CLIMATE EFFECTS ON STABLE CARBON ISOTOPE PROXIES FOR PALEOVEGETATION IN MEADE BASIN, KANSAS

by

CARA MARIE LAURIA

B.S., COLLEGE OF CHARLESTON, 2015

A thesis submitted to the

Faculty of the Graduate School of the

University of Colorado in partial fulfillment

of the requirement for the degree of

Master of Science

Environmental Studies Program

2017

This thesis entitled:

Climate effects on stable carbon isotope proxies for paleovegetation in Meade Basin, Kansas

written by Cara Marie Lauria

has been approved for the Environmental Studies Program

Eve-Lyn S. Hinckley, Ph.D.

Kathryn Snell, Ph.D.

November 29, 2017

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

Lauria, Cara Marie (M.S., Environmental Studies Program)

Climate effects on stable carbon isotope proxies for paleovegetation in Meade Basin, Kansas

Thesis directed by Assistant Professor Eve-Lyn Hinckley and Assistant Professor Kathryn Snell

Abstract

Paleovegetation proxies inform scientists not only about what climate and ecosystems may have looked like through Earth's history, but also give us the ability to predict what today's global change may bring for modern ecosystems. Carbon isotope ratios of soil organic matter (SOM) and pedogenic carbonates record relative proportions of C_4-derived biomass. Each soil constituent is thought to form under different soil climate conditions. Soil organic matter is thought to form under cooler and wetter conditions when climates favor the production of C_3 plant biomass. Pedogenic carbonates are thought to precipitate during the warmest and driest parts of the year, when climates favor the production of C_4 plants and C_3 plants may exhibt water stress. In this study, I investigate if the stable carbon isotopic signatures of SOM and pedogenic carbonates record climate induced vegetation signals. I analyzed and compared the carbon isotope ratio of vegetation collected under drought conditions and wet conditions, SOM, and pedogenic carbonates from four sites that vary in vegetation community and topography in Meade Basin, Kansas. Results from this study suggest carbon isotope values of carbonates and SOM reflect carbon isotope values of vegetation from warm and dry climates and/or values that are ^{13}C-enriched relative to warm and dry vegetation. The degree to which the carbon isotope ratio of SOM and carbonates are enriched relative to vegetation, may be controlled by the local topography. Carbon isotope ratios of SOM and carbonates are become heavier relative to warm and dry vegetation as topography increases. These findings suggest SOM and carbonates formed in lowlands may incorporate more of a vegetation derived carbon isotope ratio, while proxies

formed in uplands may incorporate more ^{13}C-enrichment affects from influences of heavy atmospheric CO_2 and discrimination from decomposition.

Acknowledgements

First, I would like to thank my patient and supportive advisors Dr. Kathryn Snell and Dr. Eve Hinckley for their guidance and openness to welcome me as one of their graduate students. They are my biggest role models in the fields of stable isotope geochemistry and biogeochemistry. I would also like to thank Dr. Kena Fox-Dobbs and Dr. Andrew Haveles for their immense help in generating a sample plan, gathering data, and working through results. Additionally, I would like to thank the primary investigators associated with the Meade Basin Earth-Life Transition Project (NSF-ELT Grant; EAR-1338261): Dr. David Fox, Dr. Pratigya Polissar, and Dr. Kevin Uno. Thank you as well to all the University of Puget Sound students who collected and analyzed some of the data that is included in this thesis, and a special thanks to Rita McCreesh and Hannah Richardson for helping me collect and transport 64 aboveground biomass samples. Thank you also to all those in the Environmental Biogeochemistry Lab and CU Boulder Earth Systems Stable Isotope Lab for their help in the lab, writing and discussion sessions, and support and encouragement through this process. Finally, I would like to thank the University of Colorado at Boulder Environmental Studies Program for the supportive community and opportunity to complete this level of graduate research. This department has afforded me an immense amount of personal and academic growth.

Table of Contents

List of Tables

List of Figures

1. Introduction

Stable carbon isotopes ($\delta^{13}C$) of paleosols (fossil soils) provide information about vegetation of past landscapes. The dominant photosynthetic pathway of a past landscape can provide information about whether former ecosystems were characterized by woody vegetation, i.e. trees and shrubs (C_3-dominated) or open grasslands (C_3- or C_4-dominated) (Cerling et al., 1997; Ehleringer et al., 1997; Ehleringer & Monson, 1993). To reconstruct past vegetation from paleosols, many studies use the $\delta^{13}C$ values of soil organic matter (SOM; $\delta^{13}C_{SOM}$) and pedogenic carbonates ($\delta^{13}C_{carbonates}$) to infer the proportions of C_3 and C_4 plant biomass (Cerling and Quade, 1993; Cerling et al., 1991; Johnson et al., 2007; Mariotti & Peterschmitt, 1994; Mcpherson et al., 1992; Quade et al., 1989). $\delta^{13}C_{SOM}$ values are thought to reflect relative proportions of C_3 and C_4 biomass through time (years to hundreds of years) (Stout and Rafter 1978; Dzurec et al., 1985; Nadelhoffer and Fry 1998). $\delta^{13}C_{carbonates}$ values are thought to reflect soil carbon dioxide (CO_2), which is a function of the $\delta^{13}C$ value of decomposing and aboveground vegetation; therefore, $\delta^{13}C_{carbonates}$ also reflect relative proportions of C_3 and C_4 biomass through time (Cerling, 1984).

The $\delta^{13}C$ value of SOM and soil carbonates are used to interpret relative proportions of C_3 and C_4 biomass, however, each soil component is thought to form under different soil climate conditions (Figure 1). Soil organic matter is derived from the microbial decomposition of aboveground vegetation. Environmental conditions play an important role in controlling the rate of decomposition, especially in temperate grassland regions where water is limited (Figure 1; Schlesinger & Bernhardt, 2013; Stockmann et al., 2013). Epstein et al., (2013) showed that soil moisture is the most important factor controlling rates of decomposition throughout the Great Plains of North America. Adequate soil moisture is not only necessary for plant growth and therefore litter inputs, especially in regions such as the western Great Plains where, but also microbes must uptake carbon as dissolved organic carbon (DOC) (Epstein et al., 2013; Meentemeyer, 1978; Parton et al., 1993). Regions with cool climates also are found to have large accumulations of organic matter, because warming increases soil temperatures and accelerate organic matter decomposition rates, leading to a loss of organic carbon (Hobbie et al., 2000; Post et al., 1982; D. S. Schimel & Parton, 1986).

Pedogenic carbonates form under warm and dry soil conditions, when there is a higher potential for evapotranspiration, higher potential for calcite solubility, and lower soil moisture limits soil respiration and soil CO_2 (pCO_2) (Figure 1; Eswaran et al., 2000). These conditions are necessary to limit the leaching of ions (Ca^{2+}) and dissolution of calcite and facilitate precipitation of calcium carbonate (Eswaran et al., 2000). Seasonal wetting/drying cycles are also thought to be important for the formation of soil carbonates, because wetting events transport minerals vertically in the soil profile and supersaturate the soils with dissolved Ca^{2+}, while drying events facilitate evaporation and precipitation of carbonate (Breecker et al., 2009; Stevenson et al., 2005; Zamanian et al., 2016).

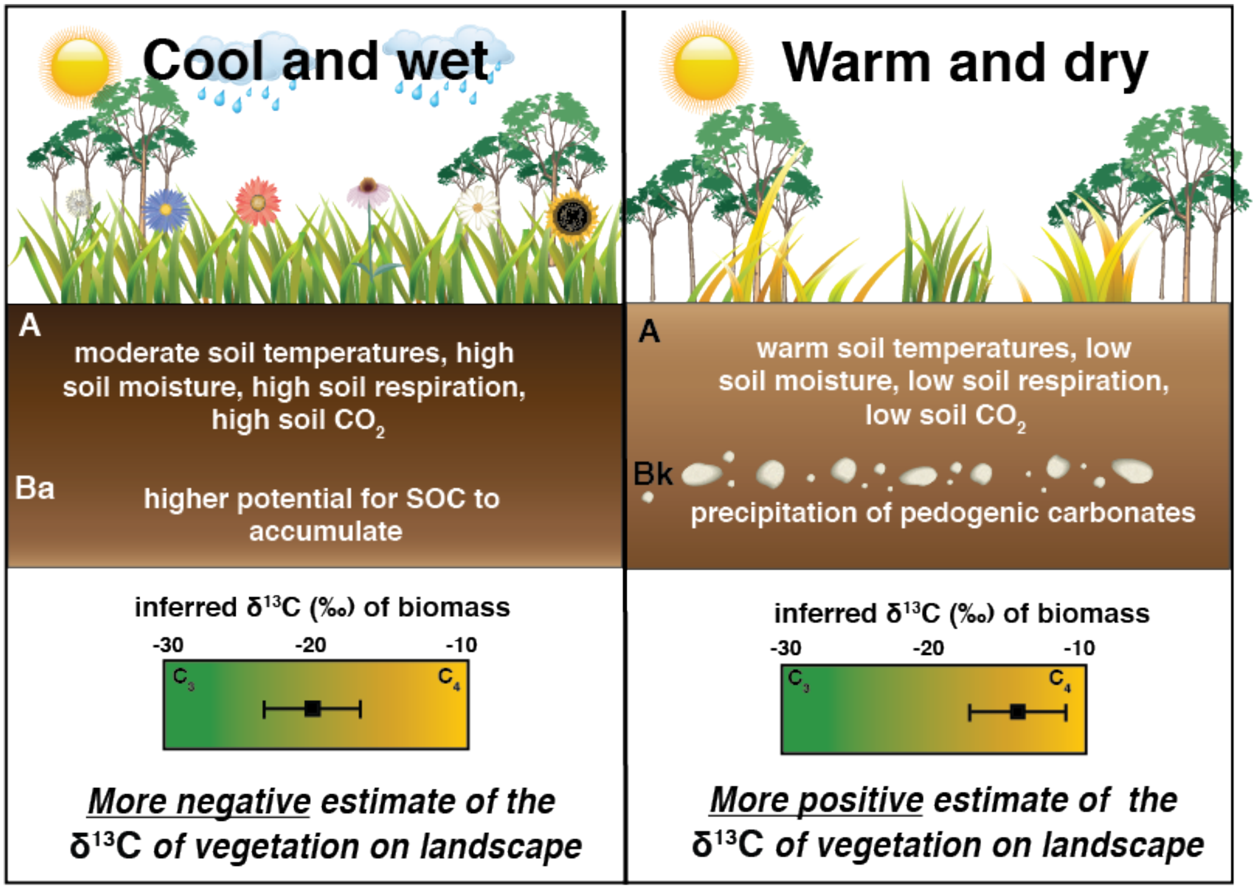

Figure 1. Conceptual model of the formation of soil-based pedogenic carbonates and soil organic matter. Warm and dry conditions present a high potential for pedogenic carbonates to form. During warm and dry periods C_4 plants have a selective advantage over C_3 plants and remaining C_3 plants may confer higher WUE (heavier δ^{13}C values). During cool and wet conditions, organic matter may have a higher potential to accumulate in the soil, because of the high rates of respiration, adequate soil moisture, and moderate temperatures. During cool and wet conditions C_4 plants do not an advantage over C_3 plants.

The proportion of C_3 to C_4 plants also vary depending on climate, and in some regions, even vary throughout the growing season (Figure 1). Increasing proportions of C_4 plants correlate best with warm and dry conditions, while increasing proportions of C_3 plants correlate best with cool and wet climate conditions (Figure 1; Edwards & Smith, 2010; Hoover et al., 2017; Mooney, 1999; Sage, 2001; Smith et al., 2015; Taylor et al., 2014; Teeri & Stowe, 1976). C_4 plants have higher water use efficiencies (WUE) compared to C_3 plants, and therefore may have an advantage over C_3 plants in regions with higher temperatures and lower soil moisture (Nobel 1996; Silvera et al. 2010; Ehleringer et al., 1997; Mooney, 1999; Teeri & Stowe 1976; Ehleringer & Monson 1993; Tieszen et al. 1997; Teeri 1988). Some C_3 species can acclimate to high temperatures and low precipitation by decreasing their stomatal conductance (increasing WUE) (Battipaglia et al., 2017; Cernusak et al., 2013; Ehleringer & Monson, 1993; Farquhar et al., 1989; Farquhar et al., 1982; Martin & Thorstenson, 1988). This ecophysiological response to water stress results in a ^{13}C-enrichment of plant tissues (Battipaglia et al., 2017; Cernusak et al., 2013; Ehleringer & Monson, 1993; Farquhar et al., 1989; Farquhar et al., 1982; Martin & Thorstenson, 1988).

When interpreting past vegetation from $\delta^{13}C_{SOM}$ and $\delta^{13}C_{carbonates}$ it is important to consider that the climate under which they form may result in a bias that drives their carbon isotope values away from "average" vegetation $\delta^{13}C$ values (Figure 1). I hypothesize that (1) under prolonged drought, pedogenic carbonates will precipitate and preserve a ^{13}C-enriched vegetation $\delta^{13}C$ value, due to a greater abundance of C_4 over C_3 plants and higher WUE conferred by C_3 plants (Figure 1). I also hypothesize that (2) under wet and cool climate conditions, SOM will accumulate and preserve ^{13}C-depleted $\delta^{13}C$ values of vegetation due to a greater abundance of C_3 plants (Figure 1). Attempts to quantify the warm and dry seasonal biases of pedogenic carbonate formation are well underway (Breecker et al., 2009; Peters et al., 2013; Quade et al., 2013), however cool and wet biases in the formation of SOM has been less examined.

The motivation for this study is to specifically understand if there are biases in $\delta^{13}C$ values of carbonates and SOM in paleovegetation records from Meade Basin, Kansas. Meade Basin contains fossil evidence for the expansion of C_4 grasslands through the paleosol $\delta^{13}C$

carbonate and SOM records (Fox et al., 2012; Fox & Koch, 2003, 2004). I measured the carbon isotopic signatures of modern (Holocene age) SOM, pedogenic carbonates, and vegetation samples collected under wet and drought conditions from four sites in Meade Basin, KS. Although Meade Basin's biomass is predominately C_4 derived (78% ± 10.9%; Fox et al., 2012), there is much heterogeneity throughout the Great Plains which may be overlooked in paleosol interpretations. For this reason, each site was chosen for its different topography and plant community.

2. Background

2.1 Carbon isotope ratios of pedogenic carbonates

Pedogenic carbonate is a mineral assemblage that is primarily derived from the pool of soil inorganic carbon (SIC), which can be of biologic or geologic sources (Zamanian et al., 2016). Carbonates tend to form in calcic soil horizons as calcite, dolomite, and aragonite (USDA, 1999). Dissolved ions, mainly Calcium (Ca^{2+}) and dissolved inorganic carbon species (DIC; i.e. HCO_3^{-}, CO_3^{2-}, H_2CO_3), are released through the dissolution of minerals in the soil. This solution then percolates or migrates through the soil and if the dissolved mineral solution becomes supersaturated with $CaCO_3$, such as from decreasing soil water content, the solute will re-precipitate as pedogenic carbonate (Breecker et al., 2009; Equation 1). Pedogenic carbonates, therefore, are typically found in soils environments that experience seasonal wetting and drying periods, where evapotranspiration exceeds precipitation, and/or in semiarid to arid regions where mean annual precipitation (MAP) does not exceed more than 250 mm year^{-1} (Breecker et al., 2009; Eswaran et al., 2000; Zamanian et al., 2016).

$$Ca^{2+} + 2HCO^{-}_{3} \Leftrightarrow CaCO_3 + H_2O + CO_2 \qquad (1)$$

The carbon isotope composition of pedogenic carbonates is controlled by the flux of soil CO_2 (Figure 2; Cerling & Quade, 1993; Cerling, 1984; Quade et al., 1989). Cerling and Quade (1993) showed the total isotopic fractionation between soil CO_2 and carbonates results in an enrichment between +16.5‰ and +13.5‰ (mean of +15‰) from diffusion of CO_2 into soil water and temperature-dependent fractionation (Figure 2). At shallow depths (< 30 cm) in the soil profile soil CO_2 may reflect a mix of atmospheric CO_2, root respired CO_2, and microbial respired CO_2 (Cerling and Quade 1993; Quade et al. 1989; Cerling 1984). Therefore the $\delta^{13}C$ may be controlled by both atmospheric CO_2 and aboveground vegetation (C_3 or C_4), resulting in ^{13}C

enrichment of the $\delta^{13}C$ of the soil CO_2 (Cerling and Quade 1993; Quade et al. 1989). At deeper depths (> 30 cm), soil CO_2 is mostly derived from root and microbial respiration, and therefore the $\delta^{13}C$ of soil CO_2 is primarily controlled by the $\delta^{13}C$ of the aboveground vegetation (Quade et al. 1989; Cerling and Quade 1993). In frozen or dry hot desert soils, when soil respiration is low, atmospheric CO_2 will partially contribute to soil CO_2 at deeper depths, resulting in enriched $\delta^{13}C$ values that may not be entirely controlled by aboveground plant communities (Cerling et al., 1993; Cerling, 1984; Quade et al., 1989). During the growing season when soil respiration is high, soil CO_2 is primarily derived from root respiration and decomposition of SOM (Cerling et al., 1993; Cerling, 1984; Quade et al., 1989). Thus, under high soil CO_2 conditions, the $\delta^{13}C$ values of soil CO_2 are controlled by the aboveground plant community (relative proportions of C_3 and C_4) (Cerling et al., 1993; Cerling, 1984; Quade et al., 1989).

Previous studies used the carbon isotope ratios of paleosol carbonates to infer past proportions of C_4 biomass (Feakins et al., 2013; Fox et al., 2012; Fox & Koch, 2003; Latorre et al., 1997; Magioncalda et al., 2004; Quade & Cerling, 1995). However, Breecker et al., (2009) showed that $\delta^{13}C$ values from carbonates reflect a biased vegetation signal due to the seasonal bias in the timing of their formation. Carbonates precipitate under warm and dry conditions, Breecker et al., (2009) argued that using carbon isotope record from paleosol carbonate as a paleovegetation proxy may be problematic, because the $\delta^{13}C$ of the soil CO_2 that is incorporated into the calcite crystal, is decoupled from the $\delta^{13}C$ value of mean growing season CO_2 (Breecker et al., 2009; Quade et al., 2012; Passey et al., 2010; Breecker et al., 2009). Under dry and warm conditions the $\delta^{13}C$ of soil CO_2 is expected to be heavier than the average $\delta^{13}C$ of soil CO_2, because of three mechanisms (1) increasing water stress in C_3 plants (higher WUE; more positive $\delta^{13}C$ values), (2) greater proportion of C_4 plants, especially in areas where seasonal changes in C_3

and C_4 distributions have been observed, and (3) when soils are more aerated during dry periods, atmospheric CO_2 may make up a greater portion of the soil CO_2; atmospheric CO_2 has an isotopic value of -8‰ (Breecker et al. 2009; (Keeling et al., 2000). Together, these processes contribute to a $\delta^{13}C$ value of soil CO_2 that is enriched in ^{13}C and therefore may be interpreted as a falsely C_4 derived dominant ecosystem (Breecker et al., 2009).

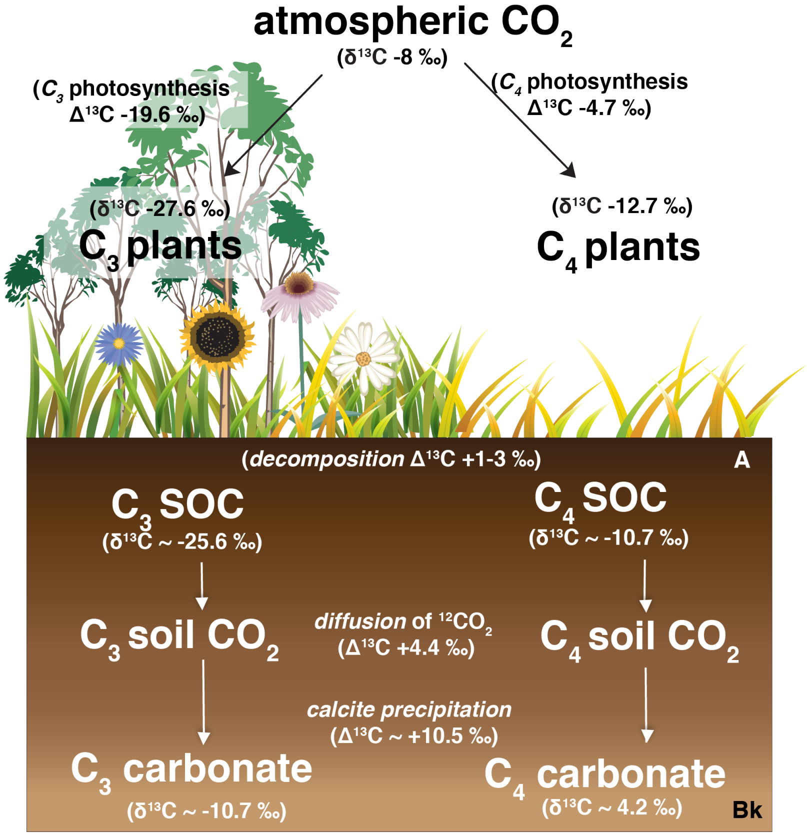

Figure 2. Carbon isotope values and fractionations of paleovegetation proxies, SOC and soil carbonates (adopted from Koch, 1998). Fractionating processes are indicated in italics. The figure uses a modern value for $\delta^{13}C$ of atmospheric CO_2 from Keeling et al. (2000).

2.2 Carbon isotope ratios of soil organic carbon

Soil organic matter is a mixture of organic materials including particulate organics, humus, charcoal, living microbial biomass, and fine plant roots compounds, and contains about

58% soil organic carbon (SOC) (Stockmann et al., 2013; Werth & Kuzyakov, 2010). The amount of SOM that accumulates in the soil is controlled primarily by net primary production and the rate of decomposition, however there are multiple climatic, biological, environmental, chemical, and physical factors that control the stabilization or turnover times of SOC in soil profiles (Lützow et al., 2006). High accumulations of SOC are found in soils where decomposition of organic matter is slow (Hobbie et al., 2000; Post et al., 1982). In semiarid grasslands such as the western Great Plains of North America, the large accumulation of above and belowground biomass, promotes high rates of decomposition and nutrient cycling (Seastedt & Knapp, 1993; Knapp et al., 1998). Soil moisture and temperature are also important controls on microbial activity and the rate of decomposition (Meentemeyer, 1978; Sala et al., 1988; Stockmann et al., 2013). Regional patterns of decomposition throughout the Great Plains, suggest that precipitation contributes more than both temperature and soil texture to rates of decomposition (Howard E Epstein et al., 2013a). Chemical and biological processes also control the rate of decomposition; carbon to nitrogen ratios (C:N) and lignin content are both negatively related to the rate of decomposition (Melillo et al., 1989; Melillo et al., 1982). Soil organic matter can be described based on its fraction (litter vs humus) and stability (labile vs stable). The labile pool of SOM is primarily made up of plant residues, leaf litter, and soil microorganisms and their metabolic products (Parton et al., 1993; Stockmann et al., 2013). Soil organic matter in labile pools facilitate decomposition of freshly added plant and animal residues and release inorganic nutrients like nitrogen (N) and phosphorous (P) which plants can uptake. The stable pool includes organic materials that are more resistant to decomposition such as semi-to-well-decomposed organic materials like humus, plant compounds such as lignin and lipids, or charcoal or charred materials from burning organic matter is typically physically or chemically stabilized (Parton et al., 1993; Stockmann et al., 2013). The stable pools help maintain soil structure by holding soil particles together as stable aggregates and maintain optimum pore space, which is important for improving soil water holding capacity, infiltration, gaseous exchange, and root growth. The physical fractionation of SOM can also be utilized to determine the rate of SOM turnover in soil (Benbi et al., 2014). Soil organic matter can be fractionated into coarse particulate organic matter (*c*POM; size>240 μm), fine particulate organic matter (*f*POM; 53-250 μm), and mineral associated organic matter (MinOM; size<53 μm) (Benbi et al., 2014). The degree of stability increases from *c*POM and *f*POM, which are typically associated with labile or slow pools of SOM, to MinOM which is physically and chemically resistant to decomposition (Benbi et al., 2012).

The carbon isotope signature of $\delta^{13}C_{SOM}$ is commonly used to calculate proportions of C_3 and C_4 biomass on past and present landscapes (Stout and Rafter 1978; Dzurec et al., 1985; Nadelhoffer and Fry 1998; Mcpherson et al. 1992; Mariotti & Peterschmitt 1994; Dzurec et al. 1985; Quade and Cerling, 1995; Tiezen et al., 1997). The $\delta^{13}C_{SOM}$ is thought to be ^{13}C-enriched by 1-3‰ relative to the overlying vegetation (Figure 2, Desjardins et al. 1994; Boutton 1996; Mcpherson et al. 1992; Mariotti & Peterschmitt 1994; Dzurec et al. 1985; Wynn, 2007; Wynn and Bird, 2007). The fractionation associated with decomposition is attributed to increasing carbon isotope ratios of atmospheric CO_2 due to the Seuss Effect (Friedli et al. 1987, Trolier et al. 1996), discrimination against ^{13}C during respiration (Boutton 1996; Nadelhoffer and Fry 1998), or microbial preference for labile compounds that happen to be ^{13}C-enriched (Bowling et al., 2008; Hobbie & Werner, 2004; Wiesenberg et al., 2004; Werth and Kuzyakov, 2010). The latter two mechanisms support the hypotheses that ^{13}C-enriched $\delta^{13}C_{SOM}$ at deeper depths is driven by an increasing proportion of microbial derived or altered SOM (Ehleringer et al., 2000;

Garten et al., 2000; Mariotti & Peterschmitt, 1994; Mcpherson et al., 1992; Werth & Kuzyakov, 2010; Wynn et al., 2005; Wynn et al., 2005).

2.3 C_3 vs C_4 plants and their distributions in North America

Photosynthesis is a solar-powered metabolism that transforms water and CO_2 into sugar and oxygen. There are three photosynthetic pathways that plants use to fix carbon: C_3, C_4, and Crassulacean acid metabolism (CAM). These pathways fix carbon through different anatomical and biochemical processes, and may have evolved as responses to changes in Earth's climate and environmental conditions (Edwards et al., 2010). The C_3 (Calvin-Benson) pathway - named for the three-carbon acid which is the first stable product of fixation – is the oldest photosynthetic metabolism (Gray, 1985; Hatch, 1987; Nobel, 1996; O'Leary, 1988; Rubinstein et al., 2010; Sage, 2004; Wellman & Gray, 2000). The C_4 (Hatch-Slack) pathway – is named for the first stable products during fixation, which is a four-carbon acid (Hatch, 1987; Nobel, 1996; O'Leary, 1988; Rowan F. Sage, 2004). C_4 photosynthesis is thought to have evolved independently at least 66 times within the plant kingdom and 22 to 24 times within the monocotyledonous (monocot) grass family *Poaceae* (Hattersley & Watson, 1992; Edwards et al., 2010). The expansion of C_4 grasslands was first attributed to decreasing $p\mathrm{CO}_2$ throughout the Late Miocene to Pliocene (3-8 Ma) (Ehleringer et al., 1997; Keeley & Rundel, 2003; Zhang et al., 2013). However the variability in timing of C_4 expansion events on different continents suggests there may be additional environmental changes influencing the expansion of C_4 grasslands (Fox & Koch, 2003; Francelanord & Derry, 1994; Hoetzel et al., 2013; Hynek et al., 2012; Latorre et al., 1997; Passey et al., 2002, 2009; Quade et al., 1989; Uno et al., 2011, 2016), including higher growing season temperatures, fire, and/or increased aridity (Feakins et al., 2013; Hoetzel et al., 2013; Passey et al., 2009). Lastly, CAM photosynthesis, named for the *Crassulaceae* family of succulents, switches between the two pathways and is thought to have evolved as a mechanism to improve assimilation of CO_2 in extremely water-limited habitats and is characterized by its nighttime fixation of CO_2 (Keeley & Rundel, 2003; Nobel, 1996; O'Leary, 1988; Silvera et al., 2010).

While the C_4 photosynthetic pathway is present in only about 3-5% of terrestrial plant species, it accounts for approximately 25% of the total global primary productivity (Kellogg, 2013; Kubien & Sage, 2004; Osborne & Beerling, 2006; Sage, 2016; Sage & Monson, 1999). This large amount of carbon fixation is primarily from C_4 monocotyledons (monocots) in grassland ecosystems, which make up about 61% of all C_4 species. (Ehleringer et al., 1997; Kellogg, 2013; Sage & Monson, 1999). At current atmospheric $p\mathrm{CO}_2$, C_4 plants (both monocots and dicotyledons [dicots]) are found to have a selective advantage over C_3 plants (both monocots and dicots) under high temperatures (above 30ºC) and high levels of light (Ehleringer et al., 1997; Mooney, 1999). This temperature-based model of Ehleringer et al., (1997) is consistent the findings of Teerie & Stowe (1976), where C_3 and C_4 distributions are best correlated with mean growing season temperatures in the Great Plains of North America (Teeri & Stowe 1976; Ehleringer & Monson 1993; Tieszen et al. 1997; Teeri 1988). Furthermore, the C_4 pathway is found in multiple species of the family Poaceae, which is comprised of the "PACMAD" clade (an acronym for Panicoidea, Aristidoidea, Chloridoideae, Micranirioideae, Arundinoideae, and Danthoniodeae) all of which tend to be warm-adapted species and mostly C_4 grasses, while all species within the lineage Pooidea, utilize the C_3 pathway and are cold-adapted (Edwards et al., 2010; Edwards & Smith, 2010). The selective advantage of the C_4 plants is attributed to the Kranz anatomy and two-step fixation process of the photosynthetic pathway, which concentrates CO_2 around Ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) and reduces the potential for photorespiration under extremely dry and hot climates (Ibrahim et al., 2008; Kubien & Sage, 2004; Nobel, 1996; Sage & Monson, 1999; Silvera et al., 2010).

Drought has been especially important in the promotion of grasslands over the woodlands/forests, because grasslands can withstand extreme variations in water availability, which inhibit the establishment of woody vegetation but are tolerated by C_4 grasses (Mooney 1999, Chapter 8). Seasonal changes in both temperature and precipitation may also play a role in C_3 - C_4 distribution, as observed throughout the central and northern portions of the Great Plains where primary productivity is dominated by C_3 grasses in the spring growing season and then by C_4 grasses during the summer growing season (Epstein et al., 2002; Murphy & Bowman, 2007; Teeri & Stowe, 1976; Vogel et al., 1986). This distribution of C_3 and C_4 grasses is likely attributed to the structure and biochemistry of the C_4 pathway, which confers high WUE and is an advantage in drought conditions (Mooney 1999, Chapter 8).

Overall, photosynthesis discriminates against ^{13}C (the heavier stable isotope) in favor of ^{12}C (Hayes, 2001). As a part of this fractionation, stomatal diffusion of $^{13}CO_2$ is slower than $^{12}CO_2$ because of the difference in mass (O’Leary, 1988). This discrimination against ^{13}C results in plants that contain lower $\delta^{13}C$ values than atmospheric CO_2 (-8‰; O’Leary 1988; Keeling et al. 2000). C_3 plants discriminate strongly against ^{13}C, and have a $\delta^{13}C$ range of -22‰ to -30‰, which reflects the fractionation associated with RuBisCO (-28‰) the limiting step in C_3 carbon fixation (Cerling et al., 1997; O’Leary, 1988; Roeske & O’Leary, 1984). C_4 plants discriminate less strongly and have a $\delta^{13}C$ of -10‰ to -14‰, reflecting the fractionation associated with stomatal diffusion (-12‰), the limiting step in C_4 carbon fixation (Cerling et al., 1997; O’Leary, 1988; Roeske & O’Leary, 1984).

3. Study Site

3.1 Site descriptions

Meade Basin has been a focal study site for paleoecological research on the evolutionary and ecological history of C_4 grasslands (Martin et al. 2011, Fox et al. 2015, Fox and Koch, 2003, 2004). A collection of modern sites within the Meade Basin were initially established to investigate modern ecological dynamics of small mammals, plants, and soils (Figure 3; Haveles, 2015). These sites were selected based on their proximity to paleosol sites and qualitatively based on the plant communities and topography that resulted in different habitat types. For this study, four of those modern sites were selected and sampled for this modern soil proxy study based on the availability of soil organic matter and carbonate samples (Table 1). The sites I chose for this study also contain plant communities that vary based on their local topography and climate. Cottonwoods is located underneath a cottonwood canopy and contains species characteristic of a short-grass prairie understory, this site is also the most topographically low and located along the Cimarron River. Kohn's Ranch is located on a hill but within a generally topographically lower region in Meade Basin and the vegetation is primarily sagebrush and herbaceous forbs. South Cimarron is located slightly more upland relative to Kohn's Ranch and Cottonwoods, and the vegetation is comprised primarily of sagebrush with a mixed grass prairie understory. The most upland site is Rex Road and has vegetation species primarily of shortgrass prairie.

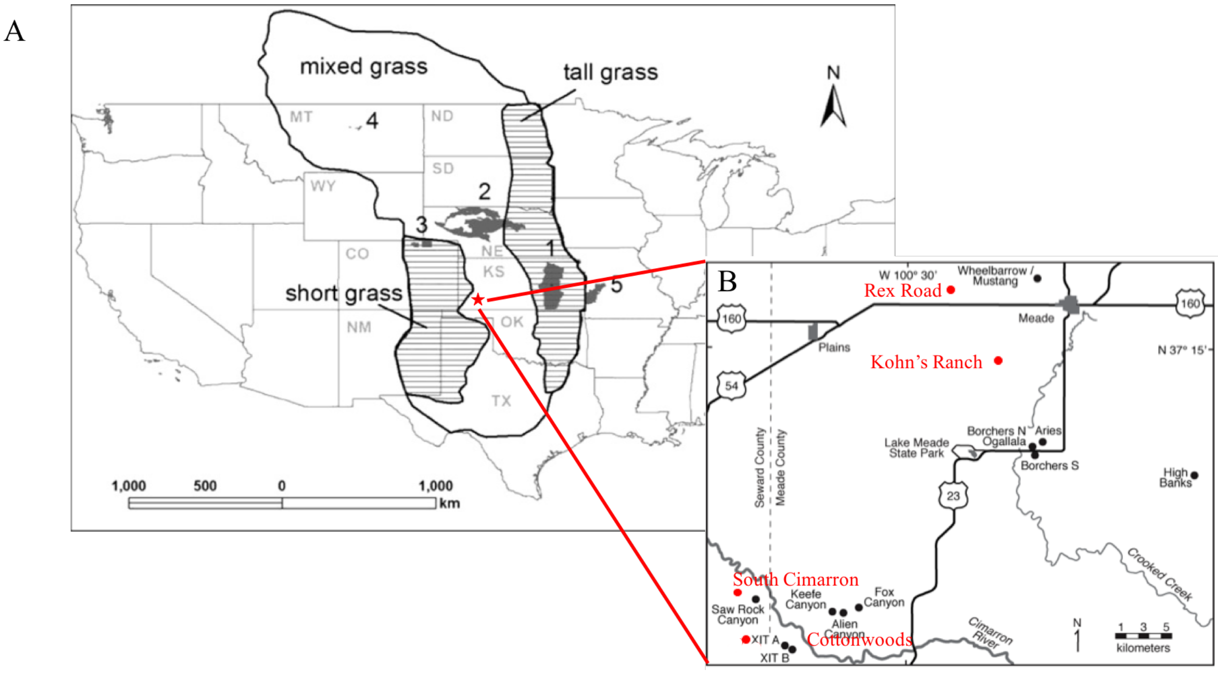

Figure 3. (A) Map adapted from Wang et al. (2013) showing the extent and range of the three floristic regions of the Great Plains: shortgrass, tallgrass, and mixed-grass prairies. Red star indicates the approximate location of Meade Basin. (B) Meade County with all modern sites (red dots), along with MBRP paleosol sites (back dots).

Table 1. Dominant vegetation types are based on visual observations. Sites are listed in order from most lowland to the most upland topography.

Site	Dominant vegetation type	Topography
Cottonwoods	Cottonwood canopy with shortgrass understory	Lowland
Kohn's Ranch	Sagebrush with forb understory	Upland
South Cimarron	Sagebrush and mixed grass prairie	Upland
Rex Road	Mixed grass prairie	Upland

3.2 Climate

Southwestern Kansas is an optimal location for studying the effects and responses of drought and wet conditions, because of the semiarid climate and susceptibility to decadal long droughts (US Drought Monitor; NOAA-NCEI; Kansa State University, Annual Reports Drought Updates). Meade Basin averages 573 mm/yr in annual precipitation with a mean annual temperature of 13.5ºC and mean high and low temperatures of 20.9ºC and 6ºC, respectively (U.S. Climate Data, 2017). Precipitation in this region is both seasonal and erratic, with the majority (66%) falling during warm months (May – September) through intense and episodic storms that can be focused on specific regions (Fox et al., 2012; Meade Station NCDC Summary of the Day, www.ncdc.noaa.gov/oa/ncdc.html). The entire state of Kansas was in "severe" (Palmer Drought Severity Index of D2) or worse drought conditions at the beginning of 2013, and during the years of 2011 to 2014, all of Meade County was in severe (D2) drought conditions throughout spring and summer months (April-August), with more than 80% of the county's land in extreme (D3) drought conditions (US Drought Monitor). During the drought period, the county received an average precipitation of 1.02 mm and a max of 61 mm, which was only 0.2% of the region's average rainfall (NOAA-NCEI). The year 2012 was ranked the warmest year on average in 119 years, and the county experienced high temperatures above 40ºC for all of July during 2011 to 2014 (NOAA-NCEI; Kansas State University, Annual Reports Drought Updates). The drought conditions began to deteriorate in the spring of 2015 resulting in only 2% of the state in abnormally dry (D0) conditions at the beginning of 2016 (Kansas State University, Annual Reports Drought Updates). While Meade Country was not in drought conditions in 2016, the average precipitation for the country was still below average, with an average of only 2.02 mm and a max of 53 mm of rainfall throughout the year (NOAA-NCEI).

3.3 Vegetation

Prairie grasslands are comprised of distinct plant communities that are determined by the local climate, precipitation, and/or topography (Knapp et al., 1998). Differences in rainfall specifically, create the three floristic regions of the shortgrass, mixed grass and tall grass prairie (Wang et al., 2013; Figure 2A). Meade Basin is located on the eastern boundary of the shortgrass prairie steppe ecosystem with a small proportion of its area lying within the western boundary of the mixed prairie ecosystem (Wang et al., 2013; Figure 2A). The shortgrass prairie is dominated by approximately 80% of warm-season (C_4) perennial grasses, most common being Blue Grama (*Bouteloua gracilis*) and Buffalo Grass (*Bouteloua dactyloides*) (Dickinson & Dodd, 1976; Ford, 1999; Küchler, 1974; Tieszen et al., 1997; Table 2). Cool-season grasses and non-graminoid species primarily from the daisy family (*Asteraceae*) and nightshade family (*Solanceae*) are also common throughout the shortgrass prairie (Jones & Cushman, 2004; Table 2). Plains Prickly Pear Cactuses (*Opuntia macrorhiza*), although a small portion of the biomass, thrive in the shortgrass prairie and are found throughout Meade Basin (Jones & Cushman, 2004; Table 2). The mixed-grass prairie regions in Meade Basin contain a mix of plants found within the tallgrass and shortgrass prairies, including the warm-season Little Bluestem (*Schizachyrium scoparium*) and cool-season Canada Wild Rye (*Elymus canadensis*) (Jones & Cushman, 2004; Table 2). While the shortgrass and mixed-grass prairie is primarily comprised of graminoids and herbaceous forbs, woody-shrubs such as Sand Sagebrush (*Artemisia filifolia*) are common throughout the prairies (Jones & Cushman 2004; Table 2). Grasslands occur where there is insufficient rain to support trees, however riparian zones can be found throughout lowland regions, such as along the Cimarron River, where Cottonwood trees (*Populus deltoides*) can be found (Jones & Cushman, 2004).

Table 2. Common species of the short-mixed grass prairie. Species list compiled from Jones and Cushman (2004)

Common species of short-mixed grass prairie
Gramminoids
Blue Grama (*Bouteloua gracilis*) [C_4]
Buffalo Grass (*Bouteloua dactyloides*) [C_4]
Western Wheatgrass (*Agropyron smithii)* [C_3]
Junegrass (*Koeleria macrantha*) [C_3]
Needle-and-Thread (*Hesperostipa comata*) [C_3]
Sideoats Grama *(Bouteloua curtipendula)* [C_4]
Hairy Grama *(Bouteloua hirsuta)* [C_4]
Little Bluestem (*Schizachyrium scoparium*) [C_4]
Canada Wild Rye (*Elymus canadensis*) [C_3]
Herbaceous Forbs
Indian blanket flower (*Gaillardia pulchella*) [C_3]
Silverleaf nightshade (*Solanum elaeagnifolium*) [C_3]
Common sunflowers (*Helianthus annuus*) [C_3]
Daisy Fleabane (*Erigeron strigosus*) [C_3]
Cacti
Plains Prickly Pear Cactuses (*Opuntia macrorhiza*) [CAM]
Shrubs
Sand Sagebrush (*Artemisia filifolia*) [C_3]
Trees
Cottonwood trees (*Populus deltoides*) [C_3]

3.4 Rocks, topography, and soil

Meade Basin encompasses approximately 50 km^2 of depositional area and contains Miocene to Holocene sediment deposits, from oldest to youngest is the Ogallala (upper Miocene), Rexroad (Pliocene), and Crooked Creek (Pliocene and Pleistocene) formations (Martin et al. 2011; Fox et al., 2015; Izett and Honey, 1995). Meade Basin is located in the High Plains plateau of the Great Plains physiographic province of Southwestern Kansas (Kansas Geological Survey; Trimble, 1980) The High Plains extends from the northern border of Nebraska through the Panhandle of Texas (Trimble, 1980). The landscape of Meade Basin consists of uplands and terraces that are shaped by Quaternary fluvial activity, such as the Cimarron River system which exposes the geologic formations (Izett & Honey, 1995).

In some places, on top of the Meade Basin's sedimentary formations are well developed soil horizons. Mollisols are the dominant soil order of the Great Plains Region (USDA, 1999). The semiarid climate, seasonal and erratic rainfall, and susceptibility to frequent drought is typical of Ustolls, a suborder of Mollisols, which are found throughout the Western Great Plains (USDA, 1999). This type of semiarid climate and upland region with well-draining soils, can have relatively low soil water content during the summer months due to evaporative losses, which facilitates the accumulation of carbonates in the B horizon (Ferretti et al., 2003).

4. Methods

4.1 Aboveground biomass

I established and sampled four quadrats (0.25 m x 0.25 m; Figure 4) at South Cimarron, Cottonwoods, Rex Road, and Kohn's Ranch in June 2016 (Figure 5). I collected one aboveground biomass sample from each quadrat by clipping all standing and litter vegetation from the top of the prairie canopy to less than 1 cm above the ground. I oven-dried each sample at 60ºC for one to six weeks. Then I homogenized each sample with a Thomas Wiley Mini-Mill Cutting Mill through 20 and then 60 mesh size to achieve a fine powder samples for total weight percent C and $\delta^{13}C$ analysis.

I conducted isotopic analyses for aboveground biomass samples at the University of Colorado at Boulder Earth Systems Stable Isotope Lab. A Thermo Scientific FlashEA oxidized and combusted each sample and a Thermo Scientific Delta V Isotope Ratio Mass Spectrometer analyzed the resultant CO_2. Data are reported as $^{13}C/^{12}C$ ratios in units of relative per mil (‰) difference between the sample $^{13}C/^{12}C$ ratio (R_{sample}) and a standard $^{13}C/^{12}C$ ratio ($R_{standard}$) relative to the of Vienna Peedee Belemnite standard scale (VPBD) (Equation 2).

$$\delta^{13}C = [(^{13}C/^{12}C_{sample}/^{13}C/^{12}C_{standard}) - 1] * 1000 \text{ (‰)} \qquad (2)$$

To attain precision and accuracy in using continuous flow IRMS, I used a correcting standard of peach leaves (NIST-STRM 1547; $\delta^{13}C$ of -26.0 ‰ ±0.1‰; weight %C of 46.9 ±1.1%) to correct for linearity and drift. To monitor the correcting standard values, I utilized an accepted standard of Acetanilide (University of Indiana; $\delta^{13}C$ of -29.5 ‰ ±0.1‰; weight %C of 71.1 ±2.1%).

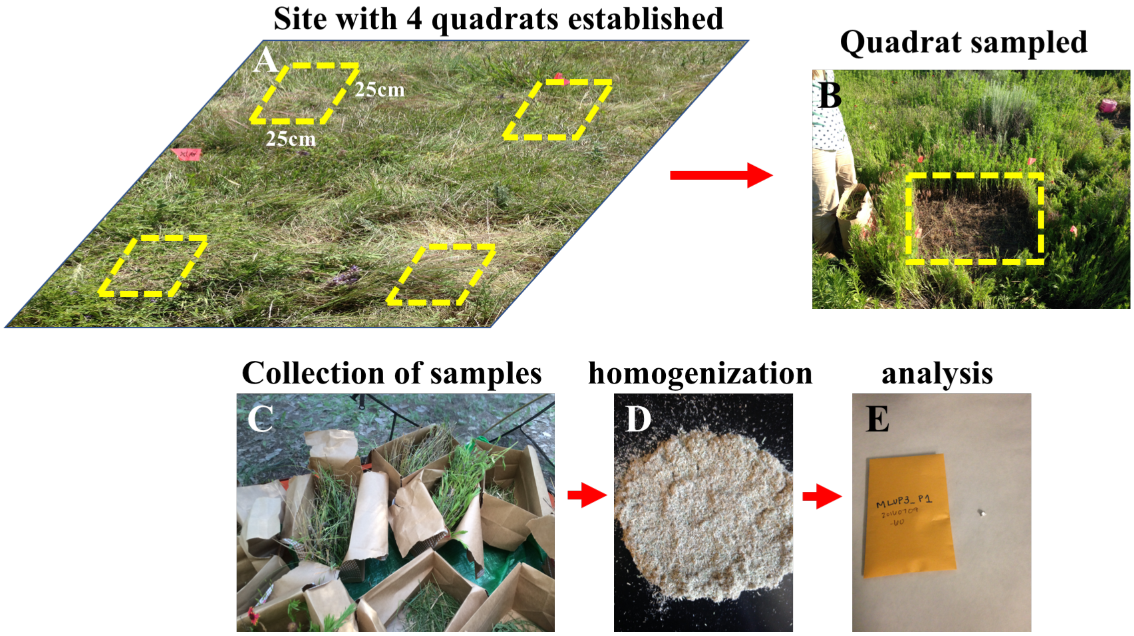

Figure 4. Aboveground biomass sampling procedure for each site. (A) Four quadrats (25 cm x 25 cm) were randomly established at each site. (B) Aboveground biomass sample was taken from each quadrat. (C) Samples collected and dried in paper bags. (D) Samples homogenized by a Wiley Mill through a 20 and then 60 mesh size. (E) Subsample of vegetation that was weighed for δ^{13}C analysis.

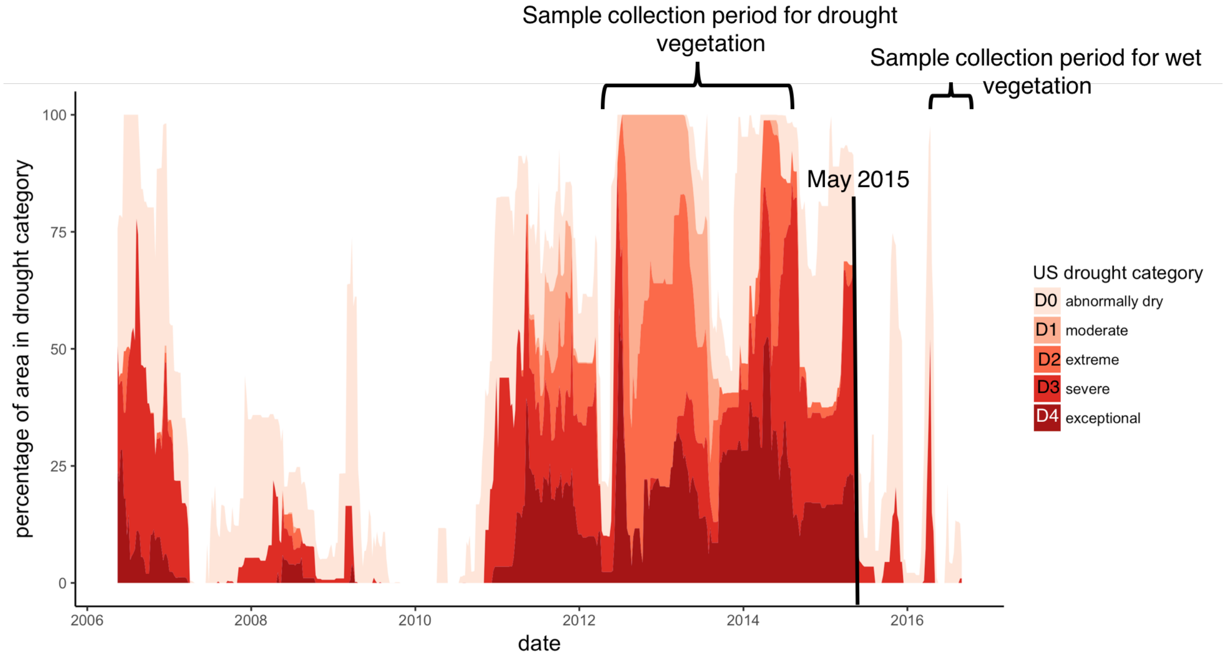

Figure 5. Percent area of Meade County, Kansas in each Palmer Drought Severity Index and US Drought Monitor category (data from US Drought Monitor). Sample collection periods are indicated for both drought and wet vegetation.

4.2 Individual plant sampling

Andrew Haveles collected a total of 29 plant specimens along transect lines established at Cottonwoods and South Cimarron in June 2012 and May 2014 (Haveles, 2015; Figure 5). Haveles collected a minimum of two specimens for the ten most abundant plants along transect lines at each site. He pressed each specimen with coin envelopes, identified to species or the lowest classification possible, and then oven-dried at 60ºC for at 48 hours. Haveles dissected plant specimens to extract flowers, leaves, and stems and ground into a fine powder with a mortar and pestle for total weight percent C and δ^{13}C analysis. Haveles collected Elemental and isotopic analysis for Cottonwoods and South Cimarron samples were conducted at University of Minnesota Department of Earth Sciences. A Costech Elemental Analyzer oxidized and combusted samples and a a Thermo Scientific Delta V Isotope Ratio Mass Spectrometer analyzed the resultant CO_2. Data are reported using delta notation as described above (Equation 2). To correct for linearity and drift, Haveles used a correcting standard of Montana soil (NIST 2711; δ^{13}C of 17.2‰; weight %C of 1.7). To monitor the correcting standard values, he utilized a standard of peach leaves (NIST-STRM 1547; δ^{13}C of -26.0 ‰; weight %C of 46.9) to monitor standard.

Brendan Femal (Femal, 2016) collected a total of 13 plant samples from Kohn's Ranch and Rex Road sites in June 2014. He collected one specimen for the top ten most abundant species present along the transect lines previously determined by Haveles (2015). I obtained samples in Spring of 2017 and by which point I was not able to classify specimens to any taxonomic level. The samples were stored in paper envelopes for three years, and after I obtained them, I oven-dried samples at 60ºC for 48 hours. I ground with mortar and pestle and if needed through a Thomas Wiley Mini-Mill Cutting Mill through 20 and then 60 mesh size to achieve a fine powder for total weight percent C and $\delta^{13}C$ analysis. I conducted isotopic analysis for Kohn's Ranch and Rex Road plant samples at the University of Colorado at Boulder Earth Systems Stable Isotope Lab. Samples were oxidized and combusted with a Thermo Scientific FlashEA and the resultant CO_2 was then analyzed with a Thermo Scientific Delta V Isotope Ratio Mass Spectrometer. Data are reported using delta notation (Equation 2). Again, I used a correcting standard of peach leaves (NIST-STRM 1547; $\delta^{13}C$ of -26.0 ‰ ±0.1‰; weight %C of 46.9 ±1.1%) to correct for linearity and drift. To monitor the correcting standard values, I utilized an accepted standard of Acetanilide (University of Indiana; $\delta^{13}C$ of -29.5 ‰ ±0.1‰; weight %C of 71.1 ±2.1%).

4.3 Soil organic carbon

Kyle Chambers (Chambers, 2016) and Andrew Haveles (Haveles, 2015) collected soil samples at vertical intervals from 0-50 cm from soil pits established at each site. Haveles collected soil samples from two soil pits established at South Cimarron and two soil pits at Cottonwoods. Chambers collected soil samples from one pit at Kohn's Ranch and one pit at Rex Road. Chambers and Haveles oven-dried soil samples at 60ºC and then homogenized each sample with a mortar and pestle. Haveles removed inorganic carbon from samples at Cottonwoods and South Cimarron by acidifying samples with 0.5M HCl, rinsing with deionized water three times. Chambers removed inorganic carbon from samples at Kohn's Ranch and Rex Road by acidifying samples with 1M HCl and rinsing five times with deionized water or until pH was neutral. They both oven-dried samples at 45ºC for 24-48 hours and homogenized by mortar-pestle for total weight percent C and $\delta^{13}C$ analysis.

Chambers and Haveles conducted elemental and isotopic analysis of soil organic carbon samples at University of Minnesota Department of Earth Sciences. A Costech Elemental

Analyzer oxidized and combusted samples and a Thermo Scientific Delta V Isotope Ratio Mass Spectrometer analyzed the resultant CO_2. Data are expressed in delta notation (Equation 2). They used a correcting standard of Montana soil (NIST 2711; $\delta^{13}C$ of 17.2‰; weight %C of 1.7) to correct for linearity and drift. They used peach leaves (NIST-STRM 1547; $\delta^{13}C$ of -25.98 ‰; weight %C of 46.92) to monitor standard values.

4.4 Pedogenic carbonates

Katie Snell and Andrew Haveles (Haveles, 2015) collected pedogenic carbonate nodules and disseminated carbonate within the soil matrix from soil pits at each site. They collected samples at vertical intervals from 35 to 100 cm. I obtained carbonate samples in the summer of 2017. I ground carbonate samples with a mortar and pestle to homogenize samples and achieve a fine grain powder for isotopic analysis. I weighed 200-4000 µg of each powdered sample into a 12 mL Exctainer vials and 90 µg of each carbonate standard into a 12 mL Exctainer vials.

I conducted isotopic analysis of carbonate samples in the University of Colorado at Boulder Earth Systems Stable Isotope Lab. I purged each sample vail with dry He gas for 5 minutes and then before analysis, treated each vial with five drops of orthophosphoric acid held at 90ºC to dissolve the carbonate and yield CO_2 gas. A Thermo Scientific Delta V Isotope Ratio Mass Spectrometer analyzed the resultant CO_2. Data are expressed in delta notation (Equation 2). I used a correcting standard of CU Yule ($\delta^{13}C$ of -2.3‰ ±0.3‰ in VPBD) to correct for linearity and drift. I used a monitoring standard of HIS ($\delta^{13}C$ of -4.8 ‰ ±0.1‰ in VPBD).

Haveles conducted his isotopic analysis of his carbonate samples at the University of Minnesota. He roasted his samples in vacuo for one hour at 400 C to eliminate water and organic matter and then reacted with 100% phosphoric acid in a Kiel automatic carbonate extraction device. A Finnigan MAT 252 isotope ratio mass spectrometer analyzed the resulting CO_2 and all data wetized by repeated analysis of both a laboratory standard Carrara marble (2.42‰ ±0.33 in VPDB) and a certified international carbonate standard NBS-19 (-5.014‰ ±0.035‰ in VPDB).

4.5 Data analysis and corrections

4.5.1 Comparing records of $\delta^{13}C$ vegetation between drought and wet conditions

Vegetation samples collected during the wet conditions are the aboveground biomass samples discussed in Section 4.1 and were collected in June of 2016. Vegetation samples collected during "exceptional" (D4) drought conditions (US Drought Monitor) are the samples collected by Haveles (2015) discussed in Section 4.2 and were collected in May and June of 2012, 2013, and 2014.

The two records of vegetation vary in their collection methods and the range of their $\delta^{13}C$ values (Figure 6). Haveles collected the drought vegetation samples from the most common species that were present along transect lines established at each site and therefore are expected to exhibit a more bimodal distribution, typical of $\delta^{13}C$ values for C_3 and C_4 plants (Figure 6; Cerling et al., 1997). In contrast, the wet vegetation samples are from a collection of aboveground biomass and each sample incorporates a mixture of C_3 and C_4 plants from the quadrat they were sampled; therefore, their values are expected to follow a unimodal distribution (Figure 6).

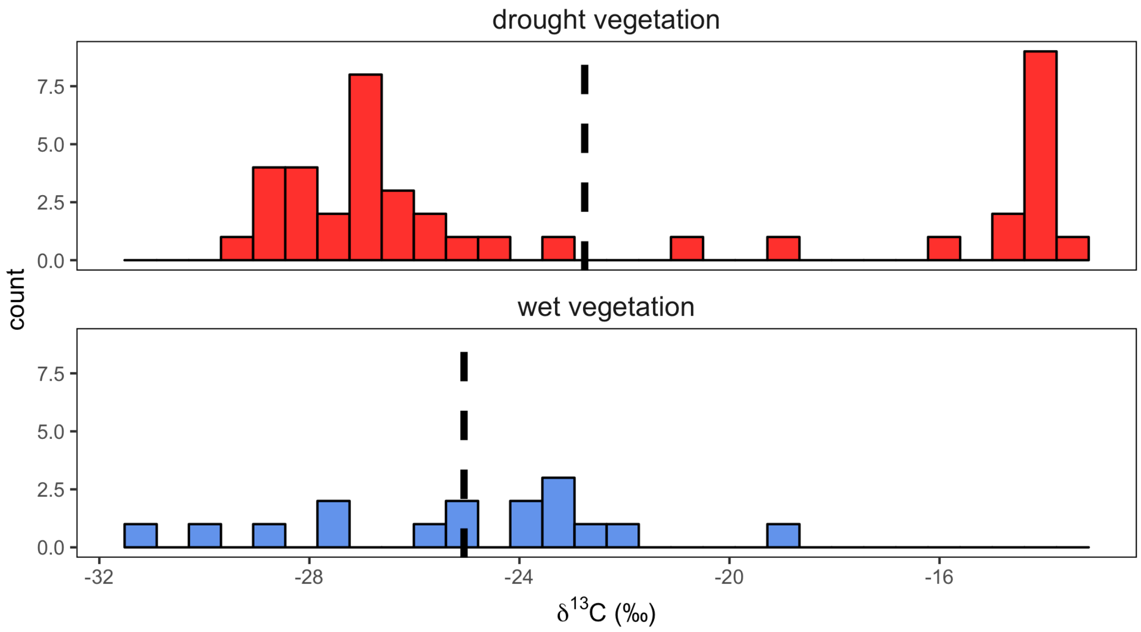

Figure 6. Histograms showing distributions of δ^{13}C values of vegetation samples collected between drought and wet climate conditions. Dashed black line indicates the mean values of vegetation samples collected for the two records.

I also compare the vegetation between drought and wet conditions through graphs and through the means and the standard deviations of δ^{13}C values of the vegetation of each site. This comparison between the two records is, appropriate because both records include some degree of proportionality with respect to their relative ratio of C_3 to C_4 biomass. The wet vegetation is inherently proportional because it represents a homogenization of all plants within each quadrat. Therefore, the δ^{13}C value of each sample reflects a relative proportion of C_3 to C_4 plants. The drought vegetation represents an aggregate of the most common species present. Therefore, the δ^{13}C also reflects a relative proportion of C_3 to C_4 species.

To compare the vegetation records, I first generated a representative mean δ^{13}C for the drought and wet vegetation from each site. For the drought record, samples from Cottonwoods and South Cimarron had multiple plant parts that were analyzed for δ^{13}C. I first calculated an average δ^{13}C value and standard deviation for each species (Table 3). Then I averaged the δ^{13}C values for each species and propagated the error through the standard deviation to attain a site average δ^{13}C value (Table 3, Figure 7). Samples from Kohn's Ranch and Rex Road were not classified to the species level, so I averaged their δ^{13}C values and calculated the standard deviation to generate a site average δ^{13}C value (Table 4, Figure 7). For the wet vegetation record, I averaged the δ^{13}C values of each of the four quadrat samples from each site, to generate a site averaged δ^{13}C value (Table 5, Figure 7). For all sites, I report the uncertainty (±1 SD) for each site, which I calculated to include the analytical error and standard deviation of the sample δ^{13}C values.

Table 3. Carbon isotope values of species samples and site averages for Cottonwoods and South Cimarron in drought period. Uncertainty (±) is reported as the standard deviation.

Site	Year	Genus and species	Common name	Plant part	δ^{13}C (‰)	Average $\delta^{13}C_{drought\text{-}vegetation}$ (‰)
Cottonwoods	2012	*Ambrosia artemisiifolia*	Pale ragweed	Leaves (n=3)	-28.83 (±0.9)	-21.0 (± 7.5)
	2012	*Elymus canadensis*	Canada wild rye	Grass	-27.90	
	2012	*Eriogonum annuum*	Annual Eriogonum	Stem/leaf	-13.80	
	2012	*Pascopyrum smithii*	Western wheatgrass	Leaf	-14.40	
	2012	*Populus deltoides*	Cottonwood	Leaf	-28.30	
	2012	*Salsola tragus*	Russian thistle	Leaves (n=2)	-14.00 (±0.3)	
	2014	*Salsola tragus*	Russian thistle	Whole plant	-14.00	
	2012	*Solidago missouriensis*	Missouri goldenrod	Leaf	-26.60	

Table 3. cont'd.

Site	**Year**	**Genus and species**	**Common name**	**Plant part**	**$\delta^{13}C$ (‰)**	**Average $\delta^{13}C_{drought-vegetation}$ (‰)**
South Cimarron	2012	*Ambrosia artemisiifolia*	Pale ragweed	Leaf	-27.10	-23.9 (±6.0)
	2012	*Artemisia filifolia*	Sagebrush	Leaves and stems (n=3)	-24.53 (±1.0)	
	2013	*Artemisia filifolia*	Sagebrush	Leaf	-27.10	
	2012	*Bulbostylis capillaris*	Hair sedge	Leaf	-16.20	
	2013	*Chamaesaracha coniodes*	Ground saracha	Leaf	-27.10	
	2013	*Chloris verticillata*	Windmill grass	Leaf	-13.80	
	2012	*Elymus canadensis*	Canada wild rye	Leaf	-29.60	
	2013	*Erigeron strigosus*	Daisy fleabane	Whole plant	-28.20	
	2012	*Eriogonum annuum*	Annual Eriogonum	Stem and leaf (n=2)	-26.05 (±1.2)	
	2013	*Evolvulus nuttallianus*	Shaggy dwarf morning glory	Whole plant	-27.00	
	2013	*Gaillardia pulchella*	Indian blanket flower	Whole plant	-27.60	
	2012	*Haplopappus spinulosus*	Cutleaf ironplant	Leaves (n=2)	-25.90 (±0.9)	
	2012	*Hordeum jubatum*	Foxtail barley	Whole plant	-28.90	
	2013	*Lipocarpha micrantha*	Small flower dwarf bulrush	Whole plant	-14.20	
	2012	*Mentzelia nuda*	Sand lily	Leaf	-25.20	
	2012	*Pascopyrum smithii*	Western wheatgrass	Whole plant	-13.80	
	2013	*Pascopyrum smithii*	Western wheatgrass	Whole plant	-14.20	
	2012	*Quincula lobata*	Chinese lantern	Leaf	-27.30	
	2012	*Solanum elaeagnifolium*	Silver-leaf nightshade	Stem and leaves (n=3)	-26.93 (±0.3)	
	2012	*Tamarix chinensis*	Tamarisk	Flower and leaf (n=2)	-28.50 (±0.9)	
	2012	*Yucca glauca*	Yucca	Leaf	-23.00	

Table 4. Carbon isotope values of species samples and site averages for Kohn's Ranch and Rex Road in drought period. Uncertainty (±) is reported as the standard deviation. There was no classification of species or plant parts.

site	Year	Sample	$\delta^{13}C$ (‰)	Average $\delta^{13}C_{drought-vegetation}$ (‰)
Kohn's Ranch	2014	Leaf litter	-20.8	-20.5 (±6.4)
	2014	Plant 1	-27.1	
	2014	Plant 2	-26.5	
	2014	Plant 3	-14.8	
	2014	Plant 4	-13.4	
Rex Road	2014	Leaf litter	-18.8	-22.9 (± 6.3)
	2014	Plant 1	-28.6	
	2014	Plant 10	-28.4	
	2014	Plant 4	-14.0	
	2014	Plant 5	-27.1	
	2014	Plant 6	-25.5	
	2014	Plant 7	-13.9	
	2014	Plant 8	-26.9	

Table 5. Carbon isotope values of quadrat samples and site averages for all sites in wet conditions. Uncertainty (±) is reported as the standard deviation.

Site	$\delta^{13}C_{wet-vegetation}$ (‰)	Average $\delta^{13}C_{wet-vegetation}$ (‰)
Cottonwoods	-28.58	-28.3 (±1.1)
	-24.03	
	-29.91	
	-31.13	
Kohn's Ranch	-27.55	-25.0 (±1.3)
	-25.35	
	-23.16	
	-23.86	
Rex Road	-22.39	-22.4 (1.8)
	-25.00	
	-18.95	
	-23.12	
South Cimarron	-25.47	-24.5 (±0.8)
	-21.95	
	-27.37	
	-23.06	

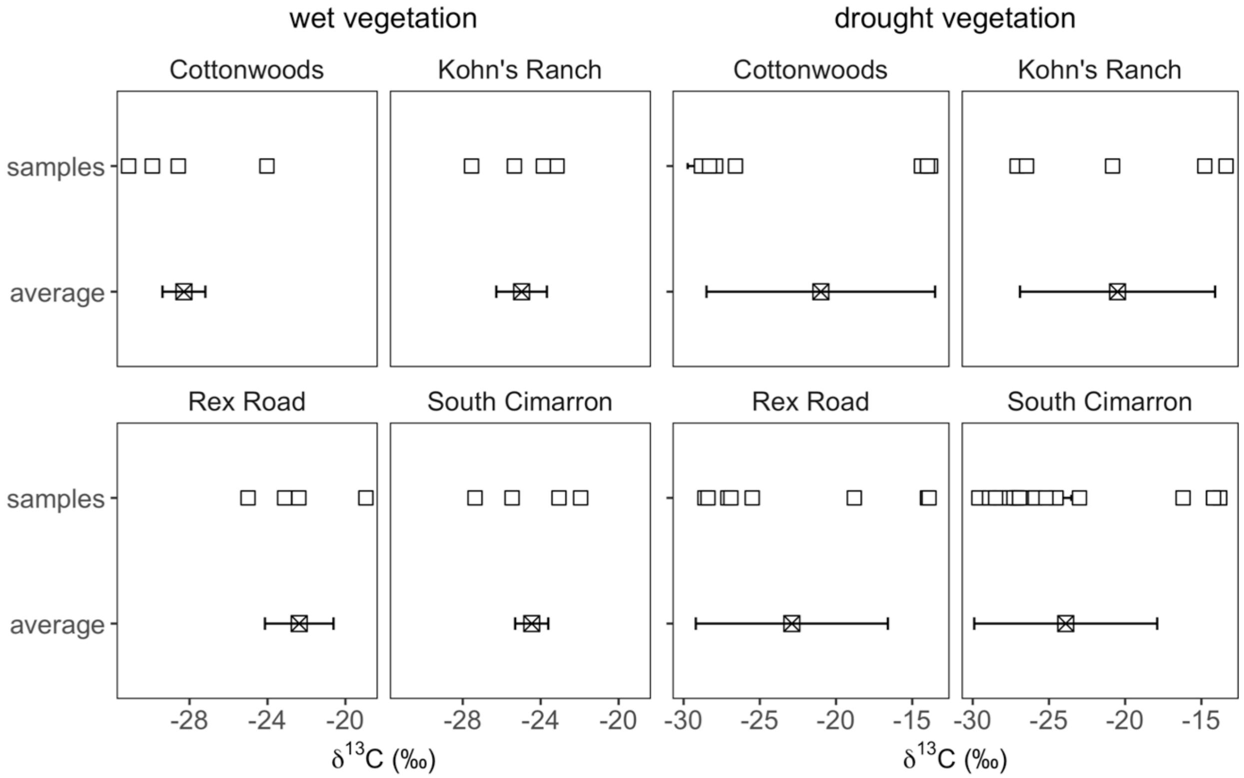

Figure 7. Vegetation $\delta^{13}C$ values of all samples and site average calculated for both wet and drought conditions. Error bars represent the propagated uncertainty.

4.5.2 Correction of $\delta^{13}C$ values of vegetation and carbonates

To compare drought and wet vegetation samples to soil organic matter and pedogenic carbonates, isotope values must be compared on a common substrate, because of the fractionation factors associated with the formations of each proxy (Figure 2). Previous studies corrected $\delta^{13}C$ values of carbonates to a soil organic matter isotopic scale by subtracting -15‰ from carbonate $\delta^{13}C$ value (Fox et al., 2012; Fox & Koch, 2003, 2004). This correcting value is based on Cerling and Quade's (1993) calculation of the total enrichment between carbonates and soil CO_2, where soil CO_2 is enriched in ^{13}C by approximately +4.4‰ relative to soil-respired CO_2 and isotopic fractionation during carbonate formation results in an enrichment of ^{13}C in carbonate samples of about 12‰ at 0ºC and 9‰ at 25ºC. In this study, I corrected all my samples to be on the same isotopic scale as soil organic carbon. Carbonate samples were adjusted by -15‰ as consistent with Cerling and Quade (1993)'s average and because the exact temperature at which these carbonate samples precipitated is unknown and therefore a middle value of ~10.5‰ is used to account for the fractionation factor (Table 6, Figure 8). After generating a site average vegetation $\delta^{13}C$ value for the drought and wet periods, I adjusted each average by +2‰ (±1‰) based on the enrichment fractionation factor of 1-3‰ documented for the decomposition of organic matter (Table 6 and 7; Figure 9 & 10; Desjardins et al. 1994; Boutton 1996; Mcpherson et al. 1992; Mariotti & Peterschmitt 1994; Dzurec et al. 1985; Wynn, 2007; Wynn and Bird, 2007). The vegetation correction value of +2‰ is also supported by the relationship between $\delta^{13}C_{SOM}$ and %C for the soil profiles in this study, which show that as decomposition occurs, or the total amount of organic C decreases, the remaining carbon becomes more enriched in ^{13}C (Table 8; Figure 10).

Table 6. Corrected $\delta^{13}C_{carbonate}$ values are calculated by subtracting 15‰ from the $\delta^{13}C_{carbonate}$ to account for diffusion and temperature dependent fractionation factor (Cerling and Quade, 1993; Fox et al., 2012).

Site	Pit	Depth (cm)	$\delta^{13}C_{carbonate}$ (‰)	Corrected $\delta^{13}C_{carbonate}$ (‰)
Cottonwoods	1	65	-0.2	-15.2
	2	21	-4.3	-19.3
		70	-2.8	-17.8
		19	-5.1	-20.1
Kohn's Ranch	1	35	-2.9	-17.9
		45	-2.5	-17.5
		60	-3.9	-18.9
		75	-2.8	-17.8
		85	0.0	-15.0
Rex Road	1	40	-4.9	-19.9
		50	-0.6	-15.6
		100	-2.2	-17.2
	2	20	0.9	-14.1
		52	2.0	-13.0
		100	1.1	-13.9
South Cimarron	1	21	-3.1	-18.4
		28	-4.3	-19.3
		32	-5.4	-20.4
		36	-5.6	-20.6
		69	-3.7	-18.7
	2	21	-3.7	-18.7

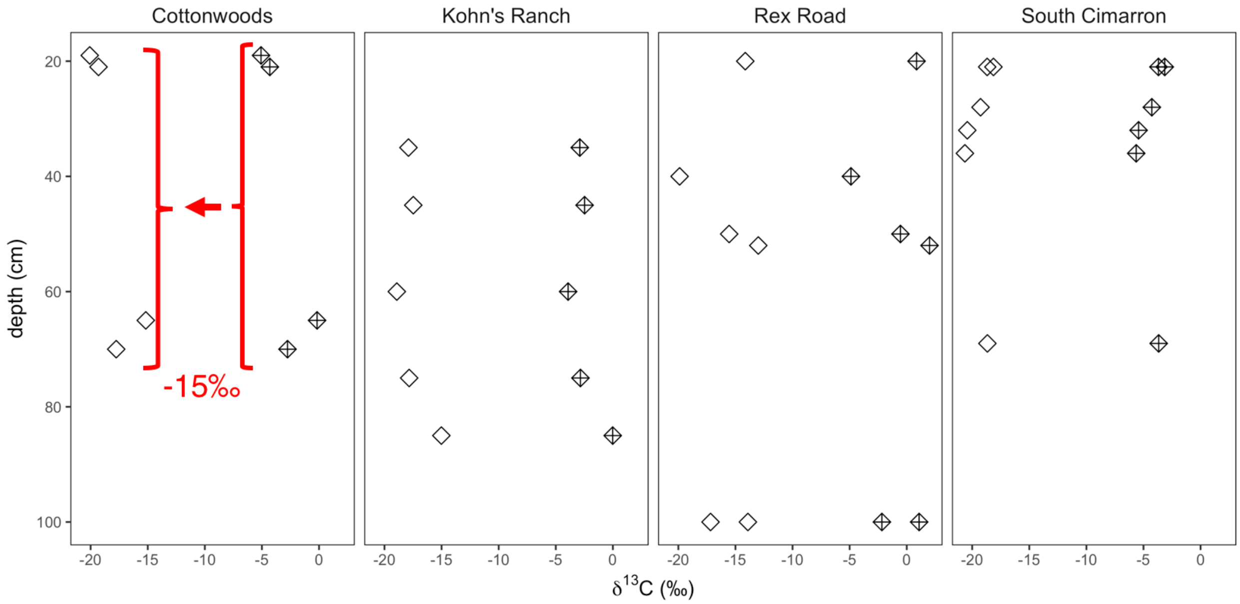

Figure 8. Schematic of $\delta^{13}C_{carbonates}$ correction. Diamonds with crosses indicate the uncorrected $\delta^{13}C_{carbonates}$, the unfilled (white) diamonds indicate the corrected $\delta^{13}C_{carbonate}$ values. These corrected values are determined by adjusting $\delta^{13}C_{carbonate}$ by -15‰ to account for diffusion and temperature dependent fractionation factor (Cerling and Quade, 1993; Fox et al., 2012).

Table 7. Corrected $\delta^{13}C$ values for wet and drought vegetation represent the values the samples may exhibit if they were to be enriched through decomposition, these values were calculated by adding 2‰ (±1‰) to the average $\delta^{13}C$ value for each site under wet and drought conditions (Desjardins et al. 1994; Boutton 1996; Mcpherson et al. 1992; Mariotti & Peterschmitt 1994; Dzurec et al. 1985; Wynn, 2007; Wynn and Bird, 2007).

Site	**Average $\delta^{13}C_{wet-vegetation}$ (‰)**	**Corrected $\delta^{13}C_{wet-vegetation}$ (‰)**	**Average $\delta^{13}C_{drought-vegetation}$ (‰)**	**Corrected $\delta^{13}C_{drought-vegetation}$ (‰)**
Cottonwoods	-28.3 (±1.1)	-26.3 (±2.2)	-21.0 (± 7.5)	-19.0 (±7.6)
Kohn's Ranch	-25.0 (±1.3)	-23.0 (±2.7)	-20.5 (±6.4)	-18.5 (±6.5)
South Cimarron	-24.5 (±0.8)	-22.5 (±1.7)	-23.9 (±6.0)	-21.9 (±6.1)
Rex Road	-22.4 (±1.8)	-20 (±4.1)	-22.9 (±6.3)	-20.9 (±6.4)

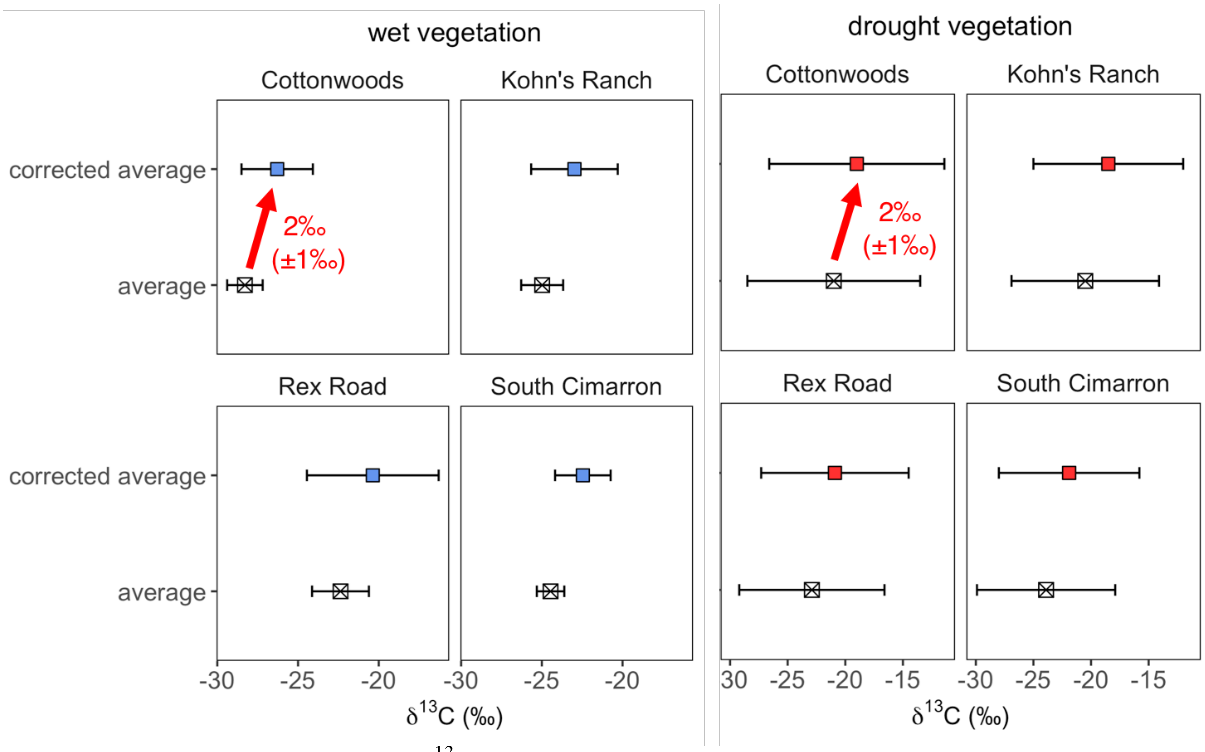

Figure 9. Schematic of corrected δ^{13}C values for wet and drought vegetation. Squares with crosses indicate the uncorrected δ^{13}C values. Blue and red squares represent the corrected $\delta^{13}C_{\text{wet-vegetation}}$ and $\delta^{13}C_{\text{drought-vegetation}}$ values. These corrected samples are calculated by adding 2‰ (±1‰) to account for enrichment that is typically associated with decomposition (Desjardins et al. 1994; Boutton 1996; Mcpherson et al. 1992; Mariotti & Peterschmitt 1994; Dzurec et al. 1985; Wynn, 2007; Wynn and Bird, 2007).

Table 8. δ^{13}C values and weight % C of soil organic matter samples collected from soil pits.

Site	Pit	Depth (cm)	Weight % C	$\delta^{13}C_{SOM}$ (‰)
Cottonwoods	1	0	3.08	-25.6
		4	2.51	-25.2
		6	2.05	-24.9
		8	1.40	-24.1
		12	0.99	-23.0
		14	0.98	-22.8
		16	0.85	-22.6
		24	0.60	-22.2
		20	0.81	-21.8
		28	0.47	-21.1
	2	5	0.83	-20.4
		10	0.62	-20.9
		15	0.16	-20.2
		20	0.99	-20.8
		25	0.41	-20.4
		30	0.66	-20.7
Kohn’s Ranch	1	1	0.91	-15.7
		5	0.76	-16.7
		30	0.50	-18.2
		34	0.45	-19.1
Rex Road	1	0	0.31	-16.8
		40	0.42	-14.0
		50	0.65	-15.6
South Cimarron	1	0	1.01	-22.8
		4	0.79	-20.3
		6	0.48	-19.5
		8	0.48	-19.5
		12	0.71	-19.3
		16	0.46	-18.9
		20	0.46	-19.3
		24	0.71	-19.5
		28	0.79	-19.3
	2	2	3.47	-21.7
		9	0.59	-20.0
		12	0.39	-21.1
		20	1.38	-20.5

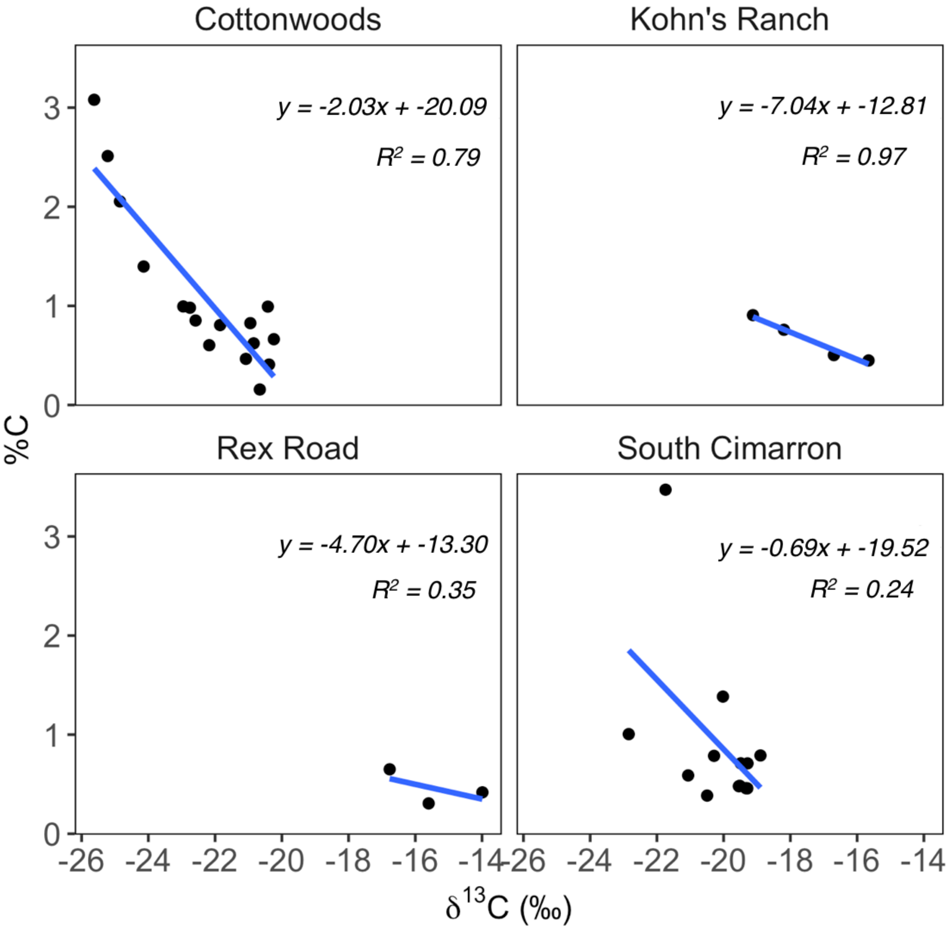

Figure 10. Weight percent organic carbon (%C) vs. δ^{13}C (‰) values of soil organic matter samples. A trend line from a simple linear regression is presented for each site.

5. Results

5.1 Carbon isotope ratios of carbonates, SOM, and wet and drought vegetation

There are three interesting patterns reflected by the $\delta^{13}C$ values of the vegetation, carbonates, and SOM across the samples collected from each site. First, the $\delta^{13}C_{carbonates}$ are enriched in ^{13}C relative the both $\delta^{13}C_{drought\text{-}vegetation}$ and $\delta^{13}C_{wet\text{-}vegetation}$ (Figure 11). Second, the $\delta^{13}C_{SOM}$ do not reflect the $\delta^{13}C_{wet\text{-}vegetation}$, but instead either fall in between the wet and drought vegetation or reflect the $\delta^{13}C_{drought\text{-}vegetation}$ (Figure 11). Lastly, the degree to which the $\delta^{13}C_{carbonates}$ and the $\delta^{13}C_{SOM}$ are enriched in ^{13}C relative to both vegetation records increases as the topography increases across the sites (Figure 11).

The topographically lowest site, Cottonwoods, is located under the cottonwood canopy with short grass prairie understory. At this site, there is the biggest differences between the $\delta^{13}C_{wet\text{-}vegetation}$ and the $\delta^{13}C_{drought\text{-}vegetation}$ and between the $\delta^{13}C_{carbonates}$ and the $\delta^{13}C_{SOM}$. The mean $\delta^{13}C_{drought\text{-}vegetation}$ is enriched in ^{13}C relative to the $\delta^{13}C_{wet\text{-}vegetation}$ by 7.3‰ (Table 6). The $\delta^{13}C_{carbonates}$ reflect a vegetation regime more similar to the $\delta^{13}C_{drought\text{-}vegetation}$ than the $\delta^{13}C_{wet\text{-}vegetation}$ (Figure 11). The most negative and positive $\delta^{13}C_{carbonates}$ samples are depleted in ^{13}C by -1.1‰ and enriched in ^{13}C by 3.8‰ relative to the $\delta^{13}C_{drought\text{-}vegetation}$ (Table 6 and 7), and are enriched in ^{13}C by 6.2‰ and 11.1‰ relative to the $\delta^{13}C_{wet\text{-}vegetation}$ (Table 6 and 7). The $\delta^{13}C_{SOM}$ samples from both pits lie in between the ranges of both the $\delta^{13}C_{drought\text{-}vegetation}$ and the $\delta^{13}C_{wet\text{-}vegetation}$ (Figure 11). The $\delta^{13}C_{SOM}$ samples of the upper (0-8 cm) from pit 1, are more reflective of the $\delta^{13}C_{wet\text{-}vegetation}$, while the $\delta^{13}C_{SOM}$ samples from pit 2 are more reflective of the $\delta^{13}C_{drought\text{-}vegetation}$ (Figure 11). At pit 1, the most negative and positive $\delta^{13}C_{SOM}$ samples are both enriched in ^{13}C by 0.7‰ and 5.2‰, relative to the mean value of the $\delta^{13}C_{wet\text{-}vegetation}$ (Table 8 and 7), but are depleted in ^{13}C by -6.6‰ and -2.1‰, respectively, relative to the mean value of the $\delta^{13}C_{drought\text{-}}$

$_{\text{vegetation}}$ (Table 8 and 7). At pit 2, the most negative and positive $\delta^{13}C_{SOM}$ samples are enriched in ^{13}C by 1.2‰ and 1.9‰ relative to the mean value of the $\delta^{13}C_{\text{drought-vegetation}}$ (Table 8 and 7), but are enriched in ^{13}C by 5.4‰ and 6.1‰, relative to the mean value of the $\delta^{13}C_{\text{wet-vegetation}}$ (Table 8 and 7).

The second most topographically lowland site is Kohn's Ranch, which is dominated by sagebrush and with an understory of herbaceous forbs. The $\delta^{13}C$ values of vegetation at this site follow a pattern similar to Cottonwoods, because the $\delta^{13}C_{\text{drought-vegetation}}$ is enriched in ^{13}C relative to the $\delta^{13}C_{\text{wet-vegetation}}$ by 4.5‰ (Table 7). However, unlike Cottonwoods, the $\delta^{13}C_{\text{carbonates}}$ and the $\delta^{13}C_{SOM}$ both reflect vegetation signals similar to the $\delta^{13}C_{\text{drought-vegetation}}$ (Figure 11). Here, the most negative and positive $\delta^{13}C_{\text{carbonates}}$ are depleted in ^{13}C by -0.4‰ and enriched in ^{13}C by 3.5‰, relative to the mean value of the $\delta^{13}C_{\text{drought-vegetation}}$ (Table 6 and 7) but are enriched in ^{13}C relative to the $\delta^{13}C_{\text{wet-vegetation}}$ by 4.1‰ and 8‰ (Table 6 and 7). Kohn's Ranch is the only site where the $\delta^{13}C_{SOM}$ does not fall within the range of the standard deviation of the $\delta^{13}C_{\text{wet-vegetation}}$ (Figure 10). Instead, the two $\delta^{13}C_{SOM}$ samples from the upper sections (1-5 cm) and one sample from 30 cm are enriched in ^{13}C by 2.8‰, 1.8‰, and 0.3‰, respectively, relative to the $\delta^{13}C_{\text{drought-vegetation}}$ (Table 8 and 7). While the $\delta^{13}C_{SOM}$ sample from 34 cm is depleted in ^{13}C by -0.6‰, relative to the $\delta^{13}C_{\text{drought-vegetation}}$. All the $\delta^{13}C_{SOM}$ samples are enriched in ^{13}C relative to the $\delta^{13}C_{\text{wet-vegetation}}$ by 3.9‰ to 7.9‰ (Table 8 and 7).

South Cimarron is an upland site that is dominated by sagebrush and mixed grass prairie. In some ways, the proxies and vegetation of South Cimarron are similar to the lowland sites, but in other ways they show a different pattern. Like Kohn's Ranch, the majority of the $\delta^{13}C_{\text{carbonates}}$ reflect a similar vegetation regime as the $\delta^{13}C_{SOM}$ samples, and only two of the $\delta^{13}C_{\text{carbonates}}$ are enriched in ^{13}C relative to the $\delta^{13}C_{SOM}$ by 1-2‰. However, unlike the two lowland sites, the vegetation collected during the wet and drought period at South Cimarron only differ by a 0.6‰ and both the $\delta^{13}C_{SOM}$ or $\delta^{13}C_{carbonates}$ are enriched in ^{13}C relative to both the $\delta^{13}C_{drought\text{-}vegetation}$ and $\delta^{13}C_{wet\text{-}vegetatio}$n (Figure 11). This is supported by the most negative and positive $\delta^{13}C_{carbonates}$, which are enriched in ^{13}C by 0.3‰ and 2.2‰ relative to the $\delta^{13}C_{drought\text{-}vegetation}$ (Table 6 and 7) and enriched in ^{13}C relative to the $\delta^{13}C_{wet\text{-}vegetation}$ by 1.9‰ and 4.1‰ (Table 6 and 7).The most negative and positive $\delta^{13}C_{SOM}$ samples of pit 1 are depleted in ^{13}C by only -0.9‰ and enriched in ^{13}C by 3.0‰, respectively (Table 8 and 7), and the samples of pit 2 are enriched in ^{13}C by 0.2‰ and 1.4‰, respectively, relative to the $\delta^{13}C_{drought\text{-}vegetation}$ (Table 8 and 7). The most negative and positive $\delta^{13}C_{SOM}$ samples from pit 1 are depleted in ^{13}C by only -0.3‰ and enriched in ^{13}C by 3.6‰, relative to the mean value of $\delta^{13}C_{wet\text{-}vegetation}$ (Table 8 and 7). $\delta^{13}C_{SOM}$ samples from pit 2 are enriched in ^{13}C by 0.8‰ and 2‰, relative to the mean value of the $\delta^{13}C_{wet\text{-}vegetation}$ (Table 8 and 7).

Rex Road is the most upland site and is dominated by mixed grass prairie vegetation. Like South Cimarron, the vegetation collected during the wet and drought period at Rex Road only differ by a 0.9‰ and both the $\delta^{13}C_{SOM}$ or $\delta^{13}C_{carbonates}$ are enriched in ^{13}C relative to both the $\delta^{13}C_{drought\text{-}vegetation}$ and $\delta^{13}C_{wet\text{-}vegetation}$ (Figure 11). This site reflects the most ^{13}C-enrichment of both $\delta^{13}C$ and $\delta^{13}C_{carbonate}$ relative to the $\delta^{13}C$ of vegetation of both wet and drought period. The most negative and positive $\delta^{13}C_{carbonate}$ sample are enriched in ^{13}C by 0.1‰ and by 7.0‰ relative to the $\delta^{13}C_{wet\text{-}vegetation}$ (Table 6 and 7) and are enriched in ^{13}C by 1‰ and 7.9‰, relative to the $\delta^{13}C_{drought\text{-}vegetation}$ (Table 6 and 8). The most negative and positive $\delta^{13}C_{SOM}$ samples are enriched in ^{13}C by 4.1‰ and 6.9‰, respectively, relative to the $\delta^{13}C_{drought\text{-}vegetation}$ (Table 9 and 8) and are enriched in ^{13}C by 3.2‰ and 6.9‰, respectively, relative to the $\delta^{13}C_{wet\text{-}vegetation}$.

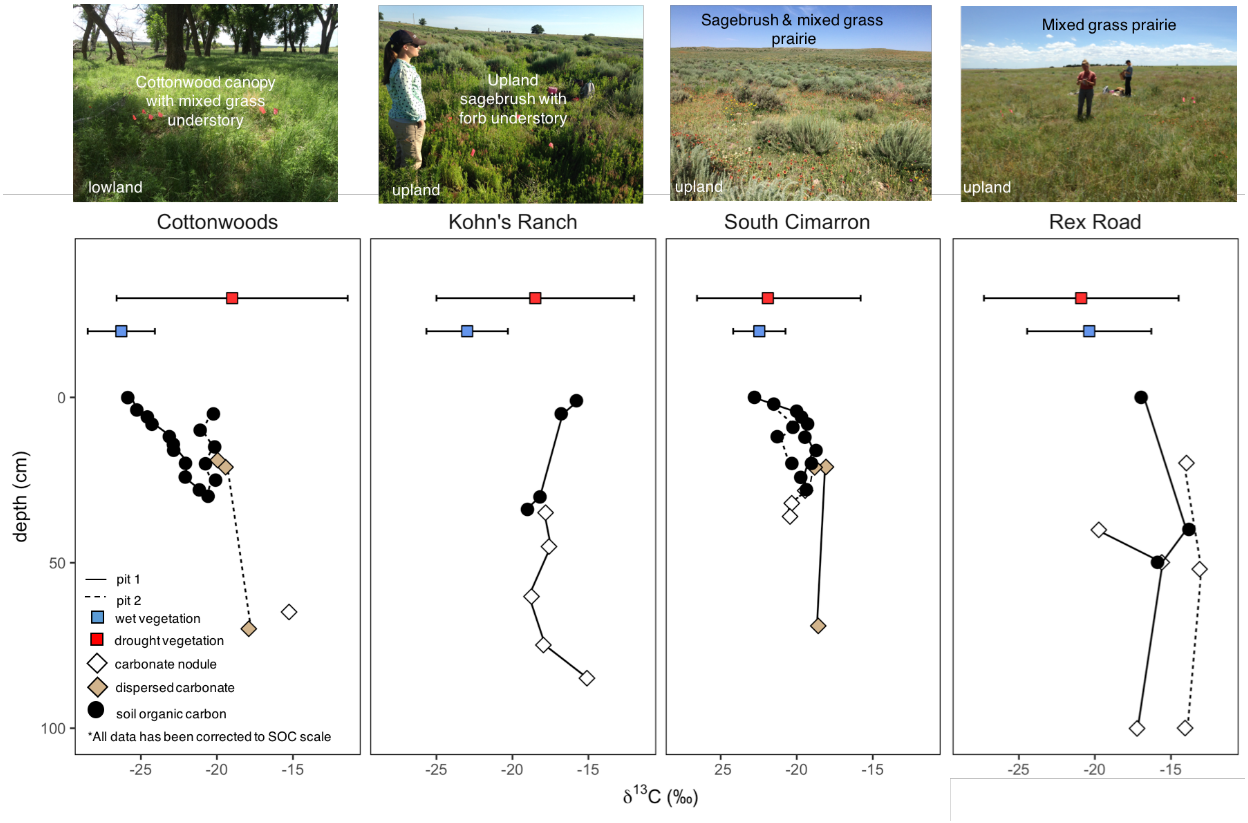

Figure 11. Carbon isotope values of drought and wet vegetation, SOC, and pedogenic carbonates. Drought and wet vegetation samples were adjusted by 2‰ (±1‰) and carbonate samples were adjusted by -15‰ (Desjardins et al. 1994; Boutton 1996; Mcpherson et al. 1992; Mariotti & Peterschmitt 1994; Dzurec et al. 1985; Wynn, 2007; Wynn and Bird, 2007; Cerling and Quade, 1993; Fox et al., 2012). Error bars indicate the standard deviation of the corrected average vegetation δ^{13}C values.

6. Discussion

6.1 Carbon isotope ratios of drought and wet vegetation

The $\delta^{13}C_{drought\text{-}vegetation}$ is enriched in ^{13}C relative to the $\delta^{13}C_{normal\text{-}vegetation}$ at all sites except Red Road. At Cottonwoods and Kohn's Ranch the $\delta^{13}C_{drought\text{-}vegetation}$ is enriched in ^{13}C relative to the $\delta^{13}C_{wet\text{-}vegetation}$ by 7.3‰ and 4.5‰, respectively, while at South Cimarron and Rex Road the $\delta^{13}C_{drought\text{-}vegetation}$ is enriched in ^{13}C by 0.6‰ and depleted in ^{13}C by 0.9‰, relative to the $\delta^{13}C_{wet\text{-}vegetation}$. The two upland sites, South Cimarron and Rex Road, are dominated by mixed grass prairie species and show the smallest difference between the $\delta^{13}C_{drought\text{-}vegetation}$ and the $\delta^{13}C_{wet\text{-}vegetation}$. This may suggest upland mixed grass communities are more tolerant to drought and do not experience C_3 or C_4 changes under water stress. Kohn's Ranch and Cottonwoods are both dominated by herbaceous and woody C_3 species and do show ^{13}C-enriched drought vegetation, which may indicate these C_3 dominated communities are more sensitive to changes in precipitation. Throughout the Great Plains, seasonal changes in both temperature and precipitation have been shown to control C_3 – C_4 distributions, where primary productivity is dominated by C_3 grasses in the spring growing season and then by C_4 grasses during the summer growing season (Epstein et al., 2002; Murphy & Bowman, 2007; Teeri & Stowe, 1976; Vogel et al., 1986). Teeri and Stowe (1976) showed that C_4 grasses were correlated not only with growing season temperatures but also with low levels of soil moisture, that are typical of drought conditions. The drought vegetation at Cottonwoods and Kohn's Ranch may also be enriched in ^{13}C because C_3 plants at these sites, notably species that are present during both the drought and wet period, such as the cottonwood trees (*Populus deltoids*) and sand sagebrush (*Artemisia filifolia*), may confer higher WUE during drought conditions and therefore produce foliar that is ^{13}C-enriched. Cottonwood trees are drought-intolerant and rely on shallow groundwater and/or high shallow soil water availability for establishment, growth and reproduction (Bushet al., 1992; Stromberg, 1993). Hultine et al. (2010) found that cottonwood trees are sensative to interannual reductions in water availability, as evidenced by high leaf carbon isotope ratios during dry summer months. Sand sagebrush are also sensitive to interannual changes in precipitation, and foliar discrimination (against ^{13}C) values of sand sagebrush significantly increased (lower $\delta^{13}C$ values) in response to simulated summer rain events (Lin, et al. 1996).

Perhaps the most important explanation for some of this differences between the $\delta^{13}C_{\text{drought-vegetation}}$ and $\delta^{13}C_{\text{wet-vegetation}}$ in this study, come from the different sampling techniques used for the two records (as discussed in section 4.5.1). A relic of these differences in methodology is observed in the standard deviations of the $\delta^{13}C_{\text{drought-vegetation}}$ which are greater than those of the $\delta^{13}C_{\text{wet-vegetation}}$. The mean and standard deviation of the drought vegetation are derived from discrete species $\delta^{13}C$ values and so encompass a broader carbon isotope range by virtue of a plant always being either C_3 or C_4 and increasing the uncertainty. The wet vegetation is from aboveground biomass samples of both C_3 and C_4 plants and therefore no $\delta^{13}C$ values are strictly C_3 or C_4 derived. While the apparent shifts in carbon isotope ratios at Cottonwoods and Kohn's Ranch to lighter $\delta^{13}C$ values during the wet period and heavier $\delta^{13}C$ values during the drought period are supported by other studies, this study is unable make conclusive remarks about differences between the $\delta^{13}C_{\text{drought-vegetation}}$ and the $\delta^{13}C_{\text{wet-vegetation}}$. Future studies should collect a greater sample size of drought and wet vegetation and decide upon a consistent sampling technique to collected vegetation.

6.2 Climate influences on carbon isotope ratios of pedogenic carbonates

Breecker et al. (2009) suggested that carbonates precipitate at times when soils are warm and dry with low soil CO_2, which may enrich $\delta^{13}C$ values of soil CO_2 in ^{13}C and drive them away from the $\delta^{13}C$ value of average growing season soil CO_2. The results from this thesis are consistent with Breecker et al.'s (2009) hypothesis and my own hypotheses (Figure 1), which predicts that the $\delta^{13}C_{carbonates}$ are controlled primarily by $\delta^{13}C_{drought\text{-}vegetation}$. Throughout all the sites, the carbonate samples and $\delta^{13}C_{drought\text{-}vegetation}$ exhibit the most positive $\delta^{13}C$ values (Figure 10). All carbonate samples were collected at depths greater than 30 cm to limit the potential influence of isotopically heavy atmospheric CO_2 (-8‰; Keeling et al., 2000). However, the pattern to which carbonates are enriched in ^{13}C increases from lowland to upland, which suggests that more perhaps the more aerated upland atmospheric CO_2 makes up a greater portion of the soil CO_2 than the lowland soils. Cottonwoods (upland) and Kohn's Ranch (upland, but within a lower region) both have $\delta^{13}C$ values that reflect $\delta^{13}C_{drought\text{-}vegetation}$ and therefore dry growing season conditions. South Cimarron and Rex Road (both uplands) have $\delta^{13}C_{carbonates}$ that are enriched in ^{13}C relative to the $\delta^{13}C_{drought\text{-}vegetation}$. Uplands have less vegetation and the soils are drier, sandy, and well-drained which means atmospheric CO_2 likely makes up a greater portion of the soil CO_2 than root and microbial respired CO_2 and therefore ^{13}C-enriches the $\delta^{13}C_{carbonates}$ of uplands. Lowlands have more vegetation and soils that are higher in silt and clay contents and therefore poorly drained, this could mean that root and microbial respired CO_2 makes up a greater proportion of soil CO_2 than atmospheric CO_2 and therefore controls the $\delta^{13}C_{carbonates}$ in lowlands. Kohn's Ranch, although an upland site, is situated in a generally lower region of Meade Basin and has denser vegetation with more herbaceous forbs than the other upland sites, and therefore the soil CO_2 may be more controlled by its high vegetative inputs than its upland topography. As a proxy for vegetation, the $\delta^{13}C$ value of pedogenic carbonates are consistently enriched relative to what may be expected for average $\delta^{13}C$ of vegetation and at upland sites the $\delta^{13}C$ of soil CO_2 may incorporate a proportion of atmospheric CO_2.

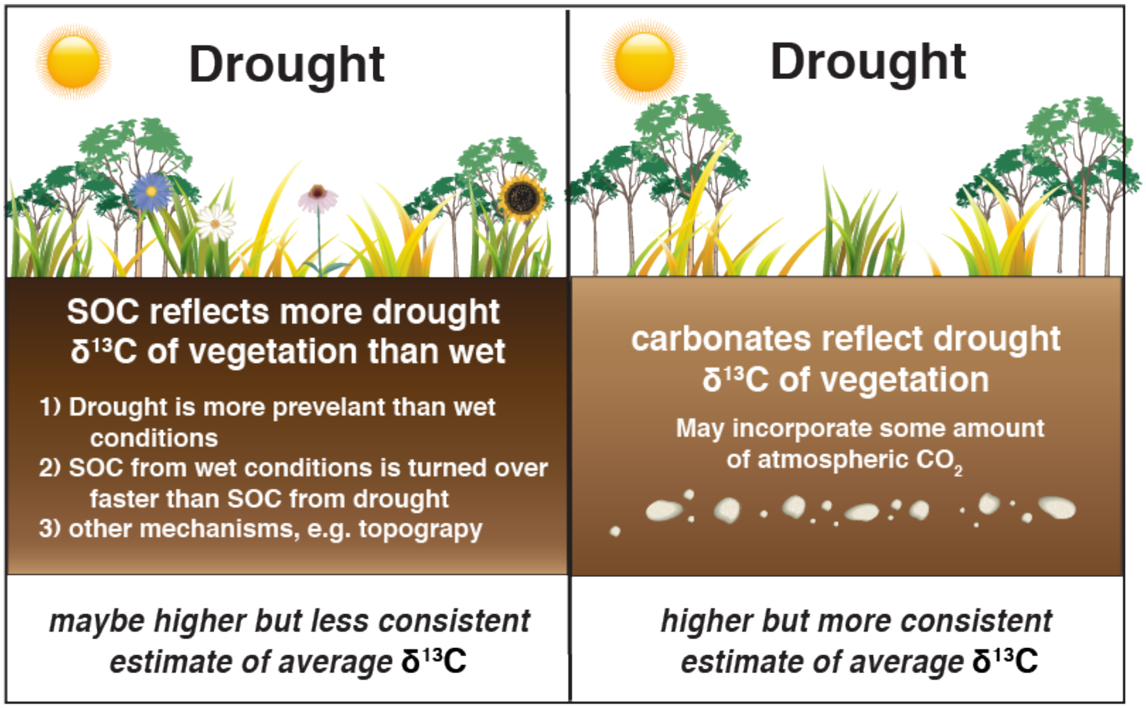

Figure 12. Revised hypothesis about of the formation of paleovegetation proxies (pedogenic carbonates and soil organic matter) and the vegetation assemblages ($\delta^{13}C$ values) they record. Carbonates may preserve $\delta^{13}C$ values indicative of warm and dry vegetation and may also incorporate atmospheric CO_2 at uplands. SOC may reflect that drought is more prevalent than wet conditions, that SOC is not preserved from wet conditions, or that other mechanisms are controlling the $\delta^{13}C$ of SOC, such as topography.

6.3 Controls on carbon isotope ratios of soil organic carbon

SOM is found to accumulate in cool and wet climates, because of high vegetative inputs and slow decomposition (Epstein et al., 2013b; Lützow & Kögel-Knabner, 2009). I predicted the $\delta^{13}C$ values of SOM will reflect vegetation growing in cool and wet growing seasons. Interestingly, the $\delta^{13}C_{SOM}$ do not reflect the $\delta^{13}C_{wet\text{-}vegetation}$, but instead fall either in between the

$\delta^{13}C$ values for wet and drought vegetation or reflect the $\delta^{13}C_{drought\text{-}vegetation}$. This finding could suggest that either 1) drought is more prevalent than wet conditions throughout the Meade Basin 2) the SOM produced during wet growing seasons is turned over more quickly than SOM produced during the drought conditions or 3) there are other mechanisms, beyond climate, that are controlling the $\delta^{13}C_{SOM}$ throughout the Great Plains (Figure 12).

Drought is a common occurrence throughout the United State and especially throughout the Midwest (Cook et al., 1999). Therefore, 1) drought could be more prevalent than wet conditions throughout the Great Plains. However, the effects of the 2012 drought on the soil organic carbon of the Great Plains does not support 2) that SOM derived from wet growing seasons is turned over more quickly than SOM produced during drought. Eddy-covariance tower data, satellite estimates of the timing of plant growth, and regional carbon-budget estimates show summer carbon losses from the Great Plains, during the 2012 drought, due to water stress and poor plant growth (Pan & Schimel, 2016). Trends toward warmer spring growing season temperature should cause initial increases in carbon uptake (through extended growing seasons) but would also cause water deficits in the late summer and therefore increased carbon losses in the late summer because of decreased plant growth, especially in drought years (Pan & Schimel, 2016).

The $\delta^{13}C_{SOM}$ follows a similar topographic pattern to the $\delta^{13}C_{carbonates}$; the $\delta^{13}C$ values become more enriched in ^{13}C from the lowland sites to the upland sites. This may provide evidence that 3) there are other mechanisms controlling the $\delta^{13}C$ values of SOM in this study. The upland sites all have lower amounts of organic carbon relative to the one lowland site (Figure 9). Hook and Burke (2000) observed a similar topographic affect; they found lowlands to have more total C and more mineral associated organic carbon than uplands. This may indicate that upland sites may turn over carbon more quickly, because they have little vegetation inputs, sandy well-drained soils, and lowland sites may have larger vegetation inputs and slower rates of decomposition because they have higher clay and silt contents in their soils which may physically and chemically protect SOM from microbes (Beare et al., 1994; Hook & Burke, 2000; Lützow et al., 2006; Schimel & Woodmansee, 1985). Cottonwoods is the only site where the $\delta^{13}C_{SOM}$ reflects that it was derived from $\delta^{13}C_{wet\text{-}vegetation}$, which suggests that more SOM may accumulate in wet and cool growing seasons at lowlands and therefore $\delta^{13}C_{SOM}$ of lowlands may reflect vegetation of cooler and wetter climates. Less organic matter accumulates at upland sites, and the SOM that does prevail in soils is likely a part of more stabilized pools. Therefore, the $\delta^{13}C_{SOM}$ of upland sites may be controlled more by SOM that has been recycled many times by microorganisms and is now biologically stabilized, because ^{13}C-enriched SOM can be an indication of increasing effects of decomposition and residuals of microorganism (Ehleringer et al., 2000; Garten et al., 2000; Mariotti & Peterschmitt, 1994; Mcpherson et al., 1992; Werth & Kuzyakov, 2010; Wynn et al., 2005; Wynn et al., 2005).

In terms of SOM as a proxy for vegetation, at uplands the soil organic matter may be enriched in ^{13}C by more than the 1-3 ‰ that is typically observed in soil profiles (Desjardins et al. 1994; Boutton 1996; Mcpherson et al. 1992; Mariotti & Peterschmitt 1994; Dzurec et al. 1985; Wynn, 2007; Wynn and Bird, 2007) At lowland sites, the $\delta^{13}C$ of soil organic matter is more variable and in some instances, reflects wet and cool conditions, while other times it appears more derived from warm and dry vegetation (Figure 11).

6.4 Topographic influences

Studies show accumulation of organic matter and formation of pedogenic carbonates is most strongly related to climate and precipitation throughout the Great Plains region (Epstein et al., 2013a; Eswaran et al., 2000; Lützow & Kögel-Knabner, 2009; Zamanian et al., 2016). This study shows that topography may also play a more important role in local variability of both the amount of organic matter that accumulates and the $\delta^{13}C$ values of SOM and pedogenic carbonates. Upland sites in semiarid grasslands contain more bare ground, less total plant coverage, sandy soils, and lower soil moisture; lowland sites contain less bare ground, greater total plant coverage, silt and clay rich soil textures, and higher soil moisture (Hook & Burke, 2000). Upland sites also generally have lower amounts of organic carbon, relative to lowland sites (Hook & Burke, 2000; D. Schimel & Woodmansee, 1985). Lowland sites may also be more sensitive to changes between drought and wet conditions, as seen with Cottonwoods site, which had the greatest accumulation of SOM and the greatest isotopic difference between the $\delta^{13}C_{carbonate}$ and $\delta^{13}C_{SOM}$. The upland sites may be less sensitive to water stress induced by drought, and therefore show smaller differences between the $\delta^{13}C_{SOM}$ and $\delta^{13}C_{carbonates}$ Kohn's Ranch, South Cimarron and Rex Road. Therefore, paleovegetation proxies collected at upland regions are more likely to deviate from average $\delta^{13}C$ value of vegetation, while lowland regions may produce proxies more indicative of average vegetation schemes.

7. Conclusions

In this study, I compare the $\delta^{13}C_{carbonate}$, $\delta^{13}C_{SOM}$, $\delta^{13}C_{drought\text{-}vegetation}$, and $\delta^{13}C_{wet\text{-}vegetation}$ from four modern sites in Meade Basin to investigate biases associated with the formation of pedogenic carbonates and soil organic matter. Meade Basin provides a unique opportunity to study how climate may influence the $\delta^{13}C$ of soil-based paleovegetation proxies, as drought has been prevalent and long term through the region. Meade Basin is also important because of the paleosol records and paleovegetation proxies which preserve the evolution of C_4 grasslands in the Great Plains of North America. I show at all sites that the $\delta^{13}C_{carbonates}$ and the $\delta^{13}C_{SOM}$ may be controlled by local topography. Upland and lowlands facilitate different biogeochemical processes that can influence the influence the vegetation communities, SOM accumulation, and nutrient cycling (D. Schimel & Woodmansee, 1985; Swanson et al., 1988). The results presented in this thesis show there is some evidence the $\delta^{13}C_{drought\text{-}vegetation}$ are enriched in ^{13}C relative to $\delta^{13}C_{wet\text{-}vegetation}$, which may be a caused by greater proportions of C_4 plants, water stress, or the differences in the sampling procedure for the two vegetation records. There is also evidence that the $\delta^{13}C_{carbonates}$ reflect signals similar to the $\delta^{13}C_{drought\text{-}vegetation}$ and/or $\delta^{13}C$ values that are enriched in ^{13}C relative to both the wet and drought vegetation. The ^{13}C-enrichment effect of $\delta^{13}C$ carbonates relative to vegetation increases as the topography increases. This indicates the $\delta^{13}C_{carbonates}$ may reflect vegetation signals of warmer and drier climates and/or isotopically heavy atmospheric CO_2 makes up a greater portion of soil CO_2 at upland sites. There is no evidence that $\delta^{13}C_{SOM}$ reflects values similar to the $\delta^{13}C_{wet\text{-}vegetation}$, instead the $\delta^{13}C_{SOM}$ reflects values that fall in between $\delta^{13}C$ of wet and drought vegetation and at some sites are enriched in ^{13}C relative to $\delta^{13}C_{drought\text{-}vegetation}$. $\delta^{13}C_{SOM}$ that is enriched in ^{13}C relative to vegetation at three of the upland sites indicate that either drought conditions are more common than wet conditions throughout the western Great Plains, or that topography is also is responsible for enriching $\delta^{13}C_{SOM}$ in ^{13}C (Figure 12). The topographic gradient that these ^{13}C enrichment patterns follow for both $\delta^{13}C$ values of SOM and carbonates, suggest uplands reflect more ^{13}C-enriched $\delta^{13}C$ values than lowland sites. To fully explore this role of topography, future studies should examine the soil texture, soil moisture, soil respiration, and aboveground biomass between lowlands and uplands.

8. References

Battipaglia, G., Pelleri, F., Lombardi, F., Altieri, S., Vitone, A., Conte, E., & Tognetti, R. (2017). Effects of associating Quercus robur L. and Alnus cordata Loisel. on plantation productivity and water use efficiency. *Forest Ecology and Management*, *391*, 106–114. https://doi.org/10.1016/j.foreco.2017.02.019

Beare, M. H., Cabrera, M. L., Hendrix, P. F., & Coleman, D. C. (1994). Aggregate-Protected and Unprotected Organic Matter Pools Conventional-and No-Tillage Soils. Retrieved from https://www.researchgate.net/profile/David_Coleman7/publication/238174789_Aggregate-Protected_and_Unprotected_Organic_Matter_Pools_in_Conventional_and_No-Tillage_Soils/links/545398da0cf2bccc490b1cde.pdf

Benbi, D. K., Boparai, A. K., & Brar, K. (2014). Decomposition of particulate organic matter is more sensitive to temperature than the mineral associated organic matter. *Soil Biology and Biochemistry*, *70*, 183–192. https://doi.org/10.1016/j.soilbio.2013.12.032

Benbi, D. K., Toor, A. S., & Kumar, S. (2012). Management of organic amendments in rice-wheat cropping system determines the pool where carbon is sequestered. *Plant and Soil*, *360*(1–2), 145–162. https://doi.org/10.1007/s11104-012-1226-3

Bowling, D. R., Pataki, D. E., & Randerson, J. T. (2008). Carbon isotopes in terrestrial ecosystem pools and CO2 fluxes. *New Phytologist*, *178*(1), 24–40. https://doi.org/10.1111/j.1469-8137.2007.02342.x

Breecker, D. O., Sharp, Z. D., & McFadden, L. D. (2009). Seasonal bias in the formation and stable isotopic composition of pedogenic carbonate in modern soils from central New Mexico, USA. *Bulletin of the Geological Society of America*, *121*(3–4), 630–640. https://doi.org/10.1130/B26413.1

Bush, D. E., Ingrahm, N. L., & Smith, S. D. (1992). Water Uptake in Woody Riparian Phreatophytes of the Southwestern United States : A Stable Isotope Study. *Ecological Applications*, *2*(4), 450–459.

Cerling, Thure E and Quade, J. (1993). Stable Carbon and Oxygen Isotopes in Soil Carbonates.

Cerling, T. E. (1984). The stable isotopic composition of modern soil carbonate and its relation to climate. *Earth Planetary Science Letters*, *71*, 229–240.

Cerling, T. E., Harris, J. M., Macfadden, B. J., Leakey, M. G., Quadek, J., Eisenmann, V., & Ehleringer, J. R. (1997). Global vegetation change through the Miocene / Pliocene boundary. *Nature*, *389*, 153–158. https://doi.org/10.1038/38229

Cerling, T. E., Solomon, D. K., Quade, J., & Bowman, J. R. (1991). On the isotopic composition of carbon in soil carbon dioxide. *Geochimica et Cosmochimica Acta*, *55*, 3403–3405. https://doi.org/10.1016/0016-7037(91)90498-T

Cernusak, L. A., Ubierna, N., Winter, K., Holtum, J. A. M., Marshall, J. D., & Farquhar, G. D. (2013). Environmental and physiological determinants of carbon isotope discrimination in terrestrial plants. *New Phytologist*. https://doi.org/10.1111/nph.12423

Cook, E. R., Meko, D. M., Stahle, D. W., & Cleaveland, M. K. (1999). Drought Reconstruction for the Continental United States. *Journal of Climate*, *12*, 1145–1162.

Dickinson, C. E., & Dodd, J. L. (1976). Phenological Pattern in the Shortgrass Praire. *The American Midland Naturalist*, *96*(2), 367–378.

Edwards, E. J., & Grass Phylogeny Working Group II. (2011). New grass phylogeny resolves deep evolutionary relationships and discovers C 4 origins. *New Phytologist*, 304–312. https://doi.org/10.1111/j.1469-8137.2011.03972.x

Edwards, E. J., Osborne, C. P., Strömberg, C. A. E., Smith, S. A., & C4 Grasses Consortium. (2010). The Origins of C 4 Grasslands: Integrating Evolutionary and Ecosystem Science. *Science*, *328*(April), 587–590. https://doi.org/10.1126/science.1177216

Edwards, E. J., & Smith, S. A. (2010). Phylogenetic analyses reveal the shady history of C4 grasses. *Proceedings of the National Academy of Sciences*, *107*(6), 2532–2537. https://doi.org/10.1073/pnas.0909672107

Ehleringer, J. R., Buchmann, N., & Flanagan, L. B. (2000). Carbon isotope ratios in belowground carbon cycle processes. *Ecological Applications*. https://doi.org/10.1890/1051-0761(2000)010[0412:CIRIBC]2.0.CO;2

Ehleringer, J. R., Buchmann, N., & Flanagan, L. B. (2000). Carbon isotope ratios in belowground carbon cycle processes. *Ecological Applications*, *10*(2), 412–422. https://doi.org/10.1890/1051-0761(2000)010[0412:CIRIBC]2.0.CO;2

Ehleringer, J. R., Cerling, T. E., & Helliker, B. R. (1997). C 4 photosynthesis, atmospheric CO 2 , and climate. *Oecologia*, *112*(3), 285–299. https://doi.org/10.1007/s004420050311

Ehleringer, J. R., & Monson, R. K. (1993). Evolutionary and Ecological Aspects of Photosynthetic Pathway Variation. *Annual Review of Ecology and Systematics*, *24*(1), 411–439. https://doi.org/10.1146/annurev.es.24.110193.002211

Epstein, H. E., Burke, I. C., & Lauenroth, W. K. (2013a). Regional Patterns of Decomposition and Primary Production Rates in the U . S . Great Plains. *Ecology*, *83*(2), 320–327. Retrieved from http://www.jstor.org/stable/2680016

Epstein, H. E., Burke, I. C., & Lauenroth, W. K. (2013b). Regional Patterns of Decomposition and Primary Production Rates in the U . S . Great Plains, *83*(2), 320–327.

Epstein, H. E., Gill, R. A., Paruelo, J. M., Lauenroth, W. K., Jia, G. J., & Burke, I. C. (2002).

The relative abundance of three plant functional types in temperate grasslands and shrublands of North and South America: effects of projected climate change. *Journal of Biogeography*, *29*(7), 875–888. https://doi.org/10.1046/j.1365-2699.2002.00701.x

Eswaran, H., Reich, P. F., Kimble, J. M., Beinroth, F. H., Padmanabhan, E., & Moncharoen, P. (2000). Global carbon stocks. In R. Lal, J. M. Kimble, B. A. Steward, & H. Eswaran (Eds.), *Global climate change and pedogenic carbonates* (pp. 15–25). Lewis Publishers, Boca Raton, FL.

Farquhar, G. D., Ehleringer, J. R., & Hubick, K. T. (1989). Carbon Isotope Discrimination and Photosynthesis. *Annual Review of Plant Physiology and Plant Molecular Biology*, *40*(1), 503–537. https://doi.org/10.1146/annurev.pp.40.060189.002443

Farquhar, G., O'Leary, M., & Berry, J. (1982). On the Relationship Between Carbon Isotope Discrimination and the Intercellular Carbon Dioxide Concentration in Leaves. *Australian Journal of Plant Physiology*, *9*(2), 121. https://doi.org/10.1071/PP9820121

Feakins, S. J., Levin, N. E., Liddy, H. M., Sieracki, A., Eglinton, T. I., & Bonnefille, R. (2013). Northeast african vegetation change over 12 m.y. *Geology*, *41*(3), 295–298. https://doi.org/10.1130/G33845.1

Ferretti, D. F., Pendall, E., Morgan, J. A., Nelson, J. A., Lecain, D., & Mosier, A. R. (2003). Partitioning evapotranspiration fluxes from a Colorado grassland using stable isotopes: Seasonal variations and ecosystem implications of elevated atmospheric CO2. *Plant and Soil*, *254*, 291–303. Retrieved from https://link-springer-com.colorado.idm.oclc.org/content/pdf/10.1023%2FA%3A1025511618571.pdf

Ford, P. L. (1999). Response of buffalograss (Buchloë dactyloides) and blue grama (Bouteloa gracilis) to fire. *Great Plains Research*, *9*(2), 261–276. Retrieved from http://digitalcommons.unl.edu/cgi/viewcontent.cgi?article=1453&context=greatplainsresearch

Fox, D. L., Honey, J. G., Martin, R. A., & Peláez-Campomanes, P. (n.d.). Pedogenic carbonate stable isotope record of environmental change during the Neogene in the southern Great Plains, southwest Kansas, USA: Oxygen isotopes and paleoclimate during the evolution of C 4 -dominated grasslands. *GSA Bulletin*, *12441*(5). https://doi.org/10.1130/B30402.1

Fox, D. L., Honey, J. G., Martin, R. A., & Peláez-Campomanes, P. (2012). Pedogenic carbonate stable isotope record of environmental change during the Neogene in the southern Great Plains, southwest Kansas, USA: Oxygen isotopes and paleoclimate during the evolution of C4-dominated grasslands. *Bulletin of the Geological Society of America*, *124*(3–4), 431–443. https://doi.org/10.1130/B30402.1

Fox, D. L., & Koch, P. L. (2003). Tertiary history of C (sub 4) biomass in the Great Plains, USA. *Geology (Boulder)*, *31*(9), 809–812. https://doi.org/10.1130/G19580.1

Fox, D. L., & Koch, P. L. (2004). Carbon and oxygen isotopic variability in Neogene paleosol carbonates: Constraints on the evolution of the C4-grasslands of the Great Plains, USA. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *207*(3–4), 305–329. https://doi.org/10.1016/S0031-0182(04)00045-8

Francelanord, C., & Derry, L. A. (1994). d13C of organic-carbon in the Bengal fan - source evolution and transport of C3 and C4 plant carbon to marine-sediments. *Geochimica et Cosmochimica Acta*, *58*(21), 4809–4814. https://doi.org/10.1016/0016-7037(94)90210-0

Garten Jr., C. T., Cooper, L. W., Post, W. M., & Hanson, P. J. (2000). Climate controls on forest soil C isotope ratios in the Southern Appalachian Mountains. *Ecology*, *81*(4), 1108–1119. Retrieved from http://www.esajournals.org/esaonline/?request=get-abstract&issn=0012-9658&volume=081&issue=04&page=1108

Gray, J. (1985). The microfossil record of early land plants: advances in understanding of early terrestrialization. *Philosophical Transactions of the Royal Society B: Biological Sciences*. Retrieved from www.jstor.org

Hatch, M. (1987). C4 Photosynthesis: a unique blend of modified biochemistry, anatomy abd ultrastructure. *Biochimica et Biophysica Acta*, *895*(2), 81–106. https://doi.org/10.1016/0003-9861(88)90351-7

Hattersley, P. W., & Watson, L. (1992). Diversification of photosynthesis. In *Grass evolution and domestication* (pp. 38–116).

Hayes, J. M. (2001). Fractionation of the Isotopes of Carbon and Hydrogen in Biosynthetic Processes. Retrieved from https://www.whoi.edu/fileserver.do?id=73288&pt=2&p=74886

Hobbie, E. A., & Werner, R. A. (2004). Bulk carbon isotope patterns in C 3 and C 4 plants : a review and synthesis. *New Phytologist*, *161*(2), 371–385. https://doi.org/10.1046/j.1469-8137.2004.00970.x

Hobbie, S. E., Schimel, J. P., Trumbore, S. E., & Randerson, J. R. (2000). Controls over carbon storage and turnover in high-latitude soils. *Global Change Biology*, *6*(SUPPLEMENT 1), 196–210. https://doi.org/10.1046/j.1365-2486.2000.06021.x

Hoetzel, S., Dupont, L., Schefuß, E., Rommerskirchen, F., & Wefer, G. (2013). The role of fire in Miocene to Pliocene C4 grassland and ecosystem evolution. *Nature Geoscience*, *6*(12), 1027–1030. https://doi.org/10.1038/ngeo1984

Hook, P. B., & Burke, I. C. (2000). Biogeochermistry in a shortgrass landscape: control by topograpy, soil texture, and microclimate. *Ecology*, *81*(10), 2686–2703. https://doi.org/10.1890/0012-9658(2000)081{[}2686:BIASLC]2.0.CO;2

Hoover, D. L., Knapp, A. K., & Smith, M. D. (2017). Photosynthetic responses of a dominant C4 grass to an experimental heat wave are mediated by soil moisture. *Oecologia*, *183*(1), 303–

313. https://doi.org/10.1007/s00442-016-3755-6

Hultine, K. R., Bush, S. E., & Ehleringer, J. R. (2010). Ecophysiology of riparian cottonwood and willow before , during , and after two years of soil water removal. *Ecological Applications*, *20*(2), 347–361.

Hynek, S. A., Passey, B. H., Luis, J., Brown, F. H., Cerling, T. E., & Quade, J. (2012). Small mammal carbon isotope ecology across the Miocene – Pliocene boundary , northwestern Argentina. *Earth and Planetary Science Letters*, *321–322*, 177–188. https://doi.org/10.1016/j.epsl.2011.12.038

Ibrahim, D. G., Gilbert, M. E., Ripley, B. S., & Osborne, C. P. (2008). Seasonal differences in photosynthesis between the C3 and C 4 subspecies of Alloteropsis semialata are offset by frost and drought. *Plant, Cell and Environment*, *31*(7), 1038–1050. https://doi.org/10.1111/j.1365-3040.2008.01815.x

Izett, G. A., & Honey, J. G. (1995). Geologic map of the Irish Flats NE Quadrangle, Meade Country, Kansas. United States Geologic Survey.

Johnson, W. C., Willey, K. L., & Macpherson, G. L. (2007). Carbon isotope variation in modern soils of the tallgrass prairie: Analogues for the interpretation of isotopic records derived from paleosols. *Quaternary International*, *162–163*, 3–20. https://doi.org/10.1016/j.quaint.2006.10.036

Jones, S. R., & Cushman, C. R. (2004). *The North American Prairie*. The Peterson Field Guide Series.

Keeley, J. E., & Rundel, P. W. (2003). Evolution of CAM and C 4 Carbon-Concentrating Mechanisms. *Source: International Journal of Plant Sciences Int. J. Plant Sci*, *1643*(164), 55–77. https://doi.org/10.1086/374192

Kansas State University. Drought Updates (2012-2014). http://climate.k-state.edu/drought/updates/

Keeling, C. D., Piper, S. C., Bacastow, R. B., Wahlen, M., Whorf, T. P., Heimann, M., & Meijer, H. A. (2000). Atmospheric CO2 and 13CO2 Exchange with the Terrestrial Biosphere and Oceans from 1978 to 2000: Observations and Carbon Cycle Implications. *A History of Atmospheric CO2 and Its Effects on Plants, Animals, and Ecosystems*, 83–113. https://doi.org/10.1007/0-387-27048-5_5

Kellogg, E. A. (2013). C4 photosynthesis. *Current Biology*, *23*(14), R594–R599. https://doi.org/10.1016/j.cub.2013.04.066

Knapp, A. K., Briggs, J. M., Hartnett, D. C., & Collins, S. L. (Eds.). (1998). *Grassland Dynamics: Long-Term Ecological Research in Tallgrass Prairie*. New York: LTER Publications Committee & Oxford Unversity Press.

Koch, P. L. (1998). Isotopic Reconstruction of Past Continental Environments. *Annual Review of Earth and Planetary Sciences*, *26*(1), 573–613. https://doi.org/10.1146/annurev.earth.26.1.573

Kubien, D. S., & Sage, R. F. (2004). Low-temperature photosynthetic performance of a C_4 grass and a co-occurring C_3 grass native to high latitudes. *Plant, Cell and Environment*, *27*(7), 907–916. https://doi.org/10.1111/j.1365-3040.2004.01196.x

Küchler, A. W. (1974). A New Vegetation Map. *Ecology*, *55*(3), 586–604.

Latorre, C., Quade, J., & McIntosh, W. C. (1997). The expansion of C4 grasses and global change in the late Miocene: Stable isotope evidence from the Americas. *Earth and Planetary Science Letters*, *146*(1–2), 83–96. https://doi.org/10.1016/S0012-821X(96)00231-2

Lin, G., Phillips, S. L., & Ehleringer, J. R. (1996). Monosoonal Precipitation Responses of Shrubs in a Cold Desert Community on the Colorado Monosoonal precipitation responses of shrubs in a cold desert community on the Colorado Plateau. *Oecologia*, *106*(106), 8–17. Retrieved from http://www.jstor.org/stable/4221226%5Cnhttp://about.jstor.org/terms

Lützow, M. V., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., & Flessa, H. (2006). Stabilization of organic matter in temperate soils: Mechanisms and their relevance under different soil conditions - A review. *European Journal of Soil Science*, *57*(4), 426–445. https://doi.org/10.1111/j.1365-2389.2006.00809.x

Magioncalda, R., Dupuis, C., Smith, T., Steurbaut, E., & Gingerich, P. D. (2004). Paleocene-Eocene carbon isotope excursion in organic carbon and pedogenic carbonate: Direct comparison in a continental stratigraphic section. *Geology*, *32*(7), 553–556. https://doi.org/10.1130/G20476.1

Mariotti, A., & Peterschmitt, E. (1994). Forest Savanna Ecotone Dynamics in India as Revealed by Carbon Isotope Ratios of Soil Organic Matter. *Oecologia*, *97*(4), 475–480.

Martin, B., & Thorstenson, Y. R. (1988). Stable Carbon Isotope Composition (deltaC), Water Use Efficiency, and Biomass Productivity of Lycopersicon esculentum, Lycopersicon pennellii, and the F(1) Hybrid. *Plant Physiol*, *88*(1), 213–217. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/16666269%5Cnhttp://www.plantphysiol.org/content/88/1/213.full.pdf

Martin, R. A., Peláez-Campomanes, P., Honey, J. G., Marcolini, F., & Akersten, W. A. (2011). Five million years of pocket gopher history in the Meade Basin of southwestern Kansas and northwestern Oklahoma. *Journal of Vertebrate Paleontology*, *31*(4), 866–884. https://doi.org/10.1080/02724634.2011.576729

Meade Station NCDC Summary of the Day, www.ncdc.noaa.gov/oa/ncdc.html

Mcpherson, A. G. R., Boutton, T. W., & Midwood, A. J. (1992). Stable Carbon Isotope Analysis of Soil Organic Matter Illustrates Vegetation Change at the grassland / woodland boundary in southeastern Arizona , USA. *Oecologia*, *93*(1), 95–101.

Meentemeyer, V. (1978). Macroclimate the Lignin Control of Litter Decomposition Rates. *Ecology*, *59*(3), 465–472.

Melillo, J. M., Aber, J. D., Linkins, A. E., Ricca, A., Fry, B., & Nadelhoffer, K. J. (1989). Carbon and nitrogen dynamics along the decay continuum: Plant litter to soil organic matter. *Plant and Soil*, *115*(2), 189–198. https://doi.org/10.1007/BF02202587

Melillo, J. M., Aber, J. D., & Muratore, J. F. (1982). Nitrogen and Lignin Control of Hardwood Leaf Litter Decomposition Dynamics. *Ecology*, *63*(3), 621–626. https://doi.org/10.2307/1936780

Mooney, H. A. (1999). *C4 Plant Biology*. (R. F. Sage & R. K. Monson, Eds.), *C4 Plant Biology*. https://doi.org/10.1016/B978-0-12-614440-6.50021-5

Murphy, B. P., & Bowman, D. M. J. S. (2007). Seasonal water availability predicts the relative abundance of C3 and C4 grasses in Australia. *Global Ecology and Biogeography*, *16*(2), 160–169. https://doi.org/10.1111/j.1466-8238.2006.00285.x

Nobel, P. S. (1996). High productivity of certain agronomic CAM species. *Crassulacean Acid Metabolism - Biochemistry, Ecophysiology and Evolution*, *114*, 255–265. https://doi.org/10.1007/978-3-642-79060-7_17

O'Leary, M. H. (1988). Carbon Isotopes in Photosynthesis Fractionation techniques may reveal new aspects of carbon dynamics in plants. *BioScience*, *38*(5), 328–336. Retrieved from http://www.jstor.org/stable/1310735

Osborne, C. P., & Beerling, D. J. (2006). Nature's green revolution: the remarkable evolutionary rise of C4 plants. *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences*, *361*(1465), 173–94. https://doi.org/10.1098/rstb.2005.1737

Pan, Y., & Schimel, D. (2016). Biogeochemistry: Synergy of a warm spring and dry summer. *Nature*, *534*(7608), 483–484. https://doi.org/10.1038/nature18450

Parton, W. J., Scurlock, J. M. O., Ojima, D. S., Gilmanov, T. G., Scholes, R. J., Schimel, D. S., … Kinyamario, J. I. (1993). Observations and modeling of biomass and soil organic matter dynamics for the grassland biome worldwide. *Global Biogeochemical Cycles*, *7*(4), 785–809. https://doi.org/10.1029/93GB02042

Passey, B. H., Ayliffe, L. K., Kaakinen, A., Zhang, Z., Eronen, J. T., Zhu, Y., … Fortelius, M. (2009). Strengthened East Asian summer monsoons during a period of high-latitude warmth? Isotopic evidence from Mio-Pliocene fossil mammals and soil carbonates from northern China. *Earth and Planetary Science Letters*, *277*(3–4), 443–452. https://doi.org/10.1016/j.epsl.2008.11.008

Passey, B. H., Cerling, T. E., Perkins, M. E., Voorhies, M. R., Harris, J. M., & Tucker, S. T. (2002). Environmental Change in the Great Plains: An Isotopic Record from Fossil Horses. *The Journal of Geology*, *110*(2), 123–140. https://doi.org/10.1086/338280

Peters, N. A., Huntington, K. W., & Hoke, G. D. (2013). Hot or not? Impact of seasonally variable soil carbonate formation on paleotemperature and O-isotope records from clumped isotope thermometry. *Earth and Planetary Science Letters*, *361*, 208–218. https://doi.org/10.1016/j.epsl.2012.10.024

Post, W. M., Emanuel, W. R., Zinke, P. J., & Stangenberger, A. G. (1982). Soil carbon pools and world life zones. *Nature*, *298*, 156. Retrieved from http://dx.doi.org/10.1038/298156a0

Quade, J. a Y., Cerling, T. E., & Bowman, J. R. (1989). Systematic variations in the carbon and oxygen isotopic composition of pedogenic Systematic variations in the carbon and oxygen isotopic composition of pedogenic carbonate along elevation transects in the southern Great Basin , United States. *Geological Society of America Bulletin*, *101*(April), 464–475. https://doi.org/10.1130/0016-7606(1989)101<0464

Quade, J., & Cerling, T. E. (1995). Expansion of C4 grasses in the Late Miocene of Northern Pakistan: evidence from stable isotopes in paleosols. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *115*(1–4), 91–116. https://doi.org/10.1016/0031-0182(94)00108-K

Quade, J., Eiler, J., Daëron, M., & Achyuthan, H. (2013). The clumped isotope geothermometer in soil and paleosol carbonate. *Geochimica et Cosmochimica Acta*, *105*, 92–107. https://doi.org/10.1016/j.gca.2012.11.031

Roeske, C. A., & O'Leary, M. H. (1984). Carbon Isotope Effects on the Enzyme-Catalyzed Carboxylation of Ribulose Bisphosphate. *Biochemistry*, *23*(1980), 6275–6284. https://doi.org/10.1021/bi00320a058

Rubinstein, C. V., Gerrienne, P., de la Puente, G. S., Astini, R. A., & Steemans, P. (2010). Early Middle Ordovician evidence for land plants in Argentina (eastern Gondwana). *New Phytologist*, *188*(2), 365–369. https://doi.org/10.1111/j.1469-8137.2010.03433.x

Sage, R. (2001). Environmental and Evolutionary Preconditionsfor the Origin and Diversification of the C4 PhotosyntheticSyndrome. *Plant Biology*, *3*(C), 202–213. https://doi.org/10.1055/s-2001-15206

Sage, R. F. (2004). The evolution of C 4 photosynthesis. *New Phytologist*, *161*(2), 341–370. https://doi.org/10.1046/j.1469-8137.2004.00974.x

Sage, R. F. (2016). A portrait of the C4 photosynthetic family on the 50th anniversary of its discovery: Species number, evolutionary lineages, and Hall of Fame. *Journal of Experimental Botany*. https://doi.org/10.1093/jxb/erw156

Sage, R. F., & Monson, R. K. (1999). *C4 plant biology*. (R. K. M. Rowan F. Sage, Ed.), *Physiological Ecology series*. Academic Press. Retrieved from https://books.google.com/books?hl=en&lr=&id=H7Wv9ZImW-QC&oi=fnd&pg=PP1&dq=c4+plant+biology&ots=uZUwVZlm0d&sig=KGMk3bA4JZiB9SP3YP4AKEmFbas#v=onepage&q&f=false

Sala, A. O. E., Parton, W. J., Joyce, L. A., & Lauenroth, W. K. (1988). Primary Production of the Central Grassland Region of the United States. *Ecological Monographs*, *69*(1), 40–45. https://doi.org/10.2307/1943158

Schimel, D. S., & Parton, W. J. (1986). Microclimatic controls of nitrogen mineralization and nitrification in shortgrass steppe soils. *Plant and Soil*, *93*(3), 347–357. https://doi.org/10.1007/BF02374285

Schimel, D., & Woodmansee, M. A. S. R. G. (1985). Biogeochemisty of C, N, and P in a Soil Catena of the Shortgrass Steppe. *Ecology*, *66*(1), 276–282.

Schlesinger, W. H., & Bernhardt, E. S. (2013). *Biogeochemistry An Analysis of Global Change* (3rd ed.). Academic Press.

Seastedt, T. R., & Knapp, a K. (1993). Consequences of nonequilibrium resource availability across multiple time scales: the transient maxima hypothesis. *The American Naturalist*, *141*(4), 621–633. https://doi.org/10.1086/285494

Silvera, K., Neubig, K. M., Whitten, W. M., Williams, N. H., Winter, K., & Cushman, J. C. (2010). Evolution along the crassulacean acid metabolism continuum. *Functional Plant Biology*. https://doi.org/10.1071/FP10084

Smith, M., Hoover, D. L., Wilcox, K. R., Felton, A. J., & Knapp, A. (2015). Ecosystem response to multiple drought events: the role of legacy effects. *American Geophysical Union, Fall Meeting 2015, Abstract #B52C-06*. Retrieved from http://adsabs.harvard.edu/abs/2015AGUFM.B52C..06S

Stevenson, B. A., Kelly, E. F., McDonald, E. V., & Busacca, A. J. (2005). The stable carbon isotope composition of soil organic carbon and pedogenic carbonates along a bioclimatic gradient in the Palouse region, Washington State, USA. *Geoderma*, *124*(1–2), 37–47. https://doi.org/10.1016/j.geoderma.2004.03.006

Stockmann, U., Adams, M. A., Crawford, J. W., Field, D. J., Henakaarchchi, N., Jenkins, M., … Zimmermann, M. (2013). The knowns, known unknowns and unknowns of sequestration of soil organic carbon. *Ecosystems and Environment*, *164*, 80–99. Retrieved from http://www.elsevier.com/copyright%0Ahttp://dx.doi.org/10.1016/j.agee.2012.10.001

Stromberg, J. C. (1993). Frémont Cottonwood-Goodding Willow Riparian Forests : A Review of

Their Ecology , Threats , and Recovery Potential. *Journal of the Arizona-Nevada Academy of Science*, *27*(1).

Swanson, F. J., Kratz, T. K., Caine, N., & Woodmansee, R. G. (1988). Landform Effects on Ecosystem Patterns and Processes. *BioScience*, *38*(2), 92–98. https://doi.org/10.2307/1310614

Taylor, S. H., Ripley, B. S., Martin, T., De-Wet, L. A., Woodward, F. I., & Osborne, C. P. (2014). Physiological advantages of C4 grasses in the field: A comparative experiment demonstrating the importance of drought. *Global Change Biology*, *20*(6), 1992–2003. https://doi.org/10.1111/gcb.12498

Teeri, J. A., & Stowe, L. G. (1976). Climatic patterns and the distribution of C4grasses in North America. *Oecologia*, *23*(1), 1–12. Retrieved from http://www.jstor.org/stable/4215231

Tieszen, L. L., Reed, B. C., Bliss, N. B., Wylie, B. K., & DeJong, D. D. (1997). NDVI, C 3 and C 4 Production, and Distributions in Great Plains Grassland Land Cover Classes. *Ecological Applications*, *7*(1), 59. https://doi.org/10.2307/2269407

Trimble, D. E. (1980). The Geologic Story of the Great Plains. *Geological Survey Bulletin 1493*, (1493), 50.

Uno, K. T., Cerling, T. E., Harris, J. M., Kunimatsu, Y., Leakey, M. G., Nakatsukasa, M., & Nakaya, H. (2011). Late Miocene to Pliocene carbon isotope record of differential diet change among East African herbivores. *Proceedings of the National Academy of Sciences of the United States of America*, *108*(16), 6509–6514. https://doi.org/10.1073/pnas.1018435108

Uno, K. T., Polissar, P. J., Kahle, E., Feibel, C., Harmand, S., Roche, H., & DeMenocal, P. B. (2016). A Pleistocene palaeovegetation record from plant wax biomarkers from the Nachukui Formation, West Turkana, Kenya. *Philosophical Transactions of the Royal Society B: Biological Sciences*, *371*(1698), 20150235. https://doi.org/10.1098/rstb.2015.0235

USDA. (1999). Soil Taxonomy. *Geological Magazine*, *114*(6), 492. https://doi.org/10.1017/S0016756800045489

US Drought Monitor. (2017). Kansas Drought Monitor. http://drought.unl.edu

Vogel, J. C., Fuls, A., & Danin, A. (1986). Geographical and environmental distribution of C3 and C4 grasses in the Sinai,Negev, and Judean desert. *Oecologia*, *70*(2), 258 265.

von Lützow, M., & Kögel-Knabner, I. (2009). Temperature sensitivity of soil organic matter decomposition-what do we know? *Biology and Fertility of Soils*, *46*(1), 1–15. https://doi.org/10.1007/s00374-009-0413-8

Wang, C., Raymond Hunt Jr, E., Zhang, L., & Guo, H. (2013). Phenology-assisted classification of C 3 and C 4 grasses in the U.S. Great Plains and their climate dependency with MODIS time series. https://doi.org/10.1016/j.rse.2013.07.025

Wellman, C. H., & Gray, J. (2000). The Microfossil Record of Early Land Plants. *Philosophical Transactions: Biological Sciences*, *355*(1398), 717–732. Retrieved from https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1692785/pdf/10905606.pdf

Werth, M., & Kuzyakov, Y. (2010). 13C fractionation at the root-microorganisms-soil interface: A review and outlook for partitioning studies. *Soil Biology and Biochemistry*. https://doi.org/10.1016/j.soilbio.2010.04.009

Wiesenberg, G. L. B., Schwarzbauer, J., Schmidt, M. W. I., & Schwark, L. (2004). Source and turnover of organic matter in agricultural soils derived from n-alkane/n-carboxylic acid compositions and C-isotope signatures. *Organic Geochemistry*, *35*(11–12 SPEC. ISS.), 1371–1393. https://doi.org/10.1016/j.orggeochem.2004.03.009

Wynn, J. G., Bird, M. I., & Wong, V. N. L. (2005). Rayleigh distillation and the depth profile of 13C/ 12C ratios of soil organic carbon from soils of disparate texture in Iron Range National Park, Far North Queensland, Australia. *Geochimica et Cosmochimica Acta*, *69*(8), 1961–1973. https://doi.org/10.1016/j.gca.2004.09.003

Zamanian, K., Pustovoytov, K., & Kuzyakov, Y. (2016). Pedogenic carbonates: Forms and formation processes. https://doi.org/10.1016/j.earscirev.2016.03.003

Zhang, Y. G., Pagani, M., Liu, Z., Bohaty, S. M., Deconto, R., & A, P. T. R. S. (2013). A 40-million-year history of atmospheric CO 2 A 40-million-year history of atmospheric CO 2. *Philosophical Transactions of The Royal Society*. https://doi.org/10.1098/rsta.2013.0096