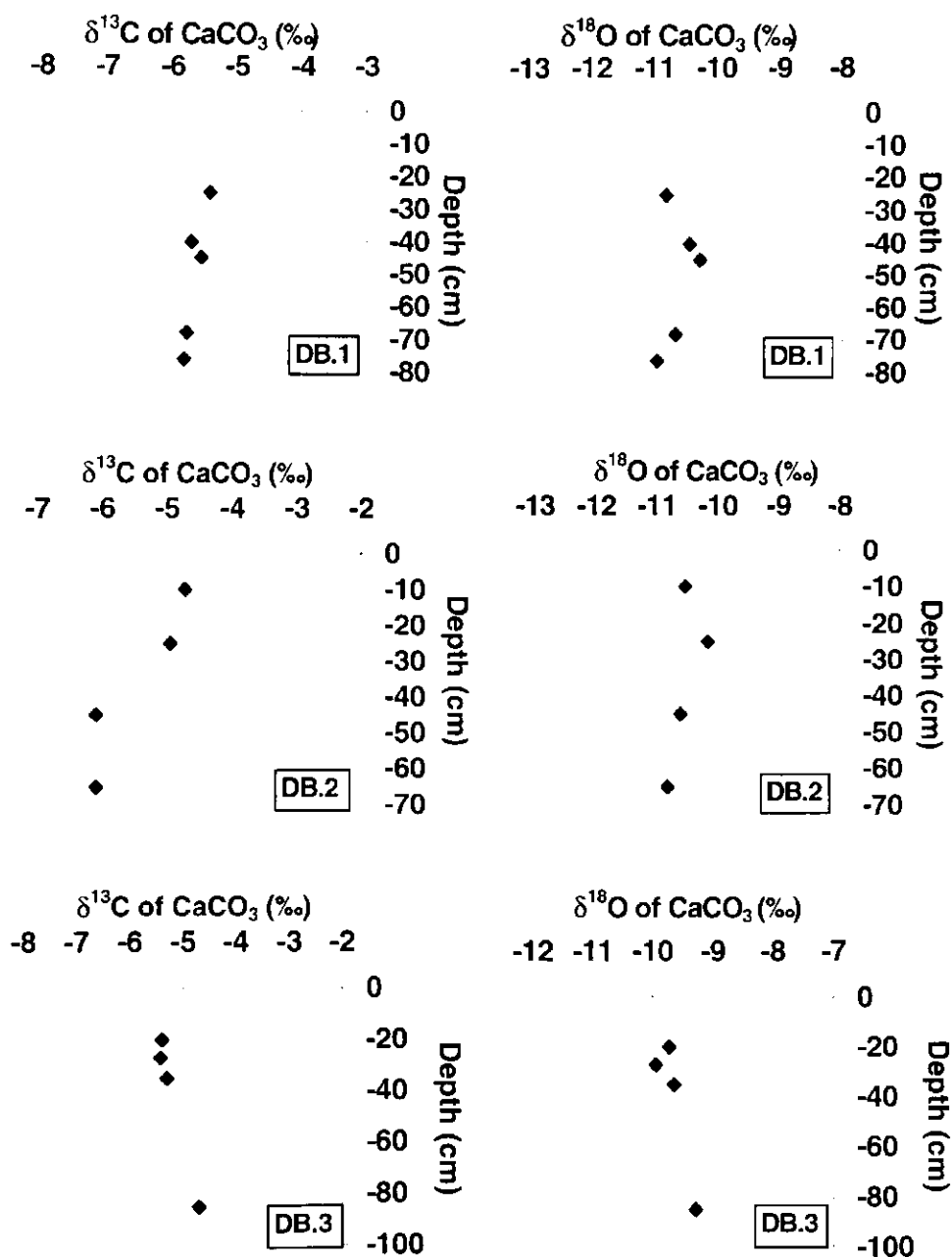


Figure 4.7 Relationship between carbon and oxygen isotopes of pedogenic carbonates with depth in Dark Brown soils. Each point is the mean of at least two replicates that are within $\pm 0.15\text{‰}$ of the mean.

Ferguson et al. (1991) also reported the high fractionation value of 19.0‰ for organic matter and calcite for Cretaceous sediments. The enrichment in ^{13}C could be due

to rapid loss of moisture and a greater gas exchange between the soil and the atmosphere through large voids and cracks between pendants and the soil. This could cause disequilibrium between CO_2 and CO_3^{2-} in soil solution (Rabenhorst et al., 1984b). Another reason could be fractionation of organic matter during respiration by decomposer organisms, resulting in more positive $\delta^{13}\text{C}$ values than the organic matter (Natelhoffer and Fry, 1988). There is also a possibility of cooler temperature during precipitation of CaCO_3 , which results in more positive $\delta^{13}\text{C}$ values.

The $\delta^{13}\text{C}$ value of pendants decreases with depth except for DB.3 (Fig. 4.7), which may be related to the composition of past vegetation. Considering all of the profiles in the Dark Brown zone, there is a good correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotopes of pendants with depth. These two isotopes, therefore, can be used to study the past vegetation and climate in the region.

For Black soils, the average $\delta^{13}\text{C}$ value of pendants is -5.9‰ with a high value of -5.2‰ occurring for profile Bl.1 at 22cm depth and a low value of -6.7‰ occurring for Bl.3 at 47cm depth. The values are slightly more positive than those of -7.4‰ and -9.0‰ reported by Wang and Anderson (1998b) for Black soils. There is a fractionation of 18.8 between the average $\delta^{13}\text{C}$ value of organic matter for the whole profile and the average $\delta^{13}\text{C}$ value of pendants. The $\delta^{13}\text{C}$ value of pendants slightly decreases with depth in Bl.1 and Bl.2, which may be related to a greater contribution from C_3 plants in the past (Fig. 4.8).

In Bl.3 there is an increase in $\delta^{13}\text{C}$ value with depth, becoming almost constant below 75 cm, suggesting that the vegetation in the past was not that much different from

the present. In this region there is a high correlation between O and C isotopes of pendants in Bl.1 and Bl.3 with depth, but in Bl.2, $\delta^{18}\text{O}$ value become more negative with depth (Fig. 4.8). This is likely due to differences in the source of water or cooler temperature in the past.

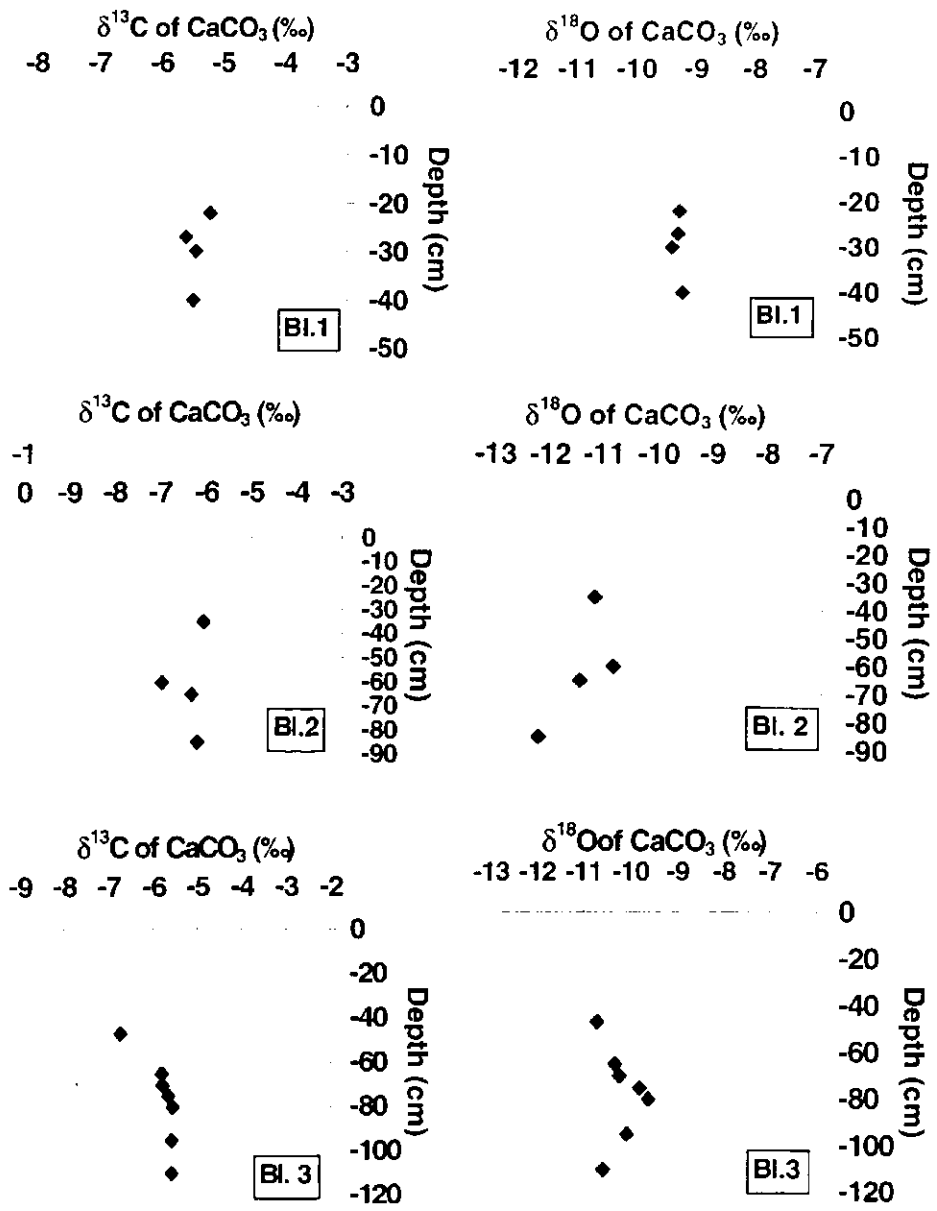


Figure 4.8 Relationship between carbon and oxygen isotopes of pedogenic carbonates with depth in Black soils. Each point is the mean of at least two replicates that are within $\pm 0.15\text{‰}$ of the mean.

The average $\delta^{13}\text{C}$ value of pendants in Gray soils is -7.8‰ with a high value of -6.9‰ for G.1 at 95cm depth and a low value of -8.6‰ for G.2 at 60cm depth (Appendix C). Considering the average $\delta^{13}\text{C}$ value of organic matter for all the profiles (-25.6‰) and average $\delta^{13}\text{C}$ value of pendants was calculated as -7.8‰ with a fractionation of 17.8‰ for Gray soils. There is a consistent relationship between the O and C isotopes of pendants in profiles G.1 and G.2 (Fig. 4.9). In profile G.3, the $\delta^{13}\text{O}$ value at depth is smaller than in the pendants in upper horizons. This is likely due to the influence of different climate conditions at the time of pedogenic carbonate formation. It is possible that a large proportion of the water was coming from the melting of snow, as in general, snow has lower $\delta^{18}\text{O}$ value than the rain.

4.3.3 Amount and Rate of Pedogenic Carbonate Accumulation

A $\delta^{13}\text{C}$ of -0.8‰ was used as an average for the parent material or lithogenic carbonates. The highest proportion of pedogenic carbonate is in the calcic horizon, where it may account for 100% of the carbonate. The lowest proportion of pedogenic carbonate is in the deepest Ck horizon, which is entirely lithogenic (Appendix C). The findings, based on stable isotope methodologies, that virtually all the CaCO_3 in Cca (Ck based on Soil Taxonomy, Soil Survey Staff 1998) horizons is pedogenic in origin is surprising. It is highly unlikely that all lithogenic carbonate was removed, and then replaced by pedogenic carbonate. Rather, it appears that there is an *in situ* reaction, during which

biogenic C from CO₂, originating initially from the vegetation, replaces the C present in lithogenic carbonates by dissolution and reprecipitation.

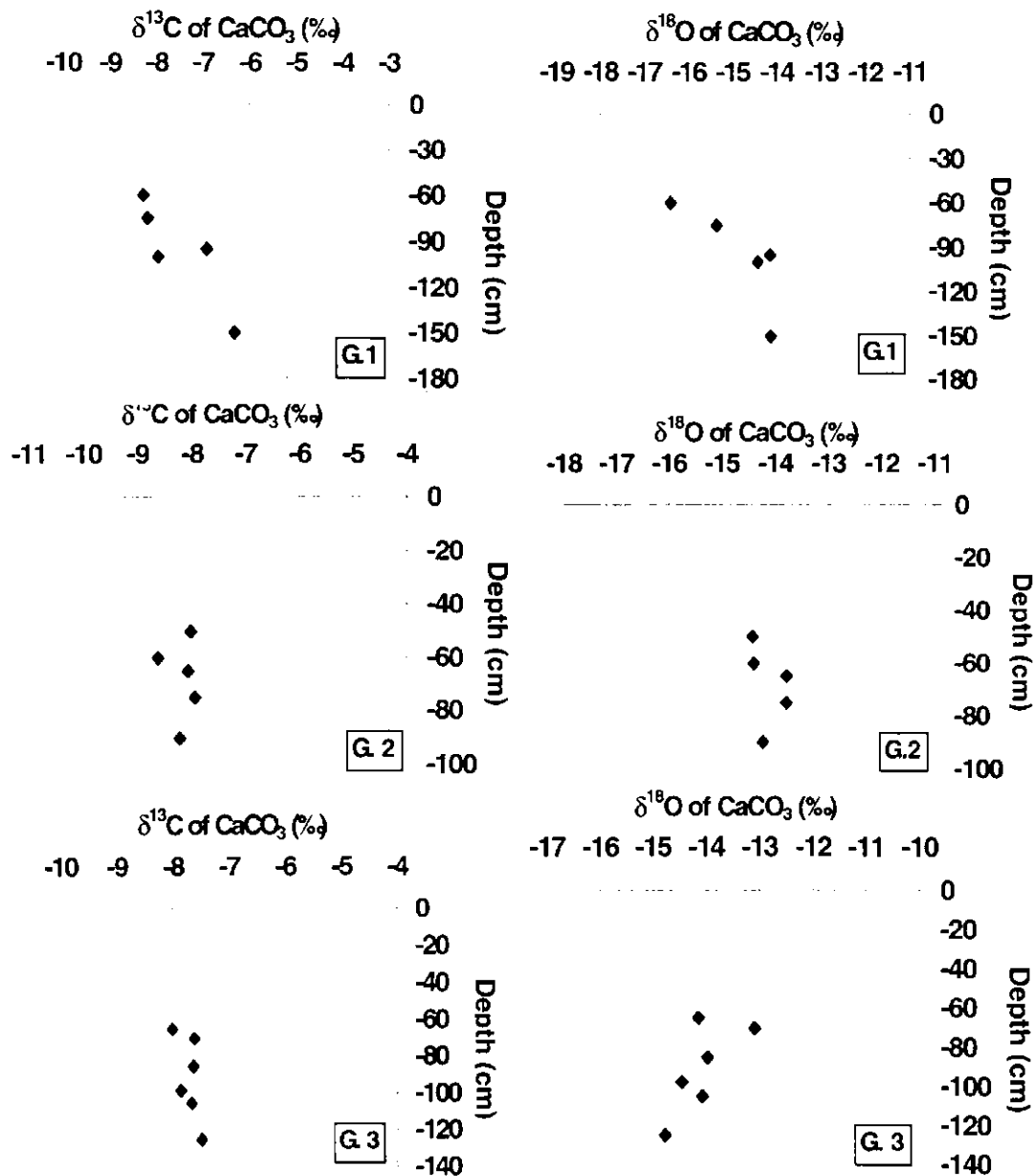


Figure 4.9 Relationship between carbon and oxygen isotopes of pedogenic carbonates with depth in Gray soils. Each point is the mean of at least two replicates that are within $\pm 0.15\text{‰}$ of the mean.

The amount of pedogenic carbonates in Brown soils ranges between 100.8 and 161.8 kg m⁻² with an average value of 132.9 kg m⁻². For Dark Brown soils, the range is

between 102.1 kg m⁻² and 172.7 kg m⁻², with an average of 143.3 kg m⁻². For Black soils, the minimum, maximum, and average values are 116.5, 156.6, and 133.8 kg m⁻², respectively, and are close to the value (100-134 kg m⁻²) reported by Wang and Anderson (2000) for Black soils. In the Gray soil zone the comparable values are 151.2, 179.4, and 163.9 kg m⁻². For Rego Black Chernozem soils the amount of pedogenic carbonates range between 98.3 and 120.9 kg m⁻², with an average of 110.0 kg m⁻² (Table 4.1).

Table 4.1 Total pedogenic carbonate (kg m⁻²) to 120-cm depth in a sequence of Brown to Gray soils

Soil Zone	Profile 1	Profile 2	Profile 3	Average	Profile 4	Profile 5	Profile 6
Brown	100.8	141.1	105.8	132.9	161.8	134.8	153.3
Dark Brown	159.6	172.7	97.7	143.3			
Black	156.6	128.2	116.5	133.8			
Gray	179.4	151.2	161.1	163.9			
Rego Black Chernozem	98.3	120.9	110.8	110.0			

According to Soil Taxonomy (Soil Survey Staff, 1998), Brown, Dark Brown and Black classified as Mollisols, and Gray soils are classified as Alfisols. We took the area covered by soil orders from Eswaran et al. (2000) to estimate total pedogenic carbonate accumulation in soils. Results from this study indicate that estimates are higher for Alfisols (Gray Luvisol) and Mollisols (Chernozems). Accepting the of Eswaran et al. (2000) numbers for pedogenic carbonate in Entisol, Inceptisol, Aridisols, Gelisol, and Vertisol orders, and with new estimates for Mollisols and Alfisols, total pedogenic carbonate accumulation in soils is calculated 1,179 Pg, which is 1.25 times the estimate by Eswaran et al. (2000).

There is an increase of total pedogenic carbonate from the southwest to northeast in Saskatchewan despite the fact that the time for soil formation decreases in the same direction (Fig. 4.10). This is similar to organic matter contents, suggesting that both organic and inorganic C pools are affected by similar environmental conditions. Biomass productivity increases with increased moisture, as does the weathering of carbonates and other minerals supplying the Ca that is precipitated with largely biogenic C from plant respiration and residues. There is more pedogenic carbonate in the Dark Brown soils than in the Black soils. The larger mass of pedogenic carbonate in Dark Brown than Black soils may be due to microtopographic effects, resulting in thicker A and B horizons, more weathering, and more Ca available to form pedogenic carbonate.

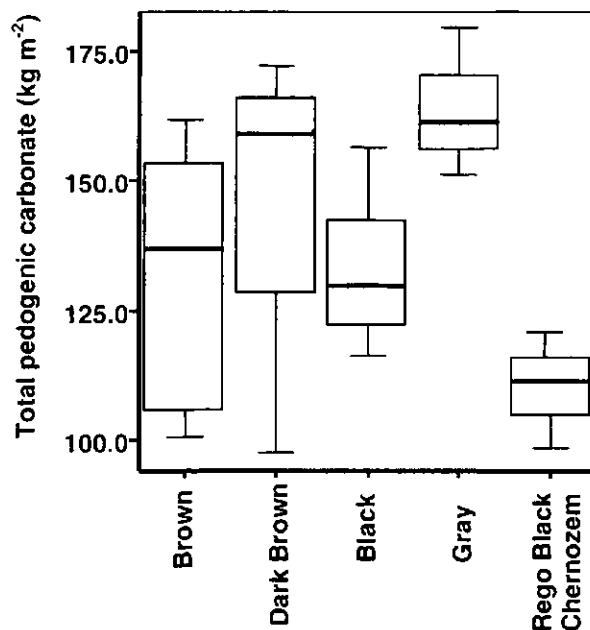


Figure 4.10 Total pedogenic carbonate storage to 1.2-m depth in a sequence of Brown to Gray soils. The boxes show the central 50% of the values with the median. Whiskers show 25th and 75th centiles. There were three or more replicates of each soil group.

The average amount of C stored in the form of pedogenic carbonate for each soil zone is 15.9, 17.2, 16.1, 19.7, and 13.2 kg C m⁻² for Brown, Dark Brown, Black, Gray and Rego Black Chernozem soils, respectively. By comparison organic C stores in the same soils are 9.1, 11.7, 14.9, 9.63, and 21.0 kg C m⁻². The mass of C stored as pedogenic carbonate is higher than the organic C, especially for the Brown and Gray soils. Radiocarbon (¹⁴C) ages suggest a mean turnover time for organic C of a few hundred years (Anderson and Paul, 1984; Trumbore et al., 1996), whereas it is likely that the pedogenic carbonate sink will continue to increase for tens of thousands of years (Lal and Kimble, 2000).

The rate of pedogenic carbonate accumulation generally increases from the southwest to northeast, at 8.3, 11.4, 11.2, 14.3, 9.6 g m⁻² yr⁻¹ for Brown, Dark Brown, Black, Gray, and Rego Black Chernozem soils (Fig. 4.11). With the time of exposure decreasing from 17,000 yr in the southwest to 11,500 yr in the northeast, however, there is a gradual increase in the rate of formation.

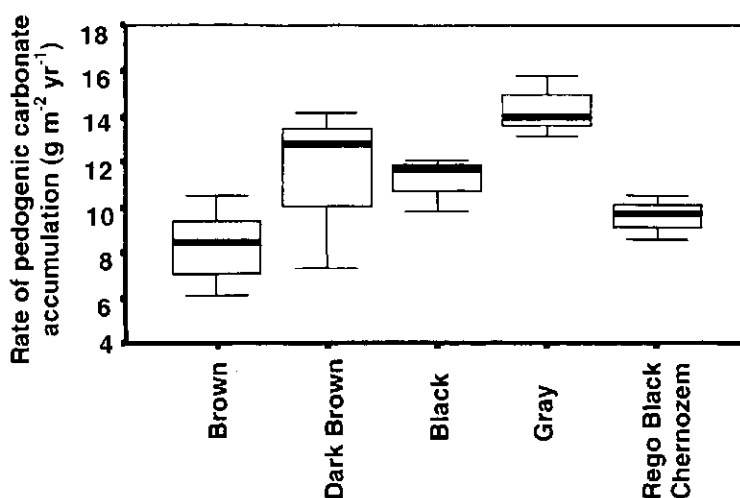


Figure 4.11 Rate of pedogenic carbonate accumulation in a sequence of Brown to Gray soils. The boxes show the central 50% of the values with the median. Whiskers show 25th and 75th centiles. There were three or more replicates of each soil group.

Using the net primary production (NPP) data and rate of C accumulation as inorganic C, it is calculated that about 0.45% of NPP C can be accumulated as inorganic C. On average the rate is about 1.4 times higher than that calculated for organic C (0.32%) (Tables 3.2, 4.2). This rate shows that in the long term, pedogenic carbonate plays an important role in the C cycle and, given enough time, will sequester more C than organic matter.

Table 4.2 Relationship between NPP and pedogenic carbon accumulation.

Soil Zone	Aboveground ^a NPP (g m ⁻² yr ⁻¹)	Belowground ^b NPP (g m ⁻² yr ⁻¹)	Rate of C (in pedogenic carbonate) accumulation (g m ⁻² yr ⁻¹)	NPP accumulation as inorganic C %
Brown	323.8	136.0	0.99	0.47
Dark Brown	464.7	195.2	1.37	0.46
Black	490.1	205.9	1.34	0.43

^a Based on Saskatchewan Agriculture and Food report (2001).

^b Calculated based on 42.6% belowground reported by Slobodian (2001).

There is a high correlation between C and O compositions of pedogenic carbonates (Fig. 4.12). The $\delta^{18}\text{O}$ value of pedogenic carbonate decreases with decreasing $\delta^{13}\text{C}$ value. Soil water and temperature mainly control the oxygen isotopic composition of pedogenic carbonate (Cerling, 1984; Amundson and Lund, 1987; Cerling and Quade, 1993). The decrease in temperature and increase in precipitation from southwest to northeast result in C_3 plants becoming more dominant, and the depletion of ^{13}C in residues, organic matter, soil CO_2 and pedogenic carbonate, sequentially. Meteoric waters

become more depleted in ^{18}O in moving toward higher latitudes because of cooler temperatures (Cerling and Wang, 1996). These findings are consistent with those from other studies (Schlesinger et al., 1989; Cerling and Quade 1993; Khademi and Mermut, 1999).

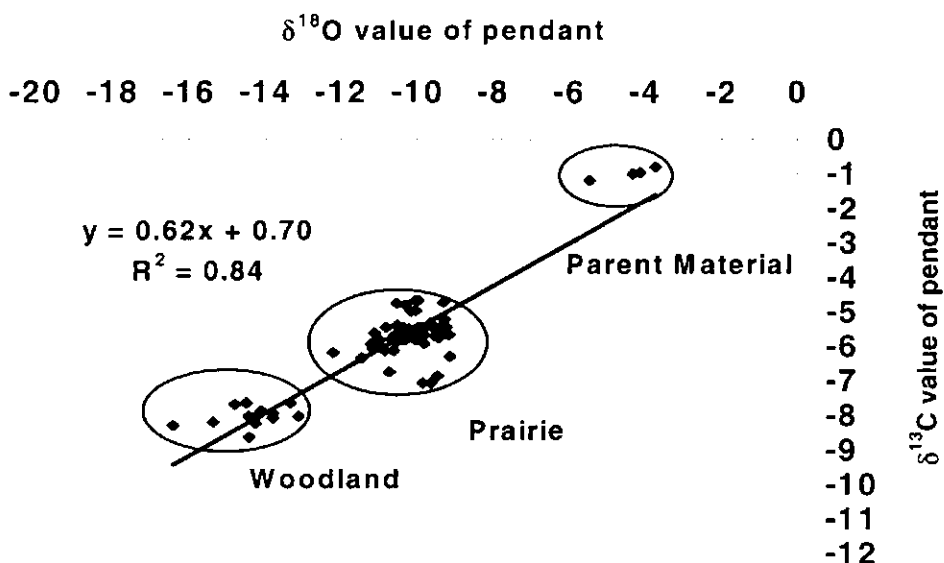


Figure 4.12 Relationship between $\delta^{13}\text{C}$ (‰ vs. VPDB) and $\delta^{18}\text{O}$ (‰ vs. VSMOW) of carbonates in Brown to Gray soils.

There is also the possibility that a larger proportion of the precipitation in the northern part of Saskatchewan is from the Pacific Ocean, and a larger proportion of the precipitation in southern Saskatchewan originate in the Gulf of Mexico (McMonagle, 1987). These two precipitation sources have different isotopic composition. Cooler meteoric water is more depleted in ^{18}O than warmer water. The O and C isotopic composition of parent materials are completely different from pedogenic carbonate, showing that they are related to marine sediments and formed under different environmental conditions than pedogenic carbonate.

Average annual rainfall of each zone is used and plotted against the rate of pedogenic carbonate formation. There is a high, positive correlation between precipitation and the average rate of pedogenic carbonate accumulation. The results show that the rate of pedogenic carbonate formation increases with precipitation (Fig 4.13).

Using the simple linear regression ($Y = 17.46X + 201.83$) from the plotted data, it is possible to use the mean annual precipitation in semiarid and subhumid regions (200-700 mm) to calculate the rate of pedogenic carbonate accumulation.

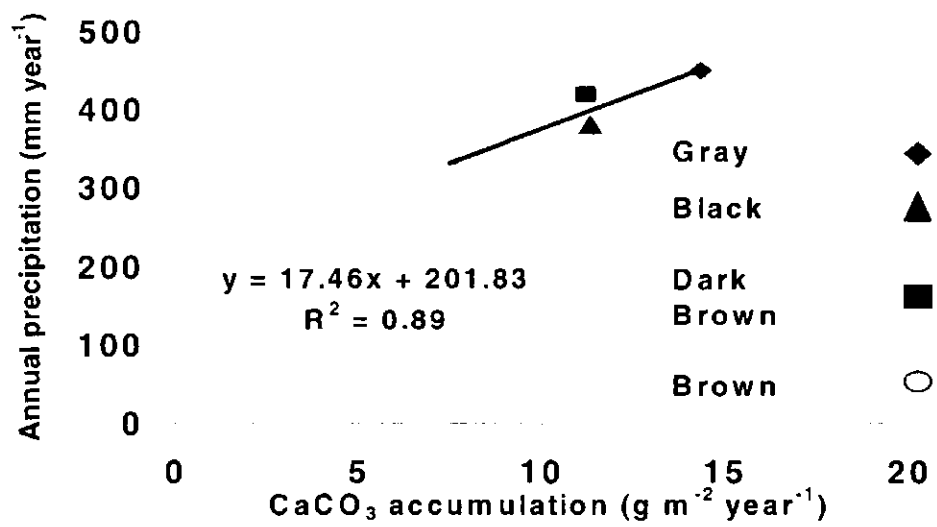


Figure 4.13 Relationship between annual precipitation and rate of pedogenic carbonate formation. There were three or more replicates of each soil group.

The rate of pedogenic carbonate formation, the total pedogenic carbonate stored in soils and the thickness of the solum all increase with increasing precipitation. This suggests that in addition to the presence of the certain amounts of bicarbonates at a given pH, the factor controlling the rate of pedogenic carbonate formation is the amount of Ca available. Deeper soils with more CaCO₃ released by weathering in the A and B horizons

will have more Ca available to precipitate again as pedogenic carbonate in Cca horizons. In addition, other Ca-bearing minerals may weather to release Ca. About 40% of the Ca-feldspars had weathered from the A and B horizons of a Gray Luvisol soil (Alfisol), double the amount weathered in a Black Chernozem or Mollisol (St Arnaud and Sudom, 1981). The precipitation of calcium carbonate from non-carbonatic sources with biogenic CO₂ represents a true additional C sink in soils.

4.4 CONCLUSIONS

Carbonate pebbles in the parent materials are dolomitic, whereas pedogenic carbonates are mainly calcite with trace amount of dolomite that are thought to be impurities. The calcite in the outer part of carbonate pendants is poorly crystalline in comparison to the more crystalline inner layers as observed by SEM.

The stable isotope data and earlier C dating reports have proven that the C in pedogenic carbonate is derived from organic matter. From the southwest to northeast across Saskatchewan, the amount and rate of pedogenic carbonate formation increases, despite the fact that the exposure time for soil formation decreases. Over the time of soil formation, the rate of C accumulation as pedogenic carbonate is 1.4 times the sequestration rate of organic C. The data obtained in this study provide an opportunity to recalculate the amount of pedogenic carbonate for the world soils. Based on available data on soils from outside of boreal regions, we calculated about 1.25 times more C in pedogenic carbonates than recent estimates.

There is a high correlation between C isotopic values of organic C and pedogenic carbonate. There is also a strong correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of pedogenic

carbonate. This means that stable isotope values of pedogenic carbonate can be utilized to reconstruct paleoclimates. There were likely cooler temperatures and more moisture, supporting more C₃ plants in the Brown, Dark Brown and parts of the Black soils in the past, which is consistent with the earlier findings that suggested a greater proportion of C₃ plants in the vegetation of southern Saskatchewan in the early Holocene.

The depth of carbonate free solum, the total pedogenic carbonate storage, and the rate of pedogenic carbonate accumulation increase with annual precipitation. Such a high correlation should enable estimations of pedogenic carbonate based on precipitation and the rate of pedogenic carbonate formation in semiarid and sub-humid environments.

The question about the significance of pedogenic carbonate formation to global C cycles remains if the main source of Ca is the dissolution of lithogenic carbonate, in that the store of C may remain relatively constant. As suggested by those carbonate accumulation horizons where the $\delta^{13}\text{C}$ methodology indicates that the carbonates are virtually all pedogenic carbonate, the reaction appears to be at least partly an *in situ* process, with carbonate of biogenic origin gradually replacing lithogenic carbonate through the dissolution of lithogenic carbonate and reprecipitation. There is more pedogenic carbonate than the amount of lithogenic carbonate lost in forest soils, especially in Rego Black Chernozem soils, suggesting that these soils sequester additional C.

CHAPTER 5

CARBON DYNAMICS IN A LANDSCAPE FROM SASKATCHEWAN, CANADA

5.1 INTRODUCTION

Soil properties vary with topographic settings due to aspect (i.e., N-facing vs S-facing) and slope shape (Birkeland, 1999). The amount and distribution of pedogenic carbonates in soils within a toposequence are controlled mainly by soil moisture. Downward movement of percolating water (descending mode), capillary rise of ground water (ascending mode), and lateral moisture flow play different roles in the different landform segments.

Knowledge about the quantitative C circulation, i.e. gains, distribution, and losses of the real amount of C that circulates within the soil system, is needed to understand soil development and ecosystem function (Warembourg and Kummerow, 1991).

Landscape position influences the nature and extent of erosion or deposition processes occurring at any given location in a field (Mermut et al., 1983; Pennock and de Jong, 1987). The degree of past erosion affects the distribution of soil organic matter in the soil profile and among various aggregates and primary particles (Bajracharya et al., 1998). With cultivation, shoulder complexes lose soil and organic C, with gains in lower slope and footslope complexes (Pennock et al., 1994). The thickness of Ap/Ah horizons follows the

same trend. The differences in soil properties among the landscape elements are related to the water movement and distribution in hummocky terrain (Pennock et al., 1987). Generally, non-carbonated and leached soils occur in concave recharge areas, and carbonated soils occur in ground water discharge areas, particularly on lower slopes adjacent to recharge depressions (Miller et al., 1985).

The depth to which calcium carbonate is leached, and the thickness, density, and percentage of calcium carbonate in the calcic horizon are closely associated with parent material, permeability, texture, structure, and with the length of time the soil has been developing (Harper, 1957). Honeycutt et al. (1990a) found that the shoulder and upper backslope had much shallower depth to carbonate accumulation zone when compared with the summit. The possible explanation for this observation was that greater erosion on the shoulder and backslope segment has resulted in shallower depths to the secondary carbonate accumulation zone.

Although the major reasons for differences in $\delta^{13}\text{C}$ of plants are the C_3 and C_4 pathways, environmental factors such as soil moisture availability, salinity, and landscape position induce small changes in $\delta^{13}\text{C}$ values, other factors such as life span, genetic variation, and photosynthesis capacity being equal. Most of these factors will change across a landscape in response to slope, aspect, elevation, soil type, and other characteristics of a landscape that result in environmental gradients (Boutton, 1996). Therefore, variation in $\delta^{13}\text{C}$ value of soil C is expected across a landscape.

The $\delta^{13}\text{C}$ value of pedogenic carbonate becomes more depleted moving from the lower slope to the middle and upper slope soils. Depressional areas with strongly eluviated Luvic Gleysols (Argiaquolls) had much less carbonate, and little or no

pedogenic carbonate, whereas Rego Black (Calcicryolls) soils just above the depression had marked gains in pedogenic carbonate (Wang and Anderson, 2000). The influence of aspect on microclimate and soils is greatest between 40° to 60° latitude, and less important in both equatorial and polar latitudes (Hunkler and Schaetzl, 1997).

The objective of this part of the work was to evaluate the effect of landscape on the formation and distribution of pedogenic carbonate and organic matter in a hummocky landscape using the stable isotope geochemistry technique.

5.2 MATERIALS AND METHODS

5.2.1 Study Area and Sampling

A non-cultivated, hummocky landscape with glacial till parent material was chosen for the study. The site located 12 km east of Saskatoon (52° 20' N, 106° 38' W) had mostly Dark Brown Chernozem (Typic Haplocryolls) soils of the Weyburn Association with some Black Chernozem (Udic Haplocryolls) soils of the Oxbow association (Acton and Ellis, 1978). The site is transitional between the Moist Mixed Grassland and Aspen Parkland ecoregions. A grid sampling design with 10-m cell spacing was constructed, and topographic observations were taken at each node using a laser-based Total Station. The dimension of the grid was 110 m by 100 m. Four transects that were part of the grid were studied in more detail, two south-north and two east-west. Soil profiles were described and sampled to a depth of one meter with an auger 7.5-cm in diameter. Samples were taken from the center of each (10 m x 10 m) grid cell. Also, two profiles, one on the shoulder complex position and the other in the

depression, were dug, described in detail, and sampled. The Topo Suite software program by Pennock and Elliott (2000) was used to specify landform elements and landform complexes for each grid cell, based on slope morphological and positional characteristics as defined by Pennock et al. (1987; 1994). A 3-D map is produced by using the Surfer software program (Fig.5.1)

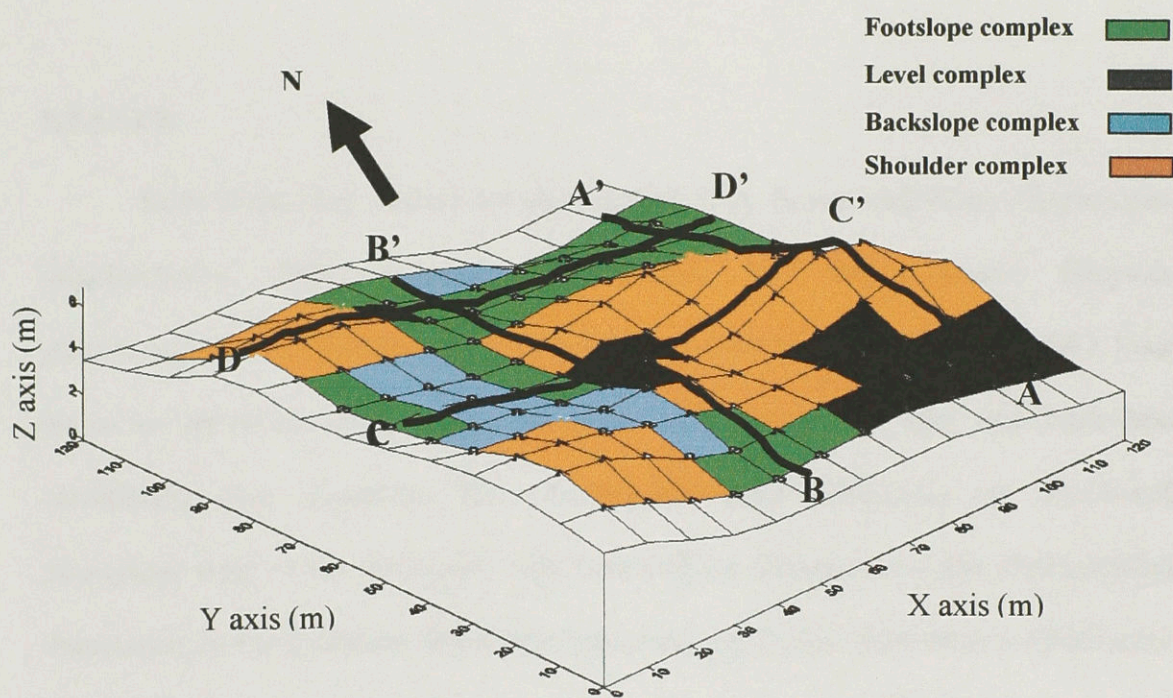


Figure 5.1 A three dimensional representation of the Dark Brown soil landscape. AA', BB', CC', and DD' are the four transects that were sampled.

5.2.2 Sample Preparation and Analytical Methods

The same methods as explained in sections 3.2.1.5, 3.2.1.6, 4.2.2.2, and 4.2.2.3 in Chapters three and four were used to measure the amount and stable isotope ratios of C and O in organic and inorganic C. The amount of pedogenic carbonates in 100 cm depth of soil can be calculated from the C isotopic composition using equation [2.4] in section 2.4.5.

In the equation, the $\delta^{13}\text{C}$ value of newly formed carbonate (pedogenic carbonate) is calculated by subtracting the calculated fractionation value for Dark Brown soils (18.6‰) from the mean $\delta^{13}\text{C}$ value of organic C for each profile.

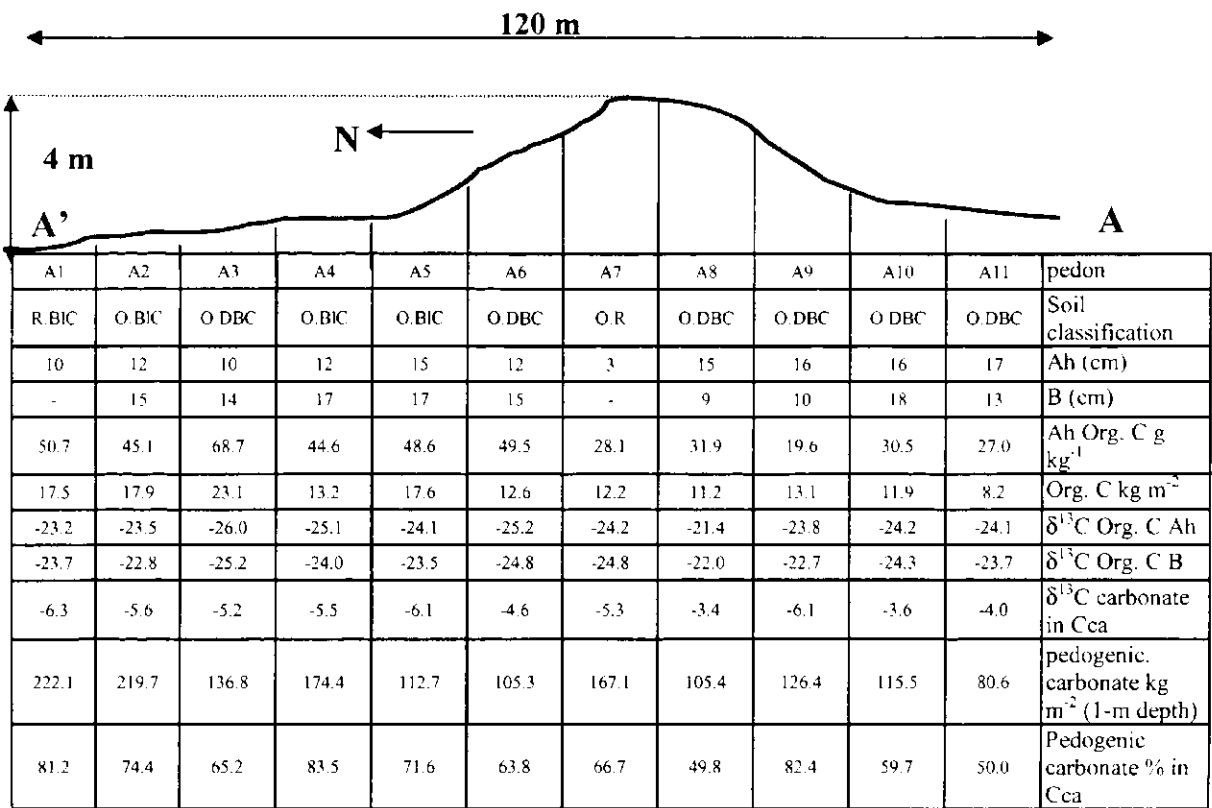
5.3 RESULTS AND DISCUSSIONS

5.3.1 Soils

Soils in the area studied are classified as Dark Brown and Black Chernozems (Haplocryolls), Orthic Regosols (Cryorthents), and Orthic Humic Gleysols (Cryoaquolls) (Soil Classification Working Group, 1998; Soil Survey Staff, 1998). Four major soil-landform element complexes (footslope, level, shoulder, and backslope complexes) were identified. The Chernozomic soils (Mollisols) are distributed throughout most of the landscape, with Orthic Black Chernozem (Udic Haplocryolls) dominating in the footslope and level complexes and Orthic Dark Brown Chernozem (Typic Haplocryolls) in the shoulder complex. Regosolic soils (Cryorthents) occur on the upper part of shoulder complexes (on knolls), and Gleysolic (Cryoaquoll) soils occur in poorly drained depressions.

The thickness of the Ah horizons ranges from 3 cm in an Orthic Regosol (Cryorthents) soil on a sharply convex shoulder position to 26 cm in a level complex position (Figs. 5.2, 5.3, 5.4, 5.5). This is consistent with Kleiss (1970) findings from northeast Iowa, and Pennock et al. (1987) from southern Saskatchewan. They reported that the thickness of A horizons and depths to calcium carbonate of the soils overall increase in the sequence of shoulder < backslope < level < footslope positions. Mermut

et al. (1983) observed thinner Ah horizons along a backslope segment in comparison to soils developed in a lower slope position of a landscape in Saskatchewan.



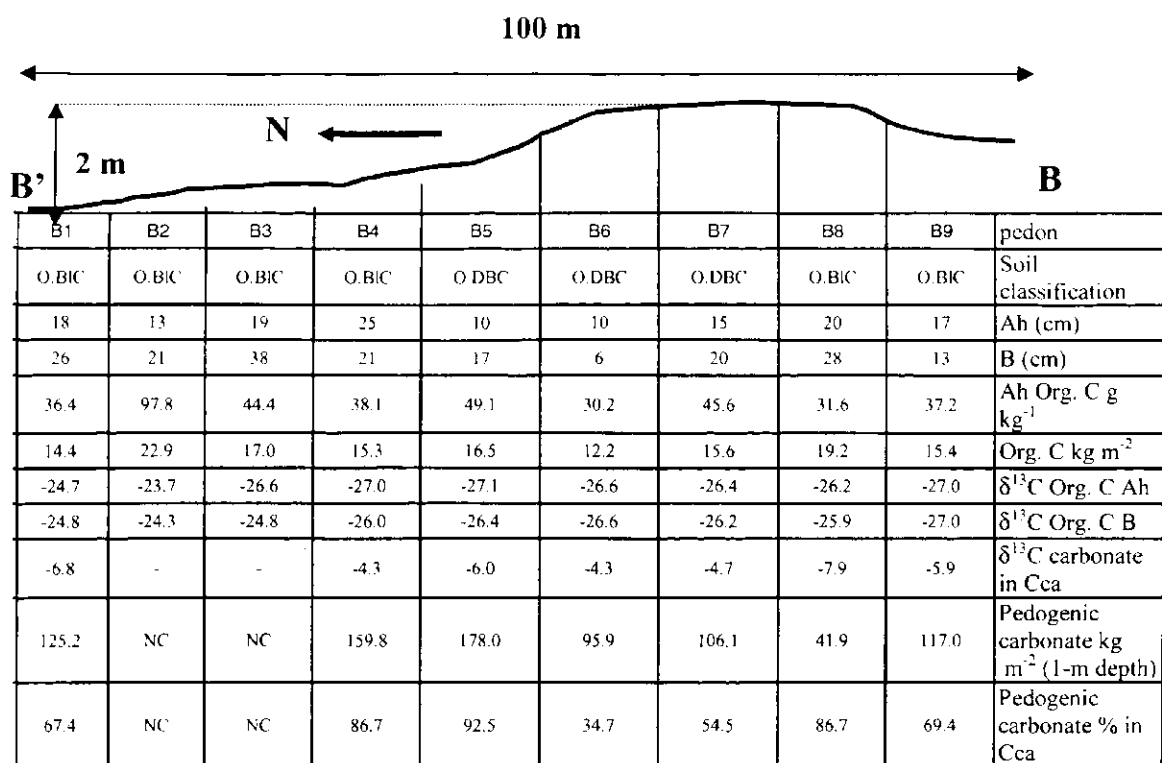
O.DBC= Orthic Dark Brown Chernozem (Typic Haplocryolls)

O.R= Orthic Regosol (Cryorthents)

O.BIC= Orthic Black Chernozem (Udic Haplocryolls)

δ¹³C= ‰ vs VPDB

Figure 5.2 Schematic cross section of AA' transect (North-South) in the Dark Brown soil landscape.

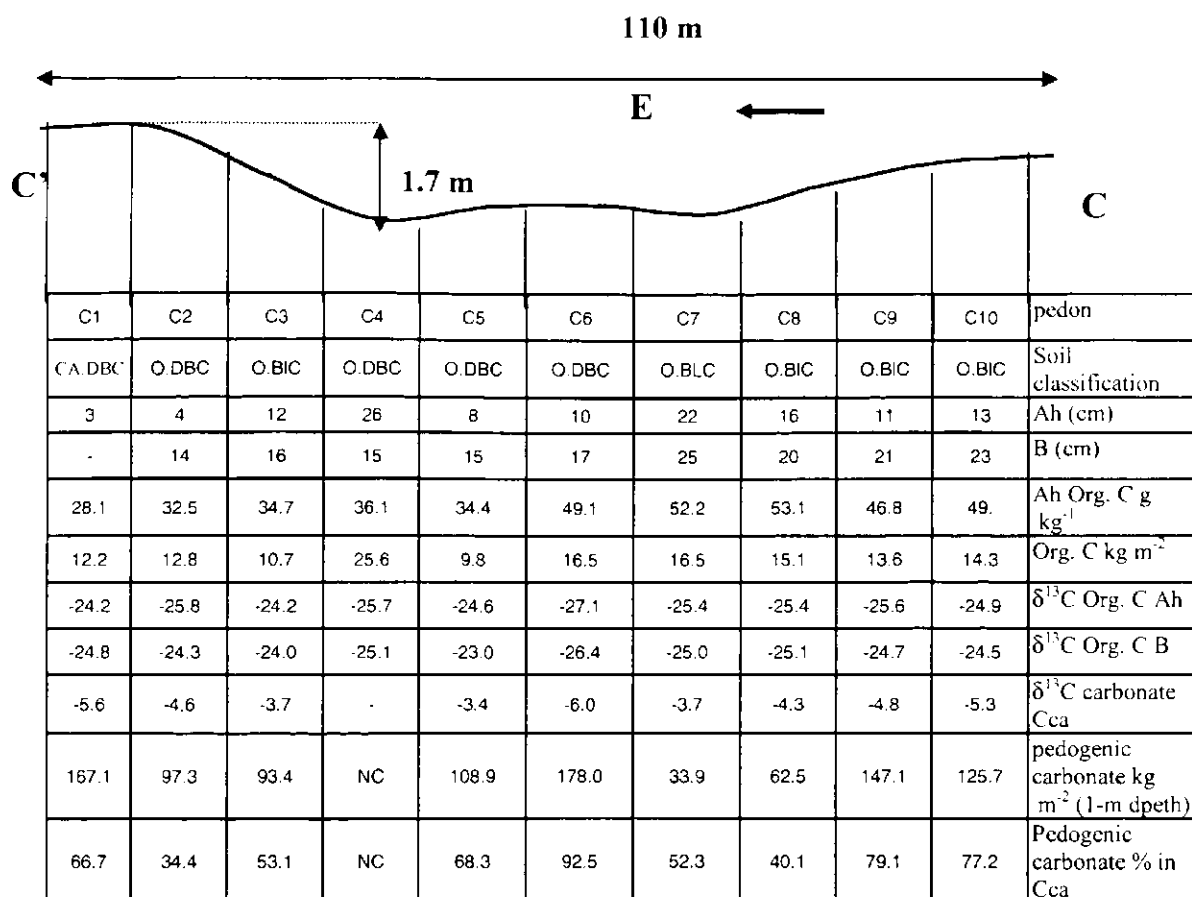


NC= No Carbonate to 1 m depth.

δ¹³C= ‰ vs VPDB

Figure 5.3 Schematic cross section BB' of transect (North-South) in the Dark Brown soil landscape.

Depth to secondary carbonates (calcic horizon) increases from 3 cm on the knoll to more than 120 cm in the depression (Appendix C). Pennock and de Jong (1987) in Saskatchewan made a similar observation. They have reported that shoulder and backslope soils have thin Ah horizons and a shallower carbonate accumulation zone (calcic horizon), and footslope and level positions have thicker Ah horizons, well developed B horizon, and calcic horizons at depth.



CA.DBC= Calcareous Dark Brown Chernozem (Calcicryolls)

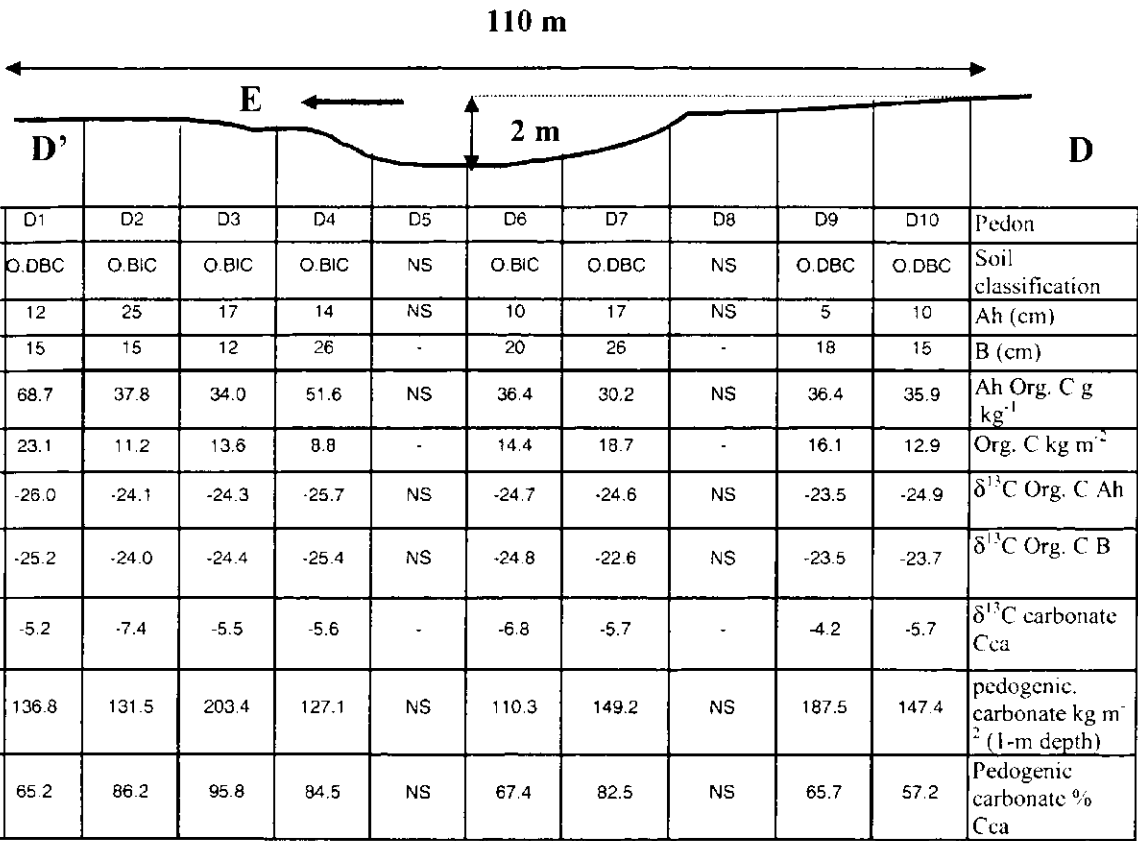
δ¹³C= ‰ vs VPDB

Figure 5.4 Schematic cross section of CC' transect (West-East) in the Dark Brown soil landscape.

5. 3.2 Organic Matter Contents and Rate of Accumulation

The organic C content of Ah horizons ranges between 27 and 98 g kg⁻¹. The amount of organic C increases from knoll to footslope. For example, in transect A' to A along a north facing slope, the organic C contents of the Ah horizons of the soils range from 48.6 to 68.7 g kg⁻¹ in lower slope and level complex landscape elements (Fig. 5.2). Ah horizons in the shoulder complex of the S-facing slope have organic C contents

between 19.6 to 38.1 g kg⁻¹. Total organic C storage is 16.7 ± 1.0 kg m⁻² in N-facing slopes in comparison to 13.9 kg m⁻² ± 1.5 in the south slopes (Table 5.1).



δ¹³C= ‰ vs VPDB

Figure 5.5 Schematic cross section of DD' transect (West-East) in the Dark Brown soil landscape.

Table 5.1 The mass of pedogenic carbonate and organic carbon, and δ¹³C value (in ‰) of organic carbon in two different aspects of the Dark Brown soil landscape.

	N-facing samples (Mean)	S-facing samples (Mean)
Pedogenic carbonate kg m ⁻² (all profiles)	153.0 ± 14.4	97.9 ± 12.9
Organic C kg m ⁻² (all profiles)	16.7 ± 1.0	13.9 ± 1.5
Organic C δ ¹³ C (Ah horizons)	-25.9 ± 0.4	-25.3 ± 0.5

The Ah horizons in south-facing and footslope soils are comparatively low in organic C, but Ah horizons and sola are thicker resulting in reasonably high stores of organic C. Similar findings were reported by other workers (Aandahl, 1948; Malo et al., 1974; Schimel et al., 1985; Aguilar et al., 1988; Pennock and Corre, 2001). A study by Honeycutt et al. (1990b) in the Great Plains reported that organic C content increases from the upper part of the landscape to footslope by as much as 23%. Kleiss (1970) reported that the amount of organic C increases from 0.9% in upper slope to 3.5% in lower slope positions. Many researchers relate this kind of trend to long-term transport of fine organic matter and lateral movement of clay from higher elevations (Reiners, 1983). Increasing organic C downslope may also be related to productivity as it is affected by moisture redistribution in the landscape.

The largest amount of organic C to a 1m depth (about 25.6 kg C m⁻²) was found in a level complex landform element (pedon C4) in west-facing slope (Fig. 5.4) and the lowest amount (about 8.2 kg C m⁻²) was found in the same landform element (pedon A11) on a south-facing slope (Fig. 5.2). The strong relationship between landscape elements and organic C storage observed for cultivated landscapes is not evident in this study of a virgin grassland. Erosion, particularly tillage erosion, likely accentuates differences in organic C, with convex upper slopes losing soil and organic C and concave areas gaining soil and organic C.

The average amount of organic C to a 1m depth in the entire landscape was 15.0 kg C m⁻², which is higher than the mean for Dark Brown soils and equivalent to the average of 14.9 kg C m⁻² for Black soils. The landscape studied does occur in the northern part of the Dark Brown soil zone, and contains Black Chernozem soils. Using

Christiansen's (1978) average age since deglaciation for this area (12,000 yr), the rate of C accumulation is about $1.25 \text{ g C m}^{-2} \text{ yr}^{-1}$, which is higher than Dark Brown ($1.0 \text{ g C m}^{-2} \text{ yr}^{-1}$) and similar to Black soils ($1.2 \text{ g C m}^{-2} \text{ yr}^{-1}$) calculated in previous chapters for level upland soils.

Increases in available moisture result in greater production of plant biomass and increased inputs to the soil organic C pool (Peterson et al., 1988). Higher clay content may also account for slower decomposition rates in downslope positions (Burke et al., 1995). A study in southern Ohio by Finney et al. (1962) showed higher amounts of organic matter occurs in soils facing NE and lower landscape position than soils on S-facing slopes. NE-facing slopes were moister, with a more dense vegetation cover. The authors suggested further that the faster organic matter decomposition rates on warmer SW-facing slopes were more rapid and some losses occur through surface runoff.

5.3.3 Carbon Stable Isotope

The $\delta^{13}\text{C}$ value for organic C ranges from -21.4‰ (pedon A8) on a dry, S-facing shoulder, to -29.6‰ in the large depression area (Appendix C). The low values of $\delta^{13}\text{C}$ associated with the lower level and footslope soils, and the significantly higher values in the upper level and shoulder landscape positions, are related to environmental controls such as moisture distribution in the landscape (van Kessel et al., 1994).

The $\delta^{13}\text{C}$ value of C_3 plants increases from -26.5‰ in moist lower areas to -24‰ on dry upper slopes (Ehleringer and Cooper, 1988). In North America and

Europe, the $\delta^{13}\text{C}$ value of C_3 plants in deciduous forests increases by 1 to 2‰ from mesic, lower positions to drier upland positions (Garten and Tylor, 1992; Balesdent et al., 1993). A study by Longpre (1986) from the Manito Sand Hills in west-central of Saskatchewan indicates that organic matter on a north-facing slope has a lower $\delta^{13}\text{C}$ than a south-facing slope (-26.1‰ and -24.2‰, respectively), and attributed the difference to a greater proportion of C_4 plants on south facing slopes. In profile 2, the Orthic Humic Gleysol (Cryoaquolls) at 70-120 cm depth, the $\delta^{13}\text{C}$ value of organic C was -18.6‰ (Appendix C). It is likely that the organic C is depositional material washed into the depression from adjacent slopes during a time when the climate was warmer and drier, perhaps thousands of years ago.

The $\delta^{13}\text{C}$ values of organic C in the soils of the north-facing slopes were slightly smaller than those facing south, especially in the AA' transect (Fig. 5.2 and Table 5.1). Wang and Anderson (2000) drew similar conclusions in their study from southern Saskatchewan. Native vegetation on N-facing slopes consists of more C_3 plants, including shrubs, grasses, and forbs with smaller $\delta^{13}\text{C}$ values. Conversely more C_4 forbs and grasses were found on S-facing slopes with higher $\delta^{13}\text{C}$ values (Lotspeich and Smith, 1953). Toward the north close to the large depression (pedons A1, A2), there is an enrichment in ^{13}C of organic C. This could be the result of deposition of organic matter from upper parts of the landscape with higher $\delta^{13}\text{C}$ values, or more humification, a consequence of generally more moist conditions favoring humification.

The $\delta^{13}\text{C}$ value of organic C in most of the sampling cores generally becomes greater with depth. Several researchers have reported similar results (Khademi and

Mermut, 1999; Balesdent et al., 1993; Skjemstad et al., 1990; Natelhoffer and Fry 1988; Volkoff and Cerri, 1987). The ^{13}C enrichment with depth may be due to higher values for roots, or an increasing degree of humification. Natelhoffer and Fry (1988) have explained the enrichment with depth as a result of discrimination against ^{13}C during humification or the preferential preservation of litter and organic material enriched in ^{13}C , and changes through time from litter inputs with high $\delta^{13}\text{C}$ values (due to more positive values for atmospheric CO_2 in the past) to litter inputs with lower $\delta^{13}\text{C}$ values. Variation in $\delta^{13}\text{C}$ values of organic C in the east-west direction are minimal. Slight changes in the $\delta^{13}\text{C}$ value of organic C may be related to slightly more moist conditions in small depressions, and drier conditions on minor convexities.

The $\delta^{13}\text{C}$ values of carbonates range from -0.9‰ (Ck horizon, totally lithogenic) (pedon A2) at the 114cm depth in a soil in the level complex, to -7.9‰ (pedon B8) at a depth of 100 cm in footslope complex near the depression (Appendix C). In some cores there is no clear change (decreasing or increasing) in $\delta^{13}\text{C}$ value of carbonate with depth. This irregularity has been observed in shoulder complexes and in the east to west direction, where there is a complexity of water flow.

5.3.4 Pedogenic Carbonate

The highest proportions and amounts of pedogenic carbonate to 1m depth were found in soils of the footslope complex position in the north-facing slope (95.8% in pedon D3, and 222.1 kg m^{-2} in pedon A1). Lowest proportions and amounts were found in the shoulder complex position on a west-facing slope (34.4% in pedon C2), and in

soil of the footslope complex (33.9 kg m^{-2} in pedon C7) (Figs. 5.4). This is generally consistent with the values of Wang and Anderson (2000) who found that the highest proportion of pedogenic carbonate occurred in lower to middle slope soils just above a strongly leached depression in which the soils have little or no pedogenic carbonate. Furthermore, we observed that in the footslope complex carbonate precipitate at a greater depth ($> 1 \text{ m}$) (Appendix C).

Gains and losses of carbonates in the landscape were calculated based on the assumption that all parent material initially contained 16% CaCO_3 or 224 kg m^{-2} to 1m depth (bulk density 1.4 Mg m^{-3}). All the soils in the AA' transect have lost substantial amount of lithogenic carbonates ($> 55\%$). The soils on footslope complexes (Pedons A1 and A2) and shoulder complex (A7) gained more pedogenic carbonate than lithogenic carbonates lost (Fig. 5.6).

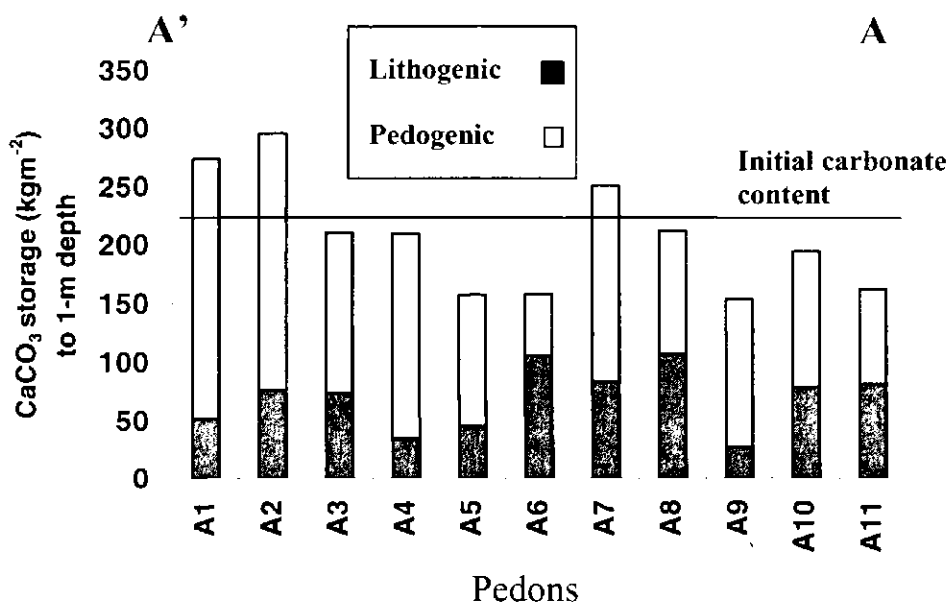


Figure 5.6 Distribution of lithogenic and pedogenic carbonates in the soils of the AA' transect in a Dark Brown soil landscape.

Accumulation of carbonate in footslopes may well be related to the upward movement of carbonate from a shallow water table or lateral flow of water from the upper slope carrying dissolved biogenic carbonates (Richardson et al., 1992).

In the CC' transect, there is a gain in pedogenic carbonate in the shoulder complex (C1, C2) which could be the result by movement from upper parts of the landscape or capillary movement of bicarbonate and precipitation in these soils. In small depressions, such as pedon C4, all or nearly all (pedon C7) of the pedogenic carbonate and original carbonates was lost from the soil. This suggests that some pedogenic carbonate may exist deeper than 1 m or that lateral transfers have moved carbonates to adjacent soils (Fig. 5.7). The carbonate balances for the majority of the soil profiles indicate that the total pedogenic carbonate and current lithogenic carbonates are less than the initial carbonates, at least when considering the upper meter (Figs. 5.6 and 5.7).

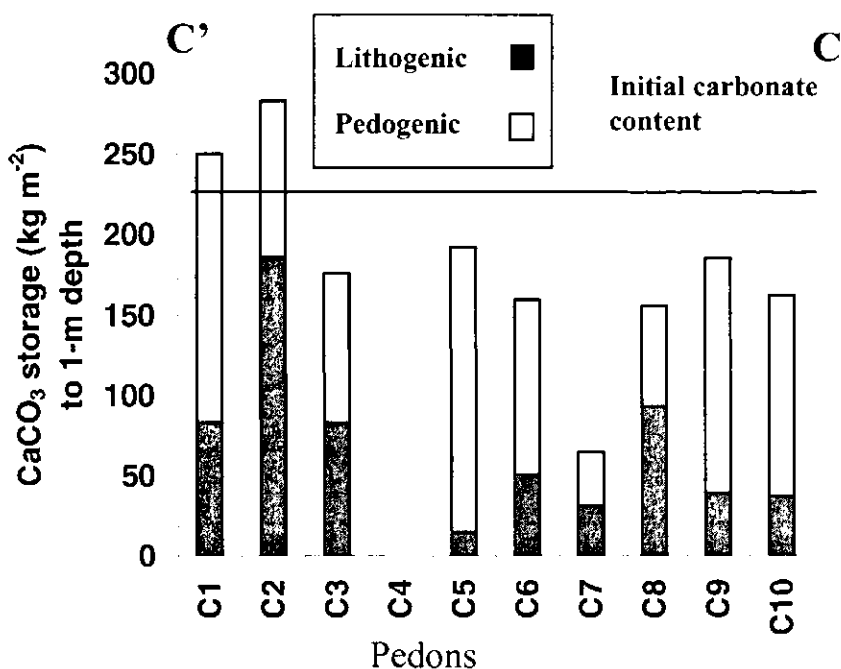


Figure 5.7 Distribution of lithogenic and pedogenic carbonates in the soils of the CC' transect in a Dark Brown soil landscape.

West et al. (1988) explain the formation of strong calcic and petrocalcic horizons in lower hillslope positions of Texas by overland movement of particulate or dissolved carbonates, or downslope movement of dissolved carbonate below the soil surface. Research by Sobecki and Wilding (1983) in the Texas Coast Prairie suggests that the formation of calcic horizons in the upper slope soils is related to the lateral redistribution of carbonates. In their conceptual model, carbonate moves from wetter concave area (with strongly leached soils) and precipitates under relatively dryer soils under micro-knolls (Calciaquolls, Haplustolls). Hall (1983) attributes the formation of strong calcic horizons in lower hillslopes to different stability of landscape elements.

In addition, there is more moisture in footslopes than middle slopes, and this causes more biomass production to produce CO_2 and more intense weathering of minerals to provide Ca. In two cores in the small depression (classified as level complex), there was no carbonate in the soil profile to 1.2m depth. In landscape positions that receive more water, carbonate may precipitate at greater depths or may leach out from the soil and reach the ground water. St. Arnaud (1979) described deep, leached soils with no salts and carbonate at considerable depth for depressional soils in a hummocky landscape in Saskatchewan.

The average amount of inorganic C as pedogenic carbonate within 1m depth in the whole landscape was 15 kg C m^{-2} . Including the two cores without carbonate within 1m depth reduces the average to 14.1 kg C m^{-2} . These values are slightly lower than the mean reported for Dark Brown (17.6 kg C m^{-2}) and Black soils (16.6 kg C m^{-2}), but represent a soil depth of 1 m rather than 1.2m. Using an age of the landscape 12,000 yr, the average rate of pedogenic carbonate accumulation was $1.25 \text{ g C m}^{-2} \text{ yr}^{-1}$, and with

those two cores without pedogenic carbonate the rate was $1.2 \text{ g C m}^{-2} \text{ yr}^{-1}$. This is close to the calculated rate of $1.4 \text{ g C m}^{-2} \text{ yr}^{-1}$ for Dark Brown, and $1.3 \text{ g C m}^{-2} \text{ yr}^{-1}$ for Black soils.

5.4 CONCLUSIONS

In the landscape studied, from knolls (shoulder complexes) to footslopes, soils become deeper, and the thickness of Ah and B horizons and depth to the secondary carbonate layer increase. The amount of organic C and pedogenic carbonate increases from the upper landscape to lower positions. Organic C contents of Ah horizons range between 20 and 98 g kg^{-1} . The amount of pedogenic carbonate to a 1 m depth shows very high variation, changing from 33.9 to 222.1 kg m^{-2} except for pedons B2, B3, and C4 in which carbonates were absent down to a 1 m depth. The amount and percentage of pedogenic carbonate is higher in north-facing slopes than those facing south. On average, the soils accumulated about $1.25 \text{ g C m}^{-2} \text{ yr}^{-1}$ of C as pedogenic carbonate and $1.25 \text{ g C m}^{-2} \text{ yr}^{-1}$ as organic C, rates that are similar to those calculated for Dark Brown soils (Mollisols) in Saskatchewan.

The $\delta^{13}\text{C}$ value of carbonate ranges from -0.9‰ at a 1.14 m depth in the Ck horizon (level complex) to -7.9‰ at a depth of 1 m in the carbonate accumulation layer (footslope complex and depression). There is an irregularity in $\delta^{13}\text{C}$ values of carbonates with depth in shoulder complexes, which may be due to vertical and lateral water flows.

While there are distinct variations in the $\delta^{13}\text{C}$ values of organic C, these variations seem to follow the following patterns: 1) the $\delta^{13}\text{C}$ value of organic C of the Ah horizon of soils occurring in the depression was -29.6‰, whereas soils in the knoll position (shoulder complex) were considerably enriched in ^{13}C , with a $\delta^{13}\text{C}$ value of -21.4‰; 2) the $\delta^{13}\text{C}$ values are more negative in north facing slopes than their south facing counterparts; 3) the $\delta^{13}\text{C}$ values vary insignificantly in the east-west direction, and 4) the $\delta^{13}\text{C}$ value of organic C increases with depth except for the depositional landscape positions.

More than 55% of lithogenic carbonates has been removed from the soil profile. Some landscape positions gained more pedogenic carbonate than the amount of lithogenic carbonates lost. Carbonate balances in the majority of the soil profiles indicate that the total pedogenic carbonate and current lithogenic carbonates are less than the initial carbonates. This suggests that carbonates have moved below the 1 m depth in certain soils, although many soils have gained carbonate. Marked differences were found in the amount and rate of organic and inorganic C accumulation in landscape segments of the area studied. This may seem to complicate the calculation of soil C fluxes and accumulation. However, when averaged for the entire landscape, the amount and rates of organic and inorganic C accumulations become similar to the soil zone in which they occur.

CHAPTER 6

SUMMARY AND CONCLUSIONS

In the past decade, increasing awareness of CO₂ build-up in the atmosphere and the threat of global warming has focused attention on the C cycle and a need for a better understanding of stocks and flows. The quantification of C pools is still far from complete. Carbon sequestration in soils can be a highly cost effective and environmentally friendly mitigation technique to offset CO₂ emissions (Mermut and Eswaran, 2001).

The pedosphere plays a significant role in influencing the gaseous composition of the atmosphere. Soil organic C (SOC) and soil inorganic C (SIC) are the two major pools in the pedosphere. The global stock of SOC has been estimated at 1500 Pg, which is three times the biotic pool located mainly in plants, and two times the atmospheric pool. Estimates of the total stock of SIC varies between 700 to 1700 Pg. The variability is at least partly due to the difficulty in separation of pedogenic and lithogenic carbonate (Lal et al., 1998). The lack of reliable information about the size and dynamics of SIC pool is emphasized in the recent literature, and the existing data on the SIC has been called sketchy, vague, and unreliable (Lal et al., 1998).

Lal et al. (2000a,b) emphasized the importance of knowledge on the SIC pool, its cycling, and its relationship to SOC within the global C cycle. Nordt et al. (2000) concluded that SIC sequestration occurs over tens to hundreds of thousands of years and

definitely plays a role in the global C cycle. Mermut et al. (2000) had several questions with respect to C cycling in the soil, two of which are important to this study: 1) how much atmospheric CO₂ is sequestered as pedogenic carbonate, and 2) how much SIC is derived from SOC during that process? Answers to the questions are important to develop a complete understanding of the C cycle.

The soils of Saskatchewan, with a well-documented deglaciation history, general similarity in glacial parent materials, and a regular environmental gradient provide an ideal opportunity to estimate the C flux in soils of the dry, cool boreal region. The results have potential for estimating more accurately the rates of C accumulation in other boreal regions. Stable isotope geochemistry was used to determine the amount and accumulation rate of pedogenic carbonate, organic C storage and accumulation rates, together with ¹³C/¹²C ratio of soil organic C in a series of zonal soils along gradients of environment and time in Saskatchewan. It was also attempted to calculate the total amount of C sequestered as pedogenic carbonate. At the local scale, I studied the effect of landscape on the formation and distribution of pedogenic carbonate and organic matter and compare of the results with the average for the same soil zone.

A southwest to northeast transect of about 500 km length was used to establish the influence of environment on SOC and SIC reserves. The transect crossed five different soil-climatic zones (Dry Brown, Brown, Dark Brown, Black, and Gray) in Saskatchewan, between 49° 13' and 53 ° 63' N latitude and 104° 92' and 107° 66' W longitude.

6.1 SOIL DEVELOPMENT

The thickness of Ah horizons, depth of solum, organic matter and pedogenic carbonate contents and rates of accumulation increases from the Dry Brown zone to the Black zone, despite the fact that the actual time for soil formation decreases. In the landscape in the Dark Brown zone, soils become deeper from knoll (shoulder complex) to footslope, and the thickness of Ah and B horizons and depth to the secondary carbonate layers increase.

6.2 ORGANIC CARBON

The amount of organic C to a 1.2 m depth generally increases from an average of 9.1, 11.7, 14.9, and 21.0 kg C m⁻² (90.8, 117.2, 148.8, and 210.2 Mg C ha⁻¹) for Brown, Dark Brown, Black, and Rego Black Chernozem soils (LFH is included for Gray and Rego Black Chernozem soils), respectively. The amount of organic C for Gray soils is 96.3 Mg C ha⁻¹, which is similar to the value (99.2 Mg C ha⁻¹) reported by Huang and Schoenau (1996) for Gray Luvisols (Alfisols) under an aspen forest in Saskatchewan. In a landscape that included Dark Brown and Black Chernozem soils there was more organic matter in soils of north-facing than south-facing slopes. For the whole landscape, the mean organic C storage was 14.9 kg C m⁻², which is higher than the values calculated for Dark Brown soils in a level landscape under natural conditions. This is probably a consequence of Black soils being present in the profiles.

At the regional scale, values for organic C stores are similar to the values reported by McGill et al. (1988) for the same soil zones in Alberta. However, our values are lower than those reported for Brown soils, and higher than Dark Brown and Black

soils studied by Anderson (1995) in Saskatchewan. Values for organic C storage for Luvisol and Chernozems are 9.6 kg C m^{-2} and 11.9 kg C m^{-2} which are in agreement with estimates by Tarnocai (1998) at 9.3 kg C m^{-2} and 12.4 kg C m^{-2} for the same two soil orders. In comparison to the global data (12.5 , 14.8 , and 13.4 kg C m^{-2} for Alfisols, Inceptisols, and Mollisols, respectively) reported by Eswaran et al. (2000), values found in this study are lower for Luvisols (Alfisols), but similar for the Black Chernozem and Dark Brown soils (Mollisols).

Annual organic C accumulation rates in the soils studied are 0.57 , 0.90 , 1.18 , 0.84 , and $1.83 \text{ g C m}^{-2} \text{ yr}^{-1}$ for Brown, Dark Brown, Black, Gray, and Rego Black Chernozems soils. At the local scale, the average rate of organic C accumulation in the landscape was $1.25 \text{ g C m}^{-2} \text{ yr}^{-1}$, which is close to the average of soils in the Black zone. The rate of accumulation for Gray soils is higher, and for Black and Dark Brown soils lower than those calculated by Harden et al. (1992) for the glaciated area of North America. Their calculation shows that Mollisols (similar to Black and Dark Brown Chernozems) store $2 \text{ g C m}^{-2} \text{ yr}^{-1}$, and Alfisols, similar to Gray soils, sequester $0.27 \text{ g C m}^{-2} \text{ yr}^{-1}$.

Anderson (1995) and many others have suggested that prairie soils have lost about 30% of their organic matter under cultivation. The loss is estimated to be about 2 kg m^{-2} by Anderson (1995), and 1.5 kg m^{-2} by Mann (1986). Considering these losses over 80 years of agriculture practices, the rate of loss is about 19 to $25 \text{ g C m}^{-2} \text{ yr}^{-1}$. This is ten to thirty times greater than the accumulation rate for Brown, Dark Brown, Black, and Gray soils. This rate is likely higher at the early stage of C losses and then levels off

and reaches a near steady state. Therefore, it may take only a few hundred years to lose the majority of the SOC.

The organic C of soils on north-facing slopes and more moist positions have smaller $\delta^{13}\text{C}$ values than south-facing and drier segments in the landscape. At regional scales, the mean $\delta^{13}\text{C}$ values of organic C are -22.9‰ for the Dry Brown, -24.3‰ for Brown, -24.8‰ for Dark Brown, -25.3‰ for Black, and -26.8‰ for Gray soil zones. These gradual changes are considered to be a consequence of increasing contribution to organic matter from C_4 plants in drier and warmer regions, with an estimated 30% C_4 plants characteristic of Dry Brown soils, and none in the Gray soils. The Dry Brown and Brown soils are more depleted in ^{13}C at depth, suggesting a greater proportion of C_3 plants in the past.

6.3 PEDOGENIC CARBONATE

X-ray diffraction analysis indicated that randomly selected carbonate pebbles from parent material were entirely dolomite, with no other carbonate materials present. Calcite with a d-spacing of 3.01 Å was the dominant mineral in pendants from carbonate accumulation zones (Cca horizons). A shift in the calcite peak from 3.03 Å to 3.01 Å is an indication of the presence of Mg-bearing calcite (Fig. 4.2).

The internal part of the pendant was much more crystalline than the surface layers as observed under SEM. The outer layers are more recently deposited, soft and porous, and consist of calcite with minor amounts of quartz and dolomite that are likely inclusions. The inner laminae were denser and more crystalline than the outer layer.

Different morphological forms of pedogenic carbonate (calcite) are typical of Saskatchewan soils (Mermut and St. Arnaud, 1981a,b; Wang and Anderson 2000).

The amount of pedogenic carbonates ranged between 100.8 and 161.8 kg m⁻² with an average value of 133.9 kg m⁻² for Brown soils. For Dark Brown soils (Mollisols), the range was between 102.1 kg m⁻² and 177.2 kg m⁻² with an average of 146.3 kg m⁻². For the Black soil zone (Mollisols) the minimum, maximum, and average values are 117.5, 156.7, and 138.2 kg m⁻², respectively. These are within the range of 100-134 kg m⁻² reported by Wang and Anderson (2000) for Black soils. In the Gray soil zone (Alfisols) the values are 151.0, 181.5, and 164.5 kg m⁻². For Rego Black Chernozem soils the amount of pedogenic carbonates range between 98.7 and 120.9 kg m⁻² with an average of 110.3 kg m⁻².

Within a typical, hummocky landscape there is a marked variation in pedogenic carbonate stores in the upper 1 m. Some soils (generally in concave, locally moist positions) have neither lithogenic nor pedogenic carbonate, indicating complete removal during soil formation. Other soils, often immediately adjacent to soils with substantial losses, contain considerably more carbonate than the initial lithogenic carbonates, with marked gains in pedogenic carbonate.

The average amount of pedogenic carbonate accumulation in the landscape was about 82 kg m⁻², which is lower than the average for the Dark Brown soils. This could be related to the depth of sampling (1 m) in the landscape studied, in comparison to the Dark Brown zone studied up to 1.2 m. On the global scale, my estimates are higher for Alfisols (Gray Luvisol) and Mollisols (Chernozems) than those published by Eswaran et al. (2000). The differences are in part related to the depth of sampling, especially for

Alfisols and Mollisols. I found that at 1.2 m depth up to 40% in Alfisols and 20% in Mollisols of the carbonates were pedogenic (Appendix C). Eswaran et al. (2000) based their estimate on the assumption that 50% of total carbonates in the soil profile were pedogenic. Data from this study shows that, in some horizons, pedogenic carbonate may account for up to 100% of the carbonates, and on average it is higher than 60% in the soil profile to 1.2 m depth. Accepting their estimates for pedogenic carbonate in Entisol, Aridisols, Inceptisols, Gelisols, and Vertisols orders, and with new estimates for Mollisols and Alfisols we calculated 1179 Pg of C as pedogenic carbonate globally, which is 1.25 times their estimate.

The rate of pedogenic carbonate accumulation increases from southwest to northeast between 8.3, 11.4, 11.2, 14.3, 9.6 g C m⁻² yr⁻¹ for Brown, Dark Brown, Black, Gray, and Rego Black Chernozem soils. Despite the fact that time for soil formation decreases from 17,000 yr in the southwest to 11,500 yr in northeast, there is a gradual increase in the rate of CaCO₃ formation from SW to NE. This is primarily due to changes in climate. At the landscape scale, the rate of accumulation was about 10.4 g m⁻² yr⁻¹, which is close to estimates for Black and Dark Brown soils. No regional data for the rate of pedogenic carbonate accumulation have been documented so far for the Canadian Prairies. Our data for dry to sub-humid boreal soils are much higher than the estimates for arid and semi arid soils reported in the literature (Buol and Yesilsoy, 1964; Bachman and Machette, 1977; McFadden, 1982; Schlesinger, 1985; Eghbal and Southard, 1993). One should remember that all the previously published estimates were made without the use of the stable isotope technique.

6.4 ASSOCIATION OF ORGANIC AND INORGANIC CARBON

Using the net primary production (NPP) data (Saskatchewan Agriculture and Food 2001) and rate of C accumulation as organic C, it is calculated that about 0.32% of NPP C can accumulate as organic C. This value appears to be less than the world average. Considering the long-term average rate for other soils such as Spodosols and peat soils, which are from 10 to more than 50 g C m⁻² yr⁻¹, my estimate seems to be quite reasonable for boreal soils. It must be noted that the annual C accumulation rates calculated are an average for soils that may have been more or less at equilibrium for thousands of years.

It is calculated that about 0.45% of NPP can be accumulated as inorganic C. On average the rate is about 1.4 times higher than that of calculated value for organic C (0.32%) (Table 6.1).

Table 6.1 Relationship between NPP and organic and inorganic carbon accumulation.

Soil Zone	Above-ground ^a NPP (g m ⁻² yr ⁻¹)	Below-ground ^b NPP (g m ⁻² yr ⁻¹)	NPP accumulation as inorganic C %	NPP accumulation as organic C %	Other ^c losses %
Brown	323.8	136.0	0.47	0.28	99.25
Dark Brown	464.65	195.2	0.46	0.30	99.24
Black	490.12	205.9	0.43	0.38	99.19

^a Based on Saskatchewan Agriculture and Food report (2001).
^b Calculated based on 42.6% belowground reported by Slobodian (2001).
^c Return to atmosphere, losses through the soil system etc.

This rate shows that, in the long term, pedogenic carbonate plays an important role in C cycle, and can sequester more C than organic matter. Adding organic and

inorganic C together, less than 1% NPP C can be accumulated in the soil. This is consistent with the findings of Chadwick et al. (1994), suggesting that in temperate grassland more than 98% of NPP eventually returns to the atmosphere through soil respiration.

The $\delta^{13}\text{C}$ values of pedogenic carbonate generally show a similar trend as the $\delta^{13}\text{C}$ values of organic C. The $\delta^{13}\text{C}$ values of pedogenic carbonate slightly decrease to a 50 cm depth, below which the values are almost constant.

There is a high correlation between C and O isotope compositions of pedogenic carbonates. Based on the data we can differentiate three different groups: 1) lithogenic group, which have higher values both for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, 2) soils of the grassland (Prairie soils), which have smaller value of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ than the first group, and 3) forest soils which have smaller value than Prairie soils. The $\delta^{18}\text{O}$ value of pedogenic carbonate decreases with decreasing $\delta^{13}\text{C}$ value. Soil water mainly controls the oxygen isotopic composition of pedogenic carbonate (Cerling, 1984; Amundson and Lund, 1987; Cerling and Quade, 1993).

There is more pedogenic carbonate formation than lithogenic carbonate loss in all soil zones (Fig. 6.1). The amount of lithogenic carbonate for each soil zone was calculated on the basis that the amount of original carbonate in the parent material was equal to the carbonate content of the present Ck horizon. The amount of lithogenic carbonate lost is calculated by subtracting the total calculated amount of lithogenic carbonate from the lithogenic carbonate left in the soil. The rate of losses is obtained by dividing the amount lost by the age of the soil. The rate of lithogenic loss is lower than the rate of formation of pedogenic carbonate, suggesting that Ca has been provided

from other sources such as weathering of non-carbonatic Ca-bearing minerals and Ca added through rainfall, to couple with biogenic CO₂ (Fig. 6.2).

The decrease in temperature and increase in precipitation from the southwest to northeast direction favors C₃ plants over C₄ plants, resulting in depletion of ¹³C. Meteoric waters become more depleted in ¹⁸O in moving toward higher latitude, because of cooler temperature (Cerling and Wang, 1996). These findings are consistent with other worker (Schlesinger et al., 1989; Cerling and Quade 1993; Khademi and Mermut 1999). Koehler (2002) and McMonagle (1987) reported the annual average value of δ¹⁸O as -15‰ for Saskatoon.

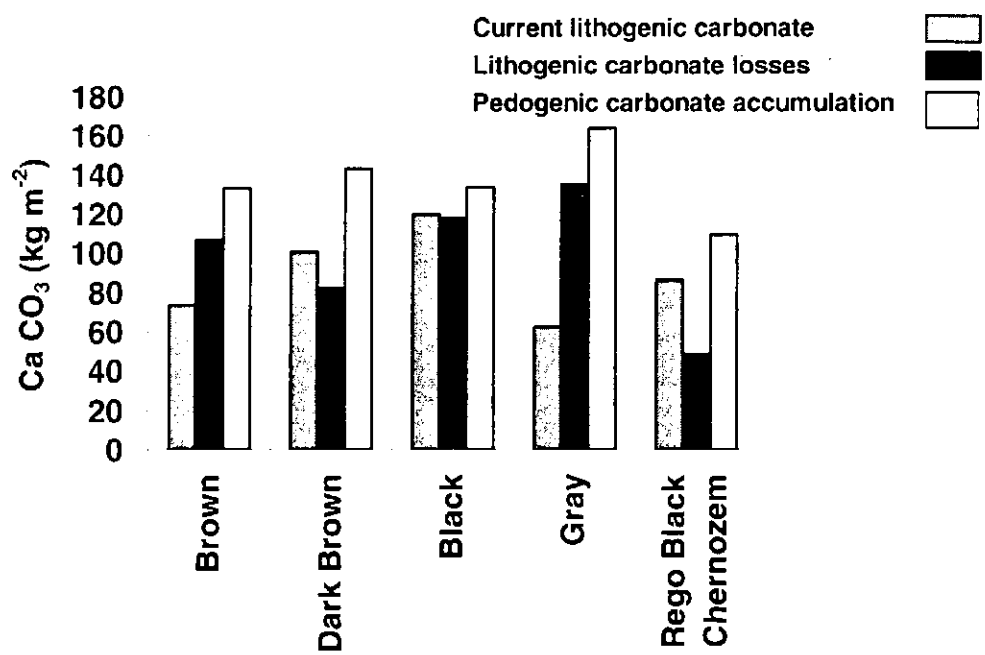


Figure 6.1 Pedogenic carbonates in comparison to the amount of lithogenic carbonate lost by weathering for a sequence of Brown to Gray soils.

The average value for δ¹⁸O of pedogenic carbonate for this area was -10‰, which is about 5‰ enriched in comparison to the precipitation value. This is probably

due to enrichment of ^{18}O by evaporation from the soil prior to carbonate precipitation (Quade et al., 1989; and Schlesinger et al., 1989).

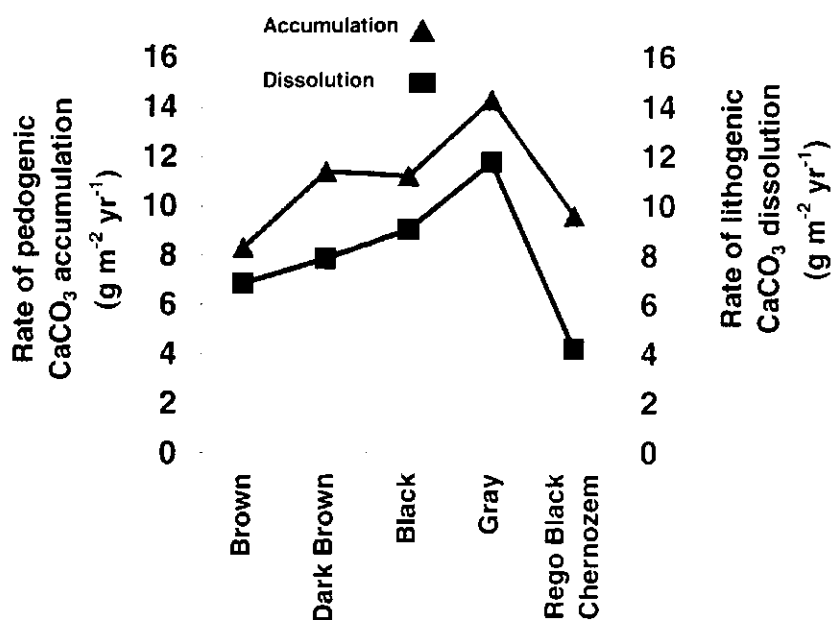


Figure 6.2 Relationship between rate of dissolution and precipitation of carbonate in a sequence of Brown to Gray soils.

The rate of pedogenic carbonate formation increases from the Brown to Gray soils, which is consistent with increases in effective precipitation and the degree of soil formation as measured by the solum thickness. My conclusion is that the availability of Ca, as related to the weathering of Ca-bearing minerals in the A and B horizons, is the rate-limiting factor in this group of cool and comparatively dry boreal soils. Using the simple linear regression ($Y = 17.46X + 201.83$, $R^2 = 0.89$), where Y is the annual precipitation (mm), and X is the rate of pedogenic carbonate accumulation ($\text{g m}^{-2} \text{yr}^{-1}$) from the plotted data, it is possible to use the mean annual precipitation in semiarid and

sub-humid regions (200-700mm) to estimate the rate of pedogenic carbonate accumulation.

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APPENDIX A

Table A.1. Concentrations of soluble ions in saturated extracts of profile B.1 (Brown Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁻	HCO ₃ ⁻	Cl ⁻	Total
Ah	0-5	0.5	0.7	2.6	4.5	8.3	2.3	5.6	0.4	8.3
Bm	5-16	1.4	0.4	3.0	4.8	9.6	3.9	5.5	0.2	9.6
Cca1	16-30	6.0	0.2	2.6	2.1	10.9	3.7	7.0	0.2	10.9
Cca2	30-50	5.6	0.2	1.4	1.1	8.3	0.2	7.7	0.4	8.3
Cca3	50-75	8.5	0.2	1.1	0.5	10.3	0.8	7.7	1.8	10.3
Ck1	75-100	28.4	0.7	10.1	1.6	40.8	28.2	5.8	6.8	40.8
Ck2	100-128	55.6	1.6	59.0	23.8	140.0	131.3	2.3	6.4	140.0

Table A.2. Concentrations of soluble ions in saturated extracts of profile B.2 (Brown Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁻	HCO ₃ ⁻	Cl ⁻	Total
Ah	0-6	0.3	0.7	4.1	7.9	13.0	6.3	6.3	0.4	13.0
Bm	6-21	0.4	0.2	2.4	5.5	8.5	3.3	4.9	0.3	8.5
Cca1	21-30	0.5	0.2	2.6	3.4	6.7	1.4	5.1	0.2	6.7
Cca2	30-59	1.6	0.2	3.4	1.9	7.1	0.3	6.5	0.3	7.1
Ck1	59-79	5.2	0.3	3.9	0.7	10.0	0.4	9.0	0.6	10.0
Ck2	79-105	22.3	1.1	75.9	24.1	123.4	112.9	4.4	6.1	123.4
Ck3	105-130	27.8	1.4	84.8	26.6	140.6	131.7	2.5	6.4	140.6

Table A.3. Concentrations of soluble ions in saturated extracts of profile B.3 (Brown Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁻	HCO ₃ ⁻	Cl ⁻	Total
Ah	0-4	2.8	0.9	6.4	8.8	18.9	4.3	6.7	7.9	18.9
Bm	4-16	0.4	0.5	3.8	6.8	11.5	4.8	6.2	0.5	11.5
Cca1	16-28	0.6	0.3	3.8	5.0	9.7	3.5	5.9	0.3	9.7
Cca2	28-52	2.1	0.3	4.0	2.6	9.0	1.5	6.6	0.9	9.0
Cca3	52-78	9.6	0.4	9.6	2.3	21.9	8.0	6.2	7.7	21.9
Ck1	78-100	20.0	0.7	32.0	3.2	55.9	37.9	4.6	13.4	55.9
Ck2	100-130	30.4	1.3	87.8	29.8	149.3	131.8	3.2	14.3	149.3

Table A.4. Concentrations of soluble ions in saturated extracts of profile B.4 (Brown Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁻	HCO ₃ ⁻	Cl ⁻	Total
Ah	0-10	0.3	0.6	2.0	3.6	6.5	0.1	5.8	0.6	6.5
Bm	10-25	0.4	0.4	1.5	1.9	4.2	0.1	3.8	0.3	4.2
Cca1	25-50	1.5	0.5	2.0	1.4	5.4	0.3	4.8	0.3	5.4
Cca2	50-75	5.5	0.6	3.1	0.7	9.9	3.6	5.2	1.1	9.9
Cca3	75-96	9.7	0.7	5.1	1.0	16.5	9.9	4.9	1.7	16.5
Ck1	96-116	14.1	0.9	7.9	1.7	24.6	18.5	4.7	1.4	24.6
Ck2	116-130	30.5	2.0	47.3	25.3	105.1	102.0	2.7	0.4	105.1

Table A.5. Concentrations of soluble ions in saturated extracts of profile B.5 (Dry Brown Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁻	HCO ₃ ⁻	Cl ⁻	Total
Ah	0-5	0.3	0.7	2.1	4.3	7.4	0.2	6.8	0.5	7.4
Bm	5-12	0.3	0.3	1.5	3.5	5.6	0.1	5.3	0.2	5.6
Cca1	12-35	0.4	0.2	1.2	2.6	4.4	0.1	4.1	0.2	4.4
Cca2	35-65	2.6	0.3	1.9	1.1	5.9	0.1	5.5	0.3	5.9
Ck1	65-88	6.5	0.2	1.1	0.7	8.5	0.1	7.7	0.7	8.5
Ck2	80-100	11.9	0.3	2.0	1.5	15.7	4.8	8.0	2.9	15.7

Table A.6. Concentrations of soluble ions in saturated extracts of profile B.6 (Dry Brown Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁻	HCO ₃ ⁻	Cl ⁻	Total
Ah	0-12	0.34	0.46	2.45	5.49	8.74	3.67	4.79	0.28	8.74
Cca1	12-43	0.65	0.18	2.12	2.57	5.53	0.32	4.94	0.27	5.53
Cca2	43-78	3.90	0.25	1.90	0.84	6.90	0.35	5.98	0.57	6.9
Cca3	78-97	13.84	0.71	15.45	8.58	38.58	35.38	2.94	0.26	38.58
Cksa	97-110	24.48	1.12	40.14	24.57	90.31	87.99	2.04	0.28	90.31
Ck	100-133	1.81	0.09	3.60	2.20	7.70	2.23	4.95	0.52	7.7

Table A.7. Concentrations of soluble ions in saturated extracts of profile DB. 1 (Dark Brown Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁻	HCO ₃ ⁻	Cl ⁻	Total
Ah	0-10	0.3	0.6	3.4	5.4	9.7	3.4	5.9	0.4	9.7
Bm	10-25	0.3	0.2	2.9	3.7	7.1	1.2	5.6	0.3	7.1
Cca1	25-45	15.8	0.7	97.2	32.6	146.3	136.9	5.2	4.2	146.3
Cca2	45-68	46.7	1.7	116.7	26.4	191.5	174.8	5.2	11.5	191.5
Ck1	68-80	50.9	1.8	109.3	14.3	176.3	159.4	4.2	12.7	176.3
Ck2	80-100	46.1	1.5	74.4	12.2	134.2	119.0	2.5	12.7	134.2
Ck3	10-120	37.5	1.3	163.4	9.7	211.9	199.1	3.9	8.9	211.9
Ck4	120-140	32.4	1.0	127.9	11.3	172.6	161.7	3.3	7.6	172.6

Table A.8. Concentrations of soluble ions in saturated extracts of profile DB. 2 (Dark Brown Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁻	HCO ₃ ⁻	Cl ⁻	Total
Ah	0-9	0.4	1.0	3.7	5.9	11.0	3.6	6.9	0.5	11.0
Bm	9-18	0.3	0.5	3.9	6.9	11.6	4.9	5.6	1.1	11.6
Cca	18-48	0.7	0.3	4.8	2.8	8.6	1.7	6.6	0.3	8.6
Ck1	48-68	8.3	1.2	56.7	27.7	93.9	90.2	3.3	0.4	93.9
Ck2	68-98	22.6	1.9	144.6	30.1	199.2	195.2	2.3	1.7	199.2
Ck3	98-138	33.4	1.7	70.7	28.9	134.7	129.1	2.5	3.1	134.7
Cg	138-175	39.2	2.3	101.4	27.1	170.0	161.9	3.1	5.0	170.0

Table A.9. Concentrations of soluble ions in saturated extracts of profile DB. 3 (Dark Brown Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁻	HCO ₃ ⁻	Cl ⁻	Total
Ah	0-6	0.3	1.0	3.1	6.1	10.5	4.2	5.8	0.5	10.5
Bm	6-20	0.4	0.6	2.7	6.2	9.9	4.0	5.6	0.3	9.9
Cca1	20-40	0.4	0.5	3.6	3.4	7.9	1.5	6.1	0.3	7.9
Cca2	40-60	2.7	0.4	5.6	0.7	9.4	1.6	7.2	0.6	9.4
Ck1	60-92	4.1	0.4	5.9	0.5	10.9	4.4	5.7	0.8	10.9
2Ck	92-125	6.8	0.5	13.1	1.9	22.3	16.8	3.8	1.7	22.3

Table A.10. Concentrations of soluble ions in saturated extracts of profile Bl. 1 (Black Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁻⁻	HCO ₃ ⁻	Cl ⁻	Total
Ah	0-10	0.5	2.5	4.4	5.9	13.3	4.6	7.8	0.9	13.3
Bm	10-32	0.5	0.8	2.8	2.5	6.6	0.3	5.9	0.4	6.6
Cca1	32-64	1.8	0.6	6.2	3.5	12.1	0.6	10.8	0.7	12.1
Cca2	64-82	21.0	1.1	65.7	20.0	107.8	93.7	5.4	8.7	107.8
Ck1	82-100	46.2	1.3	162.8	23.1	233.4	212.8	2.9	17.7	233.4
Ck2	100-120	38.4	1.1	97.9	26.4	163.8	152.5	2.1	9.2	163.8

Table A.11. Concentrations of soluble ions in saturated extracts of profile Bl. 2 (Black Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁻⁻	HCO ₃ ⁻	Cl ⁻	Total
Ah	0-14	0.3	1.1	3.9	4.6	9.9	2.3	7.1	0.5	9.9
Bm	14-34	0.6	0.3	4.8	3.2	8.9	0.2	6.9	1.9	8.9
Cca1	34-62	11.0	0.5	47.3	30.0	88.8	84.1	4.4	0.3	88.8
Cca2	62-74	13.9	0.6	98.9	26.4	139.8	137.1	2.4	0.3	139.8
Ck1	74-104	18.2	0.7	164.7	3.3	186.9	183.5	2.3	1.1	186.9
Ck2	104-134	18.3	0.7	175.7	2.9	197.6	193.6	2.4	1.6	197.6
Ck3	134-154	13.9	0.7	151.2	27.5	193.3	189.5	2.1	1.7	193.3
Ck4	154-170	10.2	0.8	71.9	29.0	111.9	107.0	2.2	2.7	111.9

Table A.12. Concentrations of soluble ions in saturated extracts of profile Bl. 3 (Black Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁻⁻	HCO ₃ ⁻	Cl ⁻	Total
Ah	0-8	0.4	1.1	2.9	6.0	10.4	3.3	6.5	0.6	10.4
Bm	8-22	0.3	0.4	2.2	4.8	7.7	1.1	6.2	0.4	7.7
Cca1	22-40	0.4	0.4	2.4	4.3	7.5	1.1	5.9	0.5	7.5
Cca2	40-52	1.7	0.6	2.4	3.4	8.1	1.0	6.4	0.7	8.1
Ck1	52-85	11.0	0.9	14.7	1.9	28.5	22.6	4.8	1.1	28.5
Ck2	85-115	20.4	1.2	50.2	4.2	76.0	70.0	4.1	1.9	76.0
Ck3	115-130	20.4	1.0	48.9	4.6	74.9	68.9	4.5	1.5	74.9

Table A.13. Concentrations of soluble ions in saturated extracts of profile G. 1 (Gray Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁼⁼	HCO ₃ ⁻	Cl ⁻	Total
LFH	5-0	0.3	3.0	3.5	7.7	14.5	4.0	9.5	1.0	14.5
Ae	0-11	0.7	0.6	1.5	2.5	5.3	0.6	4.1	0.6	5.3
Bt	11-52	0.7	0.1	0.8	1.4	3.0	0.5	1.9	0.6	3.0
Cca1	52-74	0.7	0.1	1.9	3.6	6.3	0.2	5.7	0.4	6.3
Cca2	74-114	0.7	0.1	1.5	2.3	4.6	0.0	4.3	0.3	4.6
Cca3	117-144	0.9	0.2	2.1	2.7	5.9	0.0	5.5	0.4	5.9
Ck	144-190	0.9	0.1	1.7	2.7	5.4	0.0	4.9	0.5	5.4

Table A.14. Concentrations of soluble ions in saturated extracts of profile G. 2 (Gray Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁼⁼	HCO ₃ ⁻	Cl ⁻	Total
LFH	10-0	0.2	2.6	2.3	5.5	10.6	0.0	9.3	1.3	10.6
Ae	0-32	0.7	0.1	1.1	2.6	4.5	0.3	3.5	0.7	4.5
Bt	32-57	1.7	0.0	2.7	2.2	6.6	0.5	5.4	0.7	6.6
Cca1	57-85	1.9	0.0	4.2	2.2	8.3	0.0	7.1	1.2	8.3
Cca2	85-100	2.6	0.1	2.4	1.5	6.6	0.1	6.1	0.4	6.6
Ck	100-133	1.8	0.1	3.6	2.2	7.7	2.3	4.9	0.5	7.7

Table A.15. Concentrations of soluble ions in saturated extracts of profile G. 3 (Gray Soil).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁼⁼	HCO ₃ ⁻	Cl ⁻	Total
LFH	4-0	0.2	1.5	2.5	4.9	9.1	3.7	5.0	0.4	9.1
AE	0-17	0.4	0.6	1.6	4.3	6.9	0.0	6.6	0.3	6.9
Bt	17-47	0.4	0.2	1.6	3.5	5.7	0.1	5.3	0.3	5.7
BC	47-53	0.4	0.2	1.9	4.2	6.7	0.2	6.3	0.2	6.7
Cca1	53-70	0.6	0.2	4.1	6.4	11.3	5.7	5.4	0.2	11.3
Cca2	70-92	1.0	0.4	18.9	22.9	43.2	40.2	2.9	0.1	43.2
Cca3	92-115	1.0	0.3	16.9	15.8	34.0	31.2	2.7	0.1	34.0
Ck1	115-125	1.2	0.3	13.9	13.0	28.4	25.4	2.9	0.1	28.4
Ck2	125-150	1.7	0.5	28.7	30.2	61.1	57.2	3.8	0.1	61.1

Table A.16. Concentrations of soluble ions in saturated extracts of profile W.1 (Rego Black Chernozem).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄	HCO ₃	Cl ⁻	Total
LFH	20-0	0.8	0.9	1.1	1.9	4.7	2.5	0.6	1.6	4.7
Ahk	0-25	7.5	0.6	3.9	3.3	15.3	3.8	6.7	4.8	15.3
Cca1	25-40	6.9	0.2	1.4	1.8	10.3	0.0	8.3	2.0	10.3
Cca2	40-55	5.5	0.1	2.6	3.9	12.1	4.9	5.8	1.4	12.1
Ck1	55-70	3.8	0.2	2.2	2.9	9.1	1.9	6.6	0.6	9.1
Ck2	70-100	2.6	0.2	2.4	2.4	7.6	2.2	4.9	0.5	7.6
Ck3	100-110	2.3	0.2	2.3	1.9	6.9	2.1	4.4	0.4	6.9
Ck4	110-140	2.2	0.2	2.1	1.9	6.4	1.4	4.6	0.4	6.4
Ck5	140-160	2.4	0.2	1.7	2.0	6.3	1.0	4.7	0.6	6.3

Table A.17. Concentrations of soluble ions in saturated extracts of profile W.2 (Rego Black Chernozem).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁻	HCO ₃ ⁻	Cl ⁻	Total
LFH	20-0	0.5	2.2	0.8	2.4	5.9	2.3	2.8	0.8	5.9
Ahk	0-15	6.9	0.3	2.8	2.4	12.4	4.2	4.0	4.2	12.4
Cca1	15-30	3.7	0.2	2.9	4.4	11.2	4.9	5.7	0.6	11.2
Cca2	30-50	3.1	0.1	2.1	3.2	8.5	2.7	5.5	0.3	8.5
Ck1	50-85	2.9	0.2	2.3	3.0	8.4	2.4	5.5	0.5	8.4
Ck2	85-90	1.7	0.2	0.9	1.9	4.7	1.1	3.3	0.3	4.7
Ck3	90-120	2.1	0.2	1.2	2.0	5.5	1.4	3.8	0.3	5.5
Ck4	120-150	1.8	0.2	1.1	1.8	4.9	0.8	3.7	0.4	4.9

Table A.18. Concentrations of soluble ions in saturated extracts of profile W.3 (Rego Black Chernozem).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁻	HCO ₃ ⁻	Cl ⁻	Total
LFH	20-0	1.3	0.7	0.5	8.6	11.1	1.4	8.4	1.3	11.1
Ahk	0-15	2.4	0.1	0.4	3.3	6.2	1.6	3.4	1.2	6.2
Cca1	15-30	3.4	0.1	0.5	3.6	7.6	3.3	3.3	1.0	7.6
Cca2	30-50	5.6	0.1	0.5	4.5	10.7	4.1	5.3	1.3	10.7

Table A.19. Concentrations of soluble ions in saturated extracts of profile Gleysolic soil (in a big depression).

Horizon	Depth (cm)	Cations (meq/L)					Anions (meq/L)			
		Na ⁺	K ⁺	Mg ⁺⁺	Ca ⁺⁺	Total	SO ₄ ⁺⁺	HCO ₃ ⁻	Cl ⁻	Total
LFH	3-0	0.7	1.2	0.4	4.2	6.5	0.3	5.4	0.8	6.5
Ah	0-30	0.9	0.4	0.2	1.5	3.0	0.6	1.9	0.5	3.0
B1g	30-70	0.9	0.2	0.3	2.0	3.4	1.2	1.9	0.3	3.4
B2g	70-120	0.9	0.2	0.3	2.9	4.3	2.3	1.7	0.3	4.3
Ccag	120-150	1.2	0.3	0.4	5.4	7.3	2.5	1.9	2.9	7.3
Ck1g	150-170	1.3	0.2	0.3	3.9	5.7	3.4	1.9	0.4	5.7
Ck2g	170-190	0.2	1.5	0.4	3.8	5.9	0.0	5.1	0.8	5.9

APPENDIX B

Table B.1. Physical and chemical analyses of profile B. 1 (Brown Soil).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol _c ,kg ⁻¹	Exchangeable Cations cmol _c ,kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
Ah	0-5	6.6	0.7	0.97	2.3	-	25	41	34	23.5	16	6.1	1.5	0.0
Bm	5-16	7.1	0.7	1.22	2.4	-	33	30	33	25.4	18	5.9	1.1	0.0
Cca1	16-30	7.8	0.6	1.23	1.1	17.8	34	31	35	22.6	12.2	9.0	0.7	0.3
Cca2	30-50	8.2	0.8	1.39	0.3	16.1	38	30	32	20.5	7.6	12.5	0.8	1.4
Cca3	50-75	8.7	1.0	1.38	0.3	12.9	13	37	50	21.7	3.7	14.9	1.3	3.3
Ck1	75-100	8.5	3.5	1.34	0.5	7.3	14	37	49	23.7	3.2	15.2	1.5	5.7
Ck2	100-128	8.4	9.4	1.45	0.1	6.8	15	39	46	26.2	5.2	15.0	1.3	6.2

Table B.2. Physical and chemical analyses of profile B. 2 (Brown Soil).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol _c ,kg ⁻¹	Exchangeable Cations cmol _c ,kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
Ah	0-6	6.9	1.1	1.11	2.3	-	44	34	22	19.6	14.1	4.4	1.2	0.0
Bm	6-21	7.1	0.7	1.23	2.5	-	51	24	25	20.7	15.6	4.9	0.6	0.0
Cca1	21-30	7.6	0.6	1.23	1.4	19.7	47	27	26	15.0	10.3	5.1	0.4	0.0
Cca2	30-59	7.8	0.6	1.36	0.6	18.9	49	27	24	15.2	9.0	5.8	0.5	0.2
Ck1	59-79	8.3	0.9	1.40	0.3	13.9	45	29	26	11.6	5.1	7.8	0.7	0.7
Ck2	79-105	8.1	7.8	1.40	0.2	12.0	44	29	27	13.8	3.4	10.4	0.9	1.4
Ck3	105-130	8.1	8.6	1.39	0.1	10.0	45	28	27	14.8	7.7	7.1	0.8	1.6

Table B.3. Physical and chemical analyses of profile B. 3 (Brown Soil).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol _c ,kg ⁻¹	Exchangeable Cations cmol _c ,kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
Ah	0-4	6.6	1.3	1.1	2.7	-	33	35	32	24.5	17.1	6.1	1.5	0.0
Bm	4-16	6.9	0.9	1.22	1.6	-	36	29	35	25.9	16.2	6.9	1.1	0.0
Cca1	16-28	7.5	0.8	1.25	0.6	13.8	33	34	33	23.8	15.2	7.3	0.9	0.1
Cca2	28-52	7.8	0.8	1.25	0.9	10.7	32	35	33	21.2	10.1	10.2	0.8	0.4
Cca3	52-78	8.2	1.9	1.28	0.1	11.5	28	44	28	23.3	6.9	16.1	1.1	1.4
Ck1	78-100	8.2	4.7	1.33	0.1	6.7	34	34	32	23.9	4.2	18.0	0.8	2.0
Ck2	100-130	8.1	9.4	1.38	0.0	17.6	29	43	28	15.3	4.1	10.2	0.7	2.0

Table B.4. Physical and chemical analyses of profile B. 4 (Brown Soil).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol ₍₊₎ kg ⁻¹	Exchangeable Cations cmol ₍₊₎ kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
Ah	0-10	6.9	0.6	0.94	2.5	-	49	23	28	23.2	15.9	6.0	1.0	0.0
Bm	10-25	7.0	0.4	1.27	1.3	-	42	34	24	24.8	13.1	9.3	1.2	0.0
Cea1	25-50	7.9	0.5	1.27	0.6	23.9	37	29	34	19.3	12.0	7.2	0.8	0.2
Cea2	50-75	8.3	0.9	1.38	0.3	20.1	40	27	33	25.4	12.8	10.6	1.1	0.8
Cea3	75-96	8.4	1.6	1.43	0.2	16.2	37	29	33	24.6	10.5	12.6	1.1	1.3
Ck1	96-116	8.3	2.1	1.48	0.0	14.8	36	34	30	25.6	11.2	12.7	1.1	1.5
Ck2	116-130	7.8	6.9	1.48	0.0	14.2	36	32	32	23.2	10.0	12.1	1.0	1.6

Table B.5. Physical and chemical analyses of profile B. 5 (Dry Brown Soil).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol ₍₊₎ kg ⁻¹	Exchangeable Cations cmol ₍₊₎ kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
Ah	0-5	6.8	0.7	1.14	1.7	-	47	34	19	17.6	11.6	4.8	1.0	0.0
Bm	5-12	7.0	0.5	1.30	1.3	-	44	23	33	24.7	16.3	6.2	0.7	0.0
Cea1	12-35	7.8	0.4	1.31	0.7	17.1	49	26	25	21.8	15.9	5.8	0.4	0.0
Cea2	35-65	8.2	0.6	1.30	0.4	14.5	54	23	27	16.3	9.5	6.8	0.5	0.3
Ck1	65-88	8.7	0.8	1.41	0.4	12.7	49	26	25	15.9	6.2	8.2	0.6	1.2
Ck2	80-100	8.6	1.4	1.45	0.5	12.4	50	23	27	24.7	10.3	13.9	0.6	1.8

Table B.6. Physical and chemical analyses of profile B. 6 (Dry Brown Soil).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol ₍₊₎ kg ⁻¹	Exchangeable Cations cmol ₍₊₎ kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
Ah	0-12	6.9	0.8	1.05	2.1	-	46	26	28	23.98	17.4	5.6	0.9	0.0
Cea1	12-43	7.8	0.5	1.30	0.7	22.5	35	31	34	20.98	14.4	6.5	0.4	0.1
Cea2	43-78	8.2	0.7	1.35	0.2	17.5	34	32	34	20.06	10.0	11.1	0.6	0.6
Cea3	78-97	7.9	3.2	1.36	0.2	11.5	36	30	34	19.88	7.3	10.7	0.7	1.5
Cksa	97-110	7.9	6.1	1.21	0.2	10.7	37	33	30	15.06	8.1	6.2	0.7	1.7

Table B.7. Physical and chemical analyses of profile DB.1 (Dark Brown Soil).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol ₍₊₎ kg ⁻¹	Exchangeable Cations cmol ₍₊₎ kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
Ah	0-10	7.1	0.8	1.06	3.5	-	55	22	23	18.0	14.7	3.8	0.8	0.0
Bm	10-25	7.5	0.6	1.43	1.9	-	59	23	18	12.9	9.4	3.3	0.5	0.0
Cca1	25-45	7.9	8.1	1.40	1.2	25.3	57	24	19	13.4	8.7	4.6	0.3	0.7
Cca2	45-68	8.3	19.1	1.41	0.2	26.7	64	25	11	24.5	15.9	7.3	0.2	1.5
Ck1	68-80	8.4	18.4	1.40	0.0	19.9	67	21	12	21.9	10.8	9.7	0.2	1.2
Ck2	80-100	8.3	14.5	1.56	0.0	23.4	21	44	35	30.2	17.9	10.9	0.5	2.6
Ck3	100-120	8.2	11.5	1.60	0.0	19.8	54	26	20	26.3	15.1	9.9	0.4	1.4
Ck4	120-140	8.2	10.0	1.7	0.0	19.5	40	37	23	26.4	14.6	10.3	0.5	1.6

Table B.8. Physical and chemical analyses of profile DB.2 (Dark Brown Soil).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol ₍₊₎ kg ⁻¹	Exchangeable Cations cmol ₍₊₎ kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
Ah	0-9	6.6	0.9	0.70	4.4	-	44	32	24	22.2	16.5	5.2	1.3	0.0
Bm	9-18	7.1	0.9	1.22	3.3	-	46	31	23	20.1	15.6	4.6	0.8	0.0
Cca	18-48	8.0	0.7	1.11	1.5	29.3	37	37	26	16.1	10.5	5.8	0.4	0.1
Ck1	48-68	7.9	5.5	1.35	0.3	20.2	37	34	29	16.0	9.9	7.5	0.7	0.5
Ck2	68-98	8.3	10.8	1.35	0.1	13.6	55	24	21	10.4	4.1	7.2	0.6	1.0
Ck3	98-138	8.3	13.8	1.34	0.2	14.7	38	38	24	18.9	9.1	9.5	0.6	1.7
Cg	138-175	8.2	17.8	1.42	0.1	11.9	32	41	27	18.2	5.1	12.1	0.6	2.1

Table B.9. Physical and chemical analyses of profile DB. 3 (Dark Brown Soil).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol ₍₊₎ kg ⁻¹	Exchangeable Cations cmol ₍₊₎ kg ⁻¹			
							sand %	Silt %	Clay %		Ca	Mg	K	Na
Ah	0-6	6.8	0.9	1.03	2.9	-	36	37	27	25.7	18.0	5.6	1.5	0.0
Bm	6-20	7.1	0.9	1.23	2.5	-	44	30	26	23.1	17.4	5.1	0.9	0.0
Cca1	20-40	7.8	0.7	1.14	0.9	21.5	28	44	28	18.8	12.7	6.0	0.6	0.0
Cca2	40-60	8.6	0.8	1.26	0.2	16.5	44	38	18	11.1	3.2	8.1	0.5	0.2
Ck1	60-92	8.6	0.9	1.37	0.1	9.8	38	46	16	13.7	3.4	10.4	0.5	0.3
2Ck	92-125	8.4	1.9	1.46	0.0	6.5	66	23	11	7.8	2.6	5.5	0.3	0.3

Table B.10. Physical and chemical analyses of profile Bl. 1 (Black Soil).

Profile/ horizon	Depth Cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol ₍₊₎ kg ⁻¹	Exchangable Cations cmol ₍₊₎ kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
Ah	0-10	6.6	1.2	0.87	5.7	-	39	37	24	26.1	19.0	6.0	2.1	0.0
Bm	10-32	6.6	0.6	1.26	2.0	-	48	28	24	17.5	8.8	6.4	1.4	0.0
Cca1	32-64	7.8	1.0	1.17	0.4	34.4	47	29	24	14.3	8.9	4.9	0.6	0.2
Cca2	64-82	7.9	7.0	1.41	0.2	29.3	49	28	23	17.8	10.5	6.6	0.6	1.2
Ck1	82-100	8.2	13.1	1.39	0.2	26.7	49	29	22	25.8	17.2	6.0	0.4	2.2
Ck2	100-120	8.1	9.7	1.48	0.1	24.0	50	28	22	19.5	14.1	4.1	0.4	1.9

Table B.11. Physical and chemical analyses of profile Bl. 2 (Black Soil).

Profile/ horizon	Depth Cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol ₍₊₎ kg ⁻¹	Exchangable Cations cmol ₍₊₎ kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
Ah	0-14	6.5	0.9	0.89	5.0	-	36	37	27	30.2	20.0	7.6	1.2	0.0
Bm	14-34	6.9	0.8	1.29	2.3	-	40	27	33	24.8	11.6	11.9	0.8	0.1
Cca1	34-62	7.7	5.1	1.36	0.7	19.7	40	31	29	17.7	11.5	5.9	0.4	0.2
Cca2	62-74	8.0	7.8	1.63	0.1	21.5	48	26	26	17.3	10.0	8.0	0.4	0.6
Ck1	74-104	8.1	11.2	1.66	0.1	13.5	51	25	24	16.9	7.2	9.6	0.3	0.7
Ck2	104-134	8.9	11.5	1.67	0.1	16.6	40	33	27	19.2	10.1	10.2	0.3	0.8
Ck3	134-154	7.9	9.9	1.72	0.0	18.7	42	29	29	16.5	9.3	7.4	0.4	0.6
Ck4	154-170	7.7	6.9	1.88	0.0	20.8	58	21	21	15.4	9.8	5.4	0.4	0.4

Table B.12. Physical and chemical analyses of profile Bl. 3 (Black Soil).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol ₍₊₎ kg ⁻¹	Exchangable Cations cmol ₍₊₎ kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
Ah	0-8	6.6	0.9	0.85	4.4	-	39	40	21	30.2	22.4	5.5	1.3	0.0
Bm	8-22	7.3	0.7	1.32	2.5	-	28	42	30	27.1	19.9	6.0	0.8	0.0
Cca1	22-40	7.9	0.7	1.29	2.1	23.3	27	43	30	24.0	18.1	6.1	0.5	0.0
Cca2	40-52	8.2	0.8	1.39	1.1	15.2	37	39	24	20.7	10.3	9.3	0.6	0.1
Ck1	52-85	8.5	2.7	1.48	0.3	12.5	43	35	22	20.1	5.6	12.6	0.6	0.8
Ck2	85-115	8.3	6.2	1.46	0.1	11.6	48	31	21	13.5	3.9	9.5	0.5	1.1
Ck3	115-130	8.4	5.9	1.48	0.0	11.5	40	33	27	15.0	3.1	10.9	0.6	1.4

Table B.13. Physical and chemical analyses of profile G. 1 (Gray Soil).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol ₍₊₎ kg ⁻¹	Exchangeable Cations cmol ₍₊₎ kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
LFH	5-0	6.3	1.2	0.20	24.0	-	-	-	-	-				
Ae	0-11	6.4	0.5	1.34	0.0	-	55	33	11	7.7	4.5	1.8	0.4	0.0
Bt	11-52	5.5	0.3	1.59	0.3	1.8	47	28	25	13.2	8.9	3.7	0.4	0.1
Cca1	52-74	7.9	0.6	1.23	1.5	34.2	51	27	22	16.0	14.8	2.1	0.2	0.0
Cca2	74-114	7.9	0.5	1.47	0.1	21.6	55	25	17	13.8	10.8	3.1	0.2	0.0
Cca3	117-144	8.0	0.6	1.64	0.1	13.5	54	27	19	17.9	12.9	3.4	0.3	0.1
Ck	144-190	8.1	0.5	1.70	0.1	13.0	51	30	19	12.7	7.9	3.3	0.2	0.0

Table B.14. Physical and chemical analyses of profile G. 2 (Gray Soil).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol ₍₊₎ kg ⁻¹	Exchangeable Cations cmol ₍₊₎ kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
LFH	10-0	6.4	1.0	0.12	24.4	-	-	-	-	-				
Ae	0-32	5.7	0.4	1.45	0.1	-	61	27	12	5.7	3.5	1.9	0.2	0.0
Bt	32-57	7.2	0.6	1.75	0.2	1.8	51	26	23	18.2	7.9	9.6	0.3	0.2
Cca1	57-85	8.2	0.7	1.62	0.3	23.9	58	25	17	16.4	9.4	6.8	0.1	0.1
Cca2	85-100	8.1	0.6	1.70	0.0	12.1	56	27	17	14.4	6.9	6.4	0.1	0.2
Ck	100-133	8.1	0.7	1.55	0.0	13.3	55	27	18	11.2	7.1	4.1	0.2	0.1

Table B.15. Physical and chemical analyses of profile G. 3 (Gray Soil).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol ₍₊₎ kg ⁻¹	Exchangeable Cations cmol ₍₊₎ kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
LFH	4-0	6.9	0.9	0.09	24.8	-	-	-	-	-				
Ae	0-17	6.3	0.6	1.21	0.9	-	43	45	12	7.9	5.7	1.5	0.6	0.1
Bt	17-47	6.7	0.5	1.45	0.9	-	41	20	39	19.9	12.7	6.7	0.6	0.
BC	47-53	7.9	0.6	1.49	0.9	15.8	41	32	27	15.0	10.9	4.0	0.3	0.0
Cca1	53-70	8.1	1.0	1.40	0.9	30.1	31	41	28	16.0	13.2	3.3	0.3	0.0
Cca2	70-92	8.1	3.1	1.32	0.1	30.2	40	35	25	14.5	11.0	4.1	0.2	0.0
Cca3	92-115	8.2	2.6	1.39	0.1	21.2	44	29	27	14.4	10.0	4.5	0.3	0.0
Ck1	115-125	8.3	2.3	1.39	0.1	21.3	41	27	32	19.5	13.5	6.6	0.3	0.1
Ck2	125-150	8.1	4.0	1.43	0.1	26.1	37	28	35	21.7	16.5	5.1	0.3	0.1

Table B.16. Physical and chemical analyses of profile W.1 (Rego Black Chernozem).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol _c ,kg ⁻¹	Exchangable Cations cmol _c ,kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
LFH	20-0	6.7	0.7	0.16	29.8	-	-	-	-	-				
Ahk	0-25	7.3	4.8	0.82	5.8	24.6	59	22	19	31.0	24	5.8	0.2	0.5
Cca1	25-40	7.5	2.3	1.05	0.8	14.3	66	20	14	18.8	13.5	3.2	0.2	0.4
Cca2	40-55	7.8	1.0	1.2	0.4	8.4	68	20	12	10.6	8.6	2.0	0.2	0.2
Ck1	55-70	7.9	0.7	1.3	0.2	8.0	71	20	9	6.1	5.2	1.5	0.2	0.1
Ck2	70-100	8.0	0.6	1.3	0.1	6.15	69	22	9	5.2	3.3	1.6	0.2	0.1
Ck3	100-110	8.1	0.6	1.3	0.0	4.4	76	17	7	4.5	3.9	1.6	0.4	0.2
Ck4	110-140	8.8	0.5	1.3	0.0	11.2	33	49	18	7.2	4.6	2.2	0.3	0.1
Ck5	140-160	7.9	0.6	1.3	0.0	7.0	58	27	15	7.7	6.0	1.8	0.2	0.0

Table B.17. Physical and chemical analyses of profile W.2 (Rego Black Chernozem).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol _c ,kg ⁻¹	Exchangable Cations cmol _c ,kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
LFH	20-0	6.5	0.8	0.18	24.3	-	-	-	-	-				
Ahk	0-15	7.3	3.2	0.84	5.1	33.6	31	33	36	42.3	35.9	7.4	0.2	0.5
Cca1	15-30	7.6	0.9	1.06	0.5	30.4	33	43	24	18.1	17.6	2.0	0.3	0.3
Cca2	30-50	7.7	0.7	1.2	0.3	19.0	39	40	21	13.3	11.7	2.1	0.3	0.2
Ck1	50-85	7.7	0.7	1.3	0.1	16.1	48	39	13	8.8	6.6	1.4	0.2	0.1
Ck2	85-90	8.1	0.4	1.3	0.1	9.7	49	39	12	7.5	5.0	2.1	0.2	0.1
Ck3	90-120	7.9	0.5	1.3	0.1	9.5	50	40	10	6.4	4.6	1.6	0.2	0.5
Ck4	120-150	7.9	0.4	1.3	0.0	8.9	57	34	10	6.2	4.0	1.2	0.2	1.0

Table B.18. Physical and chemical analyses of profile W.3 (Rego Black Chernozem).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol _c ,kg ⁻¹	Exchangable Cations cmol _c ,kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
LFH	20-0	6.2	1.1	0.18	34.3	-	-	-	-	-				
Ahk	0-15	7.9	2.2	0.85	4.7	30.7	45	33	22	41.5	32.6	9.2	0.2	0.9
Cca1	15-30	7.9	2.5	1.05	1.6	25.9	50	32	18	18.9	15.7	2.5	0.2	0.4
Cca2	30-50	8.2	1.3	1.10	0.3	27.0	42	40	18	11.7	10.1	1.5	0.2	0.4

Table B.19. Physical and chemical analyses of profile (Gleysolic Soil in big depression).

Profile/ horizon	Depth cm	pH	EC dS/m	BD g/cm ³	OC %	CaCO ₃ %	Texture			CEC cmol _c ,kg ⁻¹	Exchangeable Cations cmol _c ,kg ⁻¹			
							Sand %	Silt %	Clay %		Ca	Mg	K	Na
LFH	3-0	5.9	0.8	1.15	12.9	-	-	-	-	-				
Ah	0-30	5.6	0.4	1.55	4.1	-	47	31	22	22.3	14.5	6.8	0.9	0.0
B1g	30-70	6.4	0.9	1.72	0.6	-	43	27	30	17.7	7.9	8.8	0.7	0.0
B2g	70-120	7.0	0.5	1.82	0.1	1.1	52	25	23	11.6	5.1	5.8	0.4	0.0
Ccag	120-150	7.8	0.6	1.81	0.0	15.6	53	25	22	12.3	7.7	3.5	0.3	0.0
Ck1g	150-170	7.7	1.1	1.81	0.0	14.4	54	25	21	12.4	7.3	3.3	0.3	0.0
Ck2g	170-190	7.7	0.8	1.26	0.0	15.6	53	26	21	12.0	51.8	17.4	0.4	1.0

APPENDIX C

Table C.1. Carbon and oxygen isotopes of organic and pedogenic carbonate in Brown soil zone.

Profile/horizon	Depth (cm)	OC $\delta^{13}\text{C}$	Pendant depth cm	pendant $\delta^{13}\text{C}$	pendant $\delta^{18}\text{O}$	soil $\delta^{13}\text{C}$	soil $\delta^{18}\text{O}$	Pedo. CaCO_3 %	Total CaCO_3 kg m^{-2}	CaCO_3 in 120 cm kg m^{-2}	Total pedo. CaCO_3 kg m^{-2}	pedo. CaCO_3 in 120 cm kg m^{-2}
B.1												
Ah	0-5	-24.8										
Bm	5-16	-24.7	14 cm	-6.8	-9.4							
Ccal	16-30	-24.2	26 cm	-7.0	-9.8	-4.3	-8.7	55.6	30.6	30.6	17.0	17.0
Cca2	30-50	-24.3	32 cm	-7.0	-9.6	-3.5	-7.7	43.0	44.8	44.8	19.3	19.3
Cca3	50-75	-24.6	41 cm	-6.3	-9.1	-4.6	-9.3	68.8	44.5	44.5	30.6	30.6
Ck1	75-100			-6.3	-9.1	-6.0	-9.6	95.1	24.4	24.4	23.2	23.2
Ck2	100-128			-6.3	-9.1	-3.8	-8.8	54.5	17.4	17.4	15.0	10.7
									161.7		105.1	100.8
B.2												
Ah	0-6	-24.1										
Bm	6-21	-24.0	24 cm	-5.7	-9.4							
Ccal	21-30	-24.2	25 cm	-7.9	-9.5	-7.9	-9.6	100.0	21.8	21.8	21.8	21.8
Cca2	30-59	-24.5	30 cm	-5.64	-9.3	-5.5	-9.1	97.1	74.7	74.7	72.5	72.5
Ck1	59-79	-25.1	45 cm	-5.7	-9.5	-4.2	-8.0	69.8	40.8	40.8	28.5	28.5
Ck2	79-105			-5.7		-2.7	-7.5	37.7	45.2	45.2	17.1	17.1
Ck3	105-130			-5.7		-1.4	-7.0	11.6	20.9	20.9	2.4	1.2
									203.4		142.3	141.1
B.3												
Ah	0-4	-25.1										
Bm	4-16	-23.9										
Ccal	16-28	-24.3	25 cm	-6.6	-9.3	-6.6	-9.8	97.1	20.7	20.7	20.1	20.1
Cca2	28-52	-24.4	35 cm	-6.5	-9.7	-6.4	-9.1	95.5	32.0	32.0	30.5	30.5
Cca3	52-78	-24.9	45 cm	-6.7	-10.0	-6.7	-9.4	99.6	38.3	38.3	39.6	39.6
Ck1	78-100			-7.1		-5.8	-9.1	79.6	19.6	19.6	15.6	15.6
Ck2	100-130			-7.1		-0.8	-7.6	-	48.5	32.3	-	-
									159.1	142.9	105.8	105.8

Cont.' Table C.1. Carbon and oxygen isotopes of organic and pedogenic carbonate in Brown soil zone.

Profile/horizon	Depth (cm)	OC $\delta^{13}\text{C}$	Pendant depth cm	Pendant $\delta^{13}\text{C}$	Pendant $\delta^{18}\text{O}$	soil $\delta^{13}\text{C}$	soil $\delta^{18}\text{O}$	Pedo. CaCO_3 %	Total CaCO_3 kg m^{-2}	CaCO_3 in 120 cm kg m^{-2}	Total pedo. CaCO_3 kg m^{-2}	pedo. CaCO_3 in 120 cm kg m^{-2}
B.4												
Ah	0-10	-23.3	25 cm	-4.8	-10.3							
Bm	10-25	-20.5	28 cm	-5.0	-10.0							
Cca1	25-50	-21.5	42 cm	-5.5	-10.5	-4.6	-9.6	88.6	76.0	76.0	62.1	62.1
Cca2	50-75	-24.2	47 cm	-5.9	-11.2	-4.0	-9.1	66.5	69.3	69.3	46.1	46.1
Cca3	75-96		60 cm	-5.7	-10.6	-4.0	-8.7	65.4	48.6	48.6	31.8	31.8
Ck1	96-116		70 cm	-5.9	-10.6	-3.1	-8.1	44.9	43.8	43.8	19.7	19.7
Ck2	116-130					-3.0	-8.0	43.9	29.5	8.4	12.9	2.1
									246.1		172.6	161.8
B.5												
Ah	0-5	-23.5	22 cm	-4.7	-10.0							
Bm	5-12	-22.4	25 cm	-4.7	-10.0							
Cca1	12-35	-22.6	35 cm	-5.4	-10.0	-5.2	-10.1	94.2	51.4	51.4	48.4	48.4
Cca2	35-65	-23.8	41 cm	-5.4	-10.5	-3.8	-8.9	64.6	56.4	56.4	36.4	36.4
Ck1	65-88	-24.6	47 cm	-5.6	-10.2	-2.9	-8.5	42.9	41.0	41.0	17.6	17.6
Ck2	80-100		52 cm	-5.5	-10.2	-3.6	-8.7	60.0	36.0	36.0	21.6	21.6
	100-120		56 cm	-5.4	-9.9				36.0	36.0	21.6	10.8
									220.8		145.6	134.8
B.6												
Ah	0-12	-22.3	28 cm	-5.8	-10.3							
Cca1	12-43	-23.2	33 cm	-5.6	-9.5	-5.1	-9.4	83.3	90.5	90.5	75.4	75.4
Cca2	43-78	-24.0	35 cm	-5.5	-10.0	-4.1	-8.9	65.1	91.9	91.9	59.8	59.8
Cca3	78-97		56 cm	-5.6	-9.2	-2.7	-8.3	37.3	32.4	32.4	12.1	12.1
Cksa	97-110		60 cm	-5.6	-9.8	-2.0	-8.0	23.7	16.8	16.8	4.0	4.0
	110-120								16.8	16.8	4.0	2.0
									248.4		155.3	153.3

Table C.2. Carbon and oxygen isotopes of organic and pedogenic carbonate in Dark Brown soil zone.

Profile/horizon	Depth (cm)	OC $\delta^{13}\text{C}$	Pendant depth cm	Pendant $\delta^{13}\text{C}$	pendant $\delta^{18}\text{O}$	soil $\delta^{13}\text{C}$	soil $\delta^{18}\text{O}$	Pedo. CaCO_3 %	Total CaCO_3 kg m^{-2}	CaCO_3 in 120 cm kg m^{-2}	Total pedo. CaCO_3 kg m^{-2}	pedo. CaCO_3 in 120 cm kg m^{-2}	
DB.1													
Ah	0-10	-24.9											
Bm	10-25	-23.7	25 cm	-5.4	-10.8								
Cca1	25-45	-24.3	40 cm	-5.7	-10.4	-5.6	-9.7	98.2	70.8	70.8	69.5	69.5	
Cca2	45-68	-24.4	45 cm	-5.6	-20.3	-3.6	-8.5	58.1	86.7	86.7	50.3	50.3	
Ck1	68-80		68 cm	-5.8	-10.7	-2.3	-7.5	29.8	33.4	33.4	9.9	9.9	
Ck2	80-100		76 cm	-5.8	-11.0	-2.1	-7.7	26.4	66.7	66.7	17.6	17.6	
Ck3	100-120			-5.8		-1.8	-6.9	19.3	63.4	63.4	12.3	12.3	
Ck4	120-140			-5.8		-1.1	-6.6	5.4	66.4	321.0	3.6	159.6	
												163.2	
DB.2													
Ah	0-10	-26.3	10 cm	-4.7	-10.5								
Bm	10-18	-22.9	25 cm	-5.0	-10.2								
Cca1	18-48	-23.9	45 cm	-6.1	-10.6	-5.1	-9.3	81.0	97.4	97.4	78.9	78.9	
Cca2	48-68	-24.6	65 cm	-6.1	-10.8	-5.3	-10.5	85.3	56.7	56.7	48.5	48.5	
Ck2	68-98			-6.1		-3.7	-8.7	53.9	57.0	57.0	30.7	30.7	
Ck3	98-138	-24.6		-6.1		-4.1	-9.3	61.4	78.6	43.2	26.5	14.6	
Cg	138-175			-6.1		-4.1	-8.2	61.4	62.3	254.4	38.2	172.7	
												244.6	
DB.3													
Ah	0-6	-25.1	20 cm	-5.4	-9.7								
Bm	6-20	-24.9	27 cm	-5.4	-10.0								
Cca1	20-40	-24.8	35 cm	-5.3	-9.7	-5.0	-9.5	93.6	49.0	49.0	45.9	45.9	
Cca2	40-60	-24.3	85 cm	-4.7	-9.3	-3.8	-8.5	76.4	41.6	41.6	31.8	31.8	
Ck1	60-92			-4.7		-2.6	-7.3	39.0	43.0	43.0	16.7	16.7	
2Ck	92-125			-4.7		-1.5	-7.3	12.4	31.1	26.4	3.9	3.3	
												98.3	97.7

Table C.3. Carbon and oxygen isotopes of organic and pedogenic carbonate in Black soil zone.

Profile/horizon	Depth (cm)	OC $\delta^{13}\text{C}$	Pendant depth cm	$\delta^{13}\text{C}$	pendant $\delta^{18}\text{O}$	soil $\delta^{13}\text{C}$	soil $\delta^{18}\text{O}$	Pedo. CaCO_3 %	Total CaCO_3 kg m^{-2}	CaCO_3 in 120 cm kg m^{-2}	Total pedo. CaCO_3 kg m^{-2}	pedo. CaCO_3 in 120 cm kg m^{-2}
Bl.1												
Ah	0-10	-25.2										
Bm	10-32	-24.4	22	-5.2	-9.3							
Cca1	32-64	-24.4	27	-5.6	-9.3	-3.7	-8.4	63.2	128.8	128.8	81.3	81.3
Cca2	64-82	-24.3	30	-5.4	-9.4	-2.9	-7.7	44.9	74.3	74.3	33.3	33.3
Ck1	82-100	-24.8	40	-5.5	-9.2	-2.8	-7.7	43.6	66.8	66.8	29.1	29.1
Ck2	100-120			-5.5	-9.2	-1.7	-6.9	18.2	71.0	71.0	12.9	12.9
									340.9		156.6	156.6
Bl.2												
Ah	0-14	-25.2										
Bm	14-34	-24.4	35	-6.1	-11.2							
Cca1	34-62	-24.7	60	-7.0	-10.8	-7.0	-10.8	99.2	75.0	75.0	75.0	75.0
Cca2	62-74	-24.3	64	-6.1	-11.1	-3.7	-8.7	55.4	42.1	42.1	23.3	23.3
Ck1	74-104		65	-6.3	-11.5	-3.2	-7.9	43.5	67.4	67.4	29.3	29.3
Ck2	104-134		85	-6.2	-12.2	-0.9	-6.0	1.3	83.2	44.2	0.6	0.6
Ck3	134-154		100	-6.2	-12.1	-1.4	-6.6	11.4	64.3	228.1	7.3	128.2
Ck4	154-170			-6.2	-12.1	-1.0	-6.0	3.5	62.4		2.2	
											137.7	
Bl.3												
Ah	0-10	-25.5	47	-6.7	-10.7							
Bm	10-22	-24.9	65	-5.8	-10.3							
Cca1	22-40	-24.6	70	-5.8	-10.2	-5.6	-9.9	99.0	58.7	58.7	58.1	58.1
Cca2	40-52	-24.8	75	-5.7	-9.8	-4.8	-9.3	84.3	27.0	27.0	22.7	22.7
Ck1	52-85	-24.4	80	-5.6	-9.4	-2.8	-7.6	41.4	61.2	61.2	25.3	25.3
Ck2	85-115		90	-5.7	-10.0	-1.8	-7.2	19.8	50.9	50.9	10.1	10.1
Ck3	115-130		95	-5.6	-10.1	-1.3	-7.0	10.4	25.3	8.5	2.7	1.3
									206.3		117.9	116.5

Table C.4. Carbon and oxygen isotopes of organic and pedogenic carbonate in Gray soil zone.

Profile/horizon	Depth (cm)	OC $\delta^{13}\text{C}$	Pendant depth cm	pendant $\delta^{13}\text{C}$	pendant $\delta^{18}\text{O}$	soil $\delta^{13}\text{C}$	soil $\delta^{18}\text{O}$	Pedo. CaCO_3 %	Total CaCO_3 kg m^{-2}	CaCO_3 in 120 cm kg m^{-2}	Total pedo. CaCO_3 kg m^{-2}	pedo. CaCO_3 in 120 cm kg m^{-2}
G.1												
LFH	5-0	-26.7										
Ae	0-11											
Bt	11-52	-24.8	60 cm	-8.3	-16.4							
Cca1	52-74	-25.3	75 cm	-8.2	-15.3	-6.9	-14.2	82.8	92.5	92.5	76.5	76.5
Cca2	74-114	-24.6	95 cm	-6.9	-14.1	-5.6	-12.0	79.0	126.8	126.8	100.2	100.2
Cca3	117-144		100 cm	-7.9	-13.8	-3.7	-9.6	40.5	59.6	6.6	2.7	2.7
Ck	144-190		150 cm	-6.3	-14.1	-2.9	-8.9	38.0	101.7	38.6	218.0	179.4
G.2												
LFH	10-0	-26.9										
Ae	0-32	-25.5										
Bt	32-57	25.3	50 cm	-8.0	-14.4							
Cca1	57-85	-25.2	60 cm	-8.6	-14.4	-7.7	-13.2	95.2	122.0	122.0	116.1	116.2
Cca2	85-100		65 cm	-8.1	-13.8	-4.0	-9.6	44.5	39.9	39.9	17.8	17.8
Ck	100-133		75 cm	-7.9	-13.8	-3.9	-8.8	41.5	68.2	41.4	28.3	17.2
			90 cm	-8.2	-14.2					203.3	162.2	151.2
G.3												
LFH	4-0											
AE	0-17	-26.5										
Bt	17-47	-25.5										
BC	47-53	-25.6	65 cm	-8.0	-14.2	-2.7	-7.8	26.7	14.1	14.1	3.8	3.8
Cca1	53-70	-25.5	70 cm	-7.6	-13.1	-5.9	-11.3	74.5	71.5	71.5	53.2	53.2
Cca2	70-92	-25.3	80 cm	-7.4	-13.3	-5.7	-11.0	75.2	87.8	87.8	66.0	66.0
Cca3	92-115	-25.4	85 cm	-7.6	-14.0	-4.1	-9.8	47.8	67.8	67.8	32.4	32.4
Ck1	115-125		98 cm	-7.9	-14.5	-3.5	-9.0	38.4	29.6	11.8	11.4	5.7
Ck2	125-150		105 cm	-7.7	-14.1	-3.0	-8.3	31.3	93.2	253.0	166.8	161.1

Table C.5. Carbon and oxygen isotopes of organic and pedogenic carbonate in Rego Black Chernozem soils.

Profile/horizon	Depth (cm)	OC $\delta^{13}\text{C}$	Pendant depth cm	pendant $\delta^{13}\text{C}$	pendant $\delta^{18}\text{O}$	soil $\delta^{13}\text{C}$	soil $\delta^{18}\text{O}$	Pedo. CaCO_3 %	Total CaCO_3 kg m^{-2}	CaCO_3 in 120 cm kg m^{-2}	Total pedo. CaCO_3 kg m^{-2}	pedo. CaCO_3 in 120 cm kg m^{-2}
W.1												
LFH	20-0	-26.1										
Ahk	0-25	-27.0		-9.3		-9.3	-13.3	100.0	50.4	50.4	50.4	50.4
Cca1	25-40	-24.7		-9.3		-8.6	-14.3	91.2	22.5	22.5	20.5	20.5
Cca2	40-55	-23.4		-9.3		-7.0	-14.5	73.0	15.1	15.1	11.0	11.0
Ck1	55-70	-22.2		-9.3		-5.1	-12.3	50.0	15.6	15.6	7.8	7.8
Ck2	70-100			-9.3		-3.6	-10.5	32.9	24.0	24.0	7.9	7.9
Ck3	100-110			-9.3		-1.8	-7.7	12.2	5.7	5.7	0.7	0.7
Ck4	110-140			-9.3		-1.0	-6.5	2.0	43.7	132.6	0.9	98.3
Ck5	140-160			-9.3		-1.1	-6.5	3.2	18.2		0.6	
											99.8	
W.2												
LFH	20-0	-25.4		-9.3								
Ahk	0-15	-27.1		-9.3		-8.7	-13.3	93.1	42.3	42.3	39.4	39.4
Cca1	15-30	-22.2		-9.3		-5.6	-13.6	56.4	48.3	48.3	27.3	27.3
Cca2	30-50	-24.3		-9.3		-4.9	-12.4	47.8	45.6	45.6	21.8	21.8
Ck1	50-85	-23.5		-9.3		-3.9	-11.4	36.5	73.3	73.3	26.7	26.7
Ck2	85-90			-9.3		-2.7		22.3	6.3	6.3	1.4	1.4
Ck3	90-120			-9.3		-1.8	-7.8	11.7	37.0	37.0	4.3	4.3
Ck4	120-150			-9.3		-1.8	-7.9	11.6	34.7		4.0	
										252.5	124.9	120.9
W.3												
LFH	20-0	-25.7		-9.3								
Ahk	0-15			-9.3		-7.3	-13.0	75.7	39.2	39.2	29.7	29.7
Cca1	15-30	-23.1		-9.3		-5.2	-12.6	51.7	40.8	40.8	21.1	21.1
Cca2	30-50			-9.3		-4.8	-13.6	47.1	59.4	59.4	28.0	28.0
										139.4	78.8	110.8

Table C.6. Carbon and oxygen isotopes of organic and pedogenic carbonate in Orthic Humic Gleysolic (in big depression).

Profile/horizon	Depth	OC	Pendant depth	pendant	pendant	soil	soil	Pedo. CaCO ₃	Total CaCO ₃	Total pedo. CaCO ₃
P.16	(cm)	$\delta^{13}\text{C}$	cm	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	%	kg m ⁻²	kg m ⁻²
LFH	3-0	-29.6								
Ah	0-30	-28.3								
B1g	30-70	-27.7								
B2g	70-120	-18.6	125 cm	-7.9	-15.8	-2.6	-7.5	25.5	9.9	2.5
Ccag	120-150		140 cm	-7.3	-15.5	-2.0	-7.8	18.7	84.5	15.8
Ck1g	150-170		165 cm	-6.5	-14.1	-1.5	-6.9	12.7	52.3	6.6
Ck2g	170-190			-6.5		-1.3	-6.8	8.3	39.2	3.3
									185.9	28.2

Appendix D

and C₄ (high ¹³C/¹²C) pathways of photosynthesis in past plant communities, and their relative contribution to NPP through time (Boutton, 1996). Organic matter at any depth should closely reflect the relative contribution of organic matter from C₃ and C₄ plants. The surface horizons of all soils reflect the C₃ to C₄ ratios of the current vegetation (Kelly et al., 1991). The C isotope composition of pedogenic carbonate is also controlled by the plant species present in the ecosystem during the time of carbonate formation (Mermut et al., 2000).

Plants with C₃ pathway (most temperate region terrestrial plants) have δ¹³C values in the range of -21 to -32‰ with a mean value of -27‰, whereas C₄ plants (many arid plants, salt marsh species, and some tropical grasses) have relatively high δ¹³C values (-9 to -17‰), with a mean of about -13‰. Plants with the Crassulacean acid metabolism (CAM) pathway are intermediate with δ¹³C values between -9 to -19‰ with a mean value of -17‰ (Hoefs, 1980; Cerling, 1984; Nordt et al., 1996; Boutton, 1996).

Saskatchewan soils are well studied, but there are no consistent data for the isotopic composition and rate of the accumulation of organic C for soil zones. The relatively young soils of Saskatchewan along with a well-documented deglaciation history, general similarity in glacial parent materials, and a regular environmental gradient in comparison to the other parts of the world, provide the ideal situation to estimate the C flux in soils in the boreal region. The results can be used to estimate more accurate rates of C accumulation in other boreal regions of the world. The objectives of this study were to document soil development, to estimate C storage and

accumulation rates, and to determine the $^{13}\text{C}/^{12}\text{C}$ ratio of soil organic C in a sequence of soils representing gradients in climate and period of soil formation.

3.2. MATERIALS AND METHODS

Five different soil-climatic zones (Dry Brown, Brown, Dark Brown, Black, and Gray) in Saskatchewan, occurring between $49^{\circ} 13'$ and $53^{\circ} 63'$ latitude, and $104^{\circ} 92'$ and $107^{\circ} 66'$ W longitude, were included in this study. Mean annual temperature and precipitation for the Dry Brown soil zone are 4.0°C and 330 mm, for the moist mixed grassland with Dark Brown soils they are 2.4°C and 380 mm, for the Aspen parkland with Black soils they are 1.4°C and 420 mm, and for the Boreal Forest and the Gray soil zone they are 0.4°C and 450 mm. Potential evapotranspiration (PET) is about double that of precipitation (P) in the Brown, with moisture deficits decreasing to the Gray zone, where PET and P are equal (Acton et al., 1998).

Soils were sampled on well-drained, level to gently sloping upper slopes in order to minimize the influence of lateral redistribution of carbonate, i.e. in an environment where a moderate dominantly descending mode of soil moisture movement prevails. All soils sampled were developed on glacial till parent materials and were never cultivated.

There were 18 sites (two in Dry Brown, four in Brown, three in Dark Brown, three in Black, and three in Gray soil zones), representative of the major soil associations on glacial till, and three from highly calcareous Rego Black Chernozem soils (only one of them is marked on the map because they were close to each other) (Fig 3.2). At each site, one soil profile was excavated to > 120 cm depth, and described

according to the Canadian System for Soil Classification (Soil Classification Working Group, 1998). In the vicinity of each profile (the same landscape position) two more cores were sampled by auger. The data for soil chemical properties are the means of three replicates. A Global Positioning System (GPS), PRO XRS model, was used to record the elevation, longitude, and latitude of each profile.

3.2.1 Physical and Chemical Properties

3.2.1.1 pH, Electrical Conductivity, and Soluble Ions

Samples were air-dried and ground to pass a 2-mm sieve. Samples were saturated with de-ionized water to prepare a saturation paste, and an extract obtained under suction used to determine pH, electrical conductivity (EC), and concentration of soluble ions. Soluble Ca^{2+} and Mg^{2+} were determined by atomic absorption spectrometry, and soluble K^{+} and Na^{+} were determined by atomic emission spectrometry. Soluble Cl^{-} was determined by a colorimetric method using Auto Analyzer-1. Sulfate was calculated by subtracting total anions (Cl^{-} , HCO_3^{-} , CO_3^{2-}) from total cations. Bicarbonate and CO_3^{2-} were determined by acid titration (Janzen, 1993).

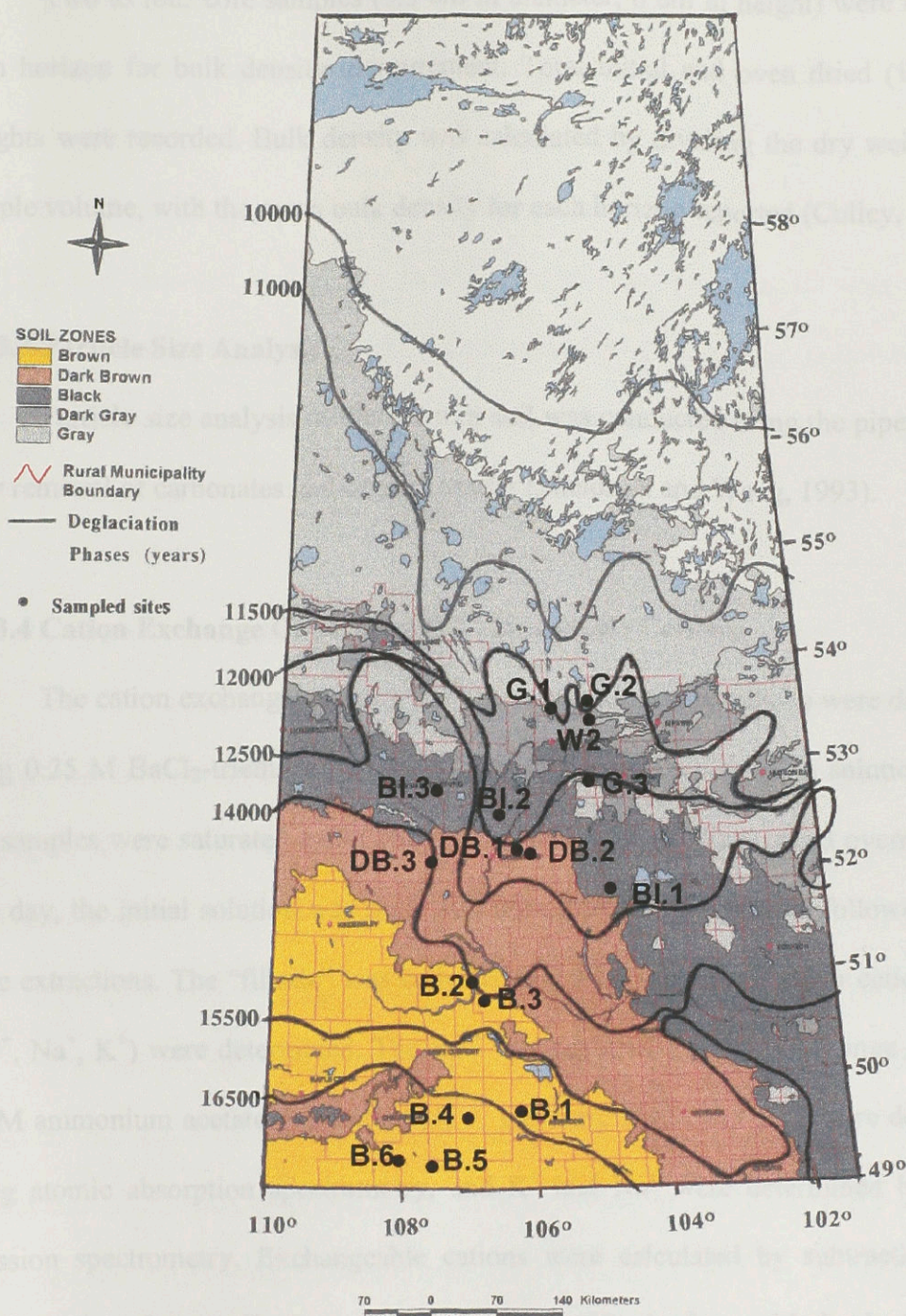


Figure 3.2 Ice margin positions during the deglaciation of Saskatchewan, the study region and soil sampling sites (produced from Saskatchewan Land Resource Centre map (1999) and deglaciation maps (Christiansen, 1979).