CONTROLS ON THE PRESENCE, CONCENTRATION, STORAGE, AND

VARIABILITY OF SOIL INORGANIC CARBON IN A SEMI-ARID WATERSHED

by

Christopher Allen Stanbery

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Christopher Allen Stanbery

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The following individuals read and discussed the thesis submitted by student Christopher Allen Stanbery, and they evaluated his presentation and response to questions during the final oral examination. They found that the student passed the final oral examination.

Jennifer Pierce, Ph.D.   Chair, Supervisory Committee

Shawn Benner, Ph.D.   Member, Supervisory Committee

Nancy Glenn, Ph.D.   Member, Supervisory Committee

Mark Seyfried, Ph.D.   Member, Supervisory Committee

The final reading approval of the thesis was granted by Jennifer Pierce, Ph.D., Chair of the Supervisory Committee. The thesis was approved by the Graduate College.

ABSTRACT

Soil inorganic carbon (SIC) constitutes approximately 40% of terrestrial soil carbon and is an integral part of the global carbon cycle; however, the controls on the storage and flux of inorganic carbon are poorly understood. Soil forming factors controlling SIC storage and flux include climate, organisms, relief, parent material, and time (Jenny, 1941). Rainfall is a primary factor controlling SIC accumulation in arid and semi-arid regions, but the hierarchy of controls on SIC development is complex. The Reynolds Creek Experimental Watershed in southwestern Idaho is an ideal location to study factors influencing SIC, as the carbon pool transitions from predominately inorganic carbon in the lower elevations, to organic carbon at higher elevations. This study builds upon fundamental studies in soil science that define and describe precipitation controls on the 'pedocal' (calcic) to 'pedalfer' (non-calcic) soil transition (e.g. Marbut, 1935; Jenny, 1941) by both defining the precipitation boundary in Reynolds Creek, and quantifying the amount of carbon storage within calcic soils.

We collected soil samples from soils developed under a wide range of soil-forming regimes: 1) along a precipitation gradient, 2) within different vegetation communities (sagebrush species (*Artimesia spp)*, bitterbrush (*Purshia tridentata),* greasewood (*Sarcobatus vermiculatus),* and juniper (*Juniperus occidentalis)*) 3) from different parent materials (granite, basalt, other volcanics, and alluvium) and 4) from terrace surfaces of different ages. Our results show SIC does not accumulate above a threshold of ~500 mm mean annual precipitation, and variability in SIC below that value

is significant. Soil inorganic carbon content from ~1 m deep soil pits and cores at 71 sites shows that 64 sites contained less than 10 kg/m^2 SIC, 5 sites contained between 10-20 kg/m^2, and 2 sites had between 24 and 29 kg/m^2. Random forest modeling and multiple linear regression of the environmental controls on SIC indicate that precipitation is the primary control on SIC accumulation, where increased precipitation correlates with lower amounts of SIC. Elevation is an effective predictor of SIC, as it is strongly auto-correlated with precipitation and vegetation. Parent material consistently ranks as an important predictor in random forest analysis; however, we were unable to quantify the importance of wind-blown dust in the soil profiles, which we believe plays a vital role in SIC accumulation.

Despite a recognition of different stages of carbonate development and accumulation rates between gravelly and non-gravelly soils, studies often ignore carbonate coatings on gravels in measurements of soil inorganic carbon (SIC). By quantifying and differentiating the fine (<2 mm) and coarse (>2 mm) fractions of SIC in the Reynolds Creek Experimental Watershed in southwestern Idaho, we show that gravel coatings contain up to 44% of total SIC at a given site. Among the 26 soil sites examined throughout the watershed, an average of 13% of the total SIC is stored as carbonate coasts within in the gravel fraction. We measured a high level of pedon-scale field variability (up to 220%) among the three faces of 1 m^3 soil pits. Analytical error associated with the modified pressure calcimeter (0.001-0.014%), is considerably less than naturally occurring heterogeneities in SIC within the soil profile. This work highlights and quantifies two sources of uncertainty in studies of SIC needed to inform future research. First, in gravelly sites, the >2 mm portion of soils may store a large

percentage of SIC. Second, SIC varies considerably at the pedon-scale, so studies

attempting to quantify carbon storage over landscape scales need to consider this

variability. This study creates a framework for understanding SIC in Reynolds Creek that

may be applied to future work.

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CHAPTER ONE: QUANTIFYING STORAGE OF INORGANIC SOIL CARBON ON

GRAVELS AND DETERMINING PEDON-SCALE VARIABILITY

1. Introduction

Soil is the third largest global pool of carbon; as such, data on soil carbon storage

and its fluxes are essential components for global climate models. Although most

research on soil carbon has focused on soil organic carbon, soil inorganic carbon (SIC)

constitutes approximately 40% of soil carbon globally and in semi-arid and arid regions

is the dominant form of carbon storage (Batjes, 1996; Eswaran et al., 2000).

Soils have very heterogeneous properties, but little work has quantified the range

of variation in SIC accumulation. Frequently, studies measuring SIC concentrations

derive their results from single measurements at a single soil site (Batjes, 1996;

Rasmussen, 2006; Hirmas et al., 2010). Soil properties are highly variable even at the

pedon-scale and we hypothesize that this heterogeneity extends to SIC accumulation

within RCEW. Taking a single profile as representative of a location can lead to

considerable under- or overestimation of SIC amounts.

The precipitation of pedogenic carbonate minerals stores SIC within the soil. As

SIC accumulates within the soil, there are differences in both the rates and characteristics

of development between SIC forming around fine soil particles (<2 mm) and gravel clasts

(>2 mm) (e.g. Gile et al., 1966; Machette, 1985; Treadwell-Steitz and McFadden, 2000).

However, many previous studies measuring the SIC pool have removed the gravel

fraction before SIC analysis (e.g. Sobecki and Wilding, 1983; Slate et al., 1991; Vincent

et al., 1994; Treadwell-Steitz and McFadden, 2000; Rasmussen, 2006; Kunkel et al., 2011; Ramnarine et al., 2012; Washbourne et al., 2012; Austreng, 2012), Other studies (e.g. Schlesinger, 1985; Reheis et al., 1992; Grinand et al., 2012) have included gravels, but have processed the soil and gravels together. When studies of SIC do not analyze the gravel fraction, they are either underestimating SIC significantly or are not fully exploring its complexities. Quantifying carbonate storage on gravels is difficult and time-consuming; we hope this work will provide a framework to help calibrate soil carbonate studies that do not include the gravel fraction with studies that do include gravels.

Our study expands the understanding of SIC storage through examination of both the carbonate coats on gravel clasts and pedon-scale variability in SIC. We extensively sampled soil pits throughout the Reynolds Creek Experimental Watershed (RCEW) in southwestern Idaho (Figure 1.1) to collect data on soils with a wide range of gravel contents. We sampled multiple profiles at several of our study sites to quantify the pedon-scale variability present throughout the watershed. By processing replicates of both field samples and known standards, we determined the precision of our methods and the natural heterogeneity present in soils. We hypothesized that the gravel SIC coatings would constitute a significant portion of the total inorganic carbon pool in the soils, and that the differences in concentration within a pit would be significant as well. The results of this work will highlight the importance of the gravel SIC fraction and quantify the range of variation for soils in the RCEW.
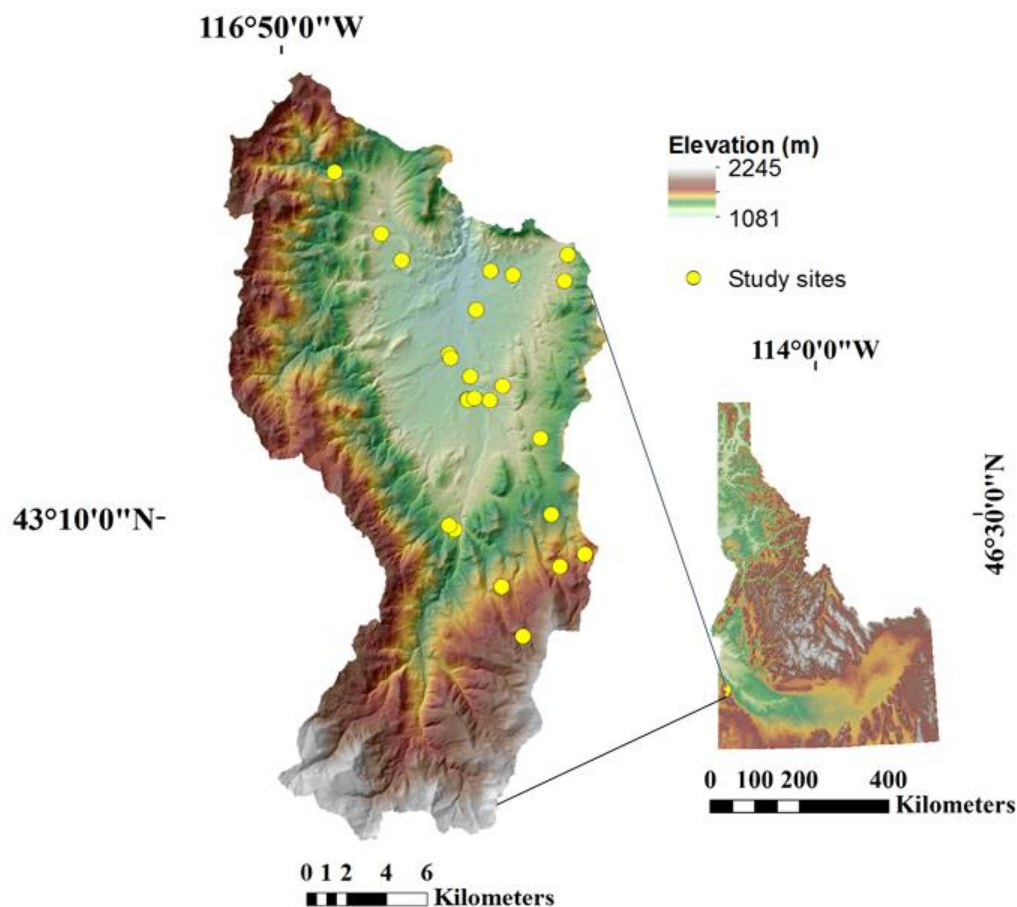
Figure 1.1 The Reynolds Creek Experimental watershed (RCEW) in southwestern Idaho. Soil sample sites used for analysis of gravel SIC are marked in yellow.

1.1. Background:

1.1.1. Inorganic carbon formation:

The precipitation of secondary carbonate minerals ($CaCO_3$ and $MgCO_3$) stores soil inorganic carbon within calcic soils. These minerals are commonly found in arid and semi-arid soils, where evaporative processes concentrate the dissolved species (Ca^{2+}, Mg^{2+}, and carbonate (CO_3^{2-}) ions) within the soil pore water, promoting precipitation of carbonate minerals (Birkeland, 1999). Although the amount of dissolved CO_2 is one of

the largest controls on SIC precipitation (McFadden et al., 1998; McFadden, 2013; Zamanian et al., 2016), adequate amounts of water can ultimately prevent carbonate from forming (Jenny, 1941; Arkley, 1963; Birkeland, 1999). When precipitation is sufficiently high and soil water evaporation is limited, infiltrating water flushes the ionic components of carbonate formation from the profile. A high pH (above ~8.2) goes hand-in-hand with the presence of calcic soil horizons and the formation of carbonates (Birkeland, 1999). The relatively low pH of rainwater, as well as mineral and organic acids forming in soils may inhibit the precipitation of these minerals. The presence of carbonate-bearing parent material (e.g. limestone or marble) will dramatically increase the potential of forming secondary calcic horizons within the associated soils.

As calcic soils accumulate carbonate over time, they go through a series of stages of development that are dependent upon the gravel content of the soil (Figure 1.2). Importantly for this study, carbonate accumulates differently in gravelly vs. non-gravelly soils. In gravelly soils, carbonates precipitate preferentially on the bottoms of clasts as surface tension holds the water to clasts and allows it to evaporate from the underside (Gile et al., 1966). Soil progresses through the initial four stages as carbonate covers soil particles (stages I-II) and then interstitial pore space is filled (stages III-IV). Studies from the southwestern US show gravelly soils reach stage IV more quickly than non-gravelly soils (Gile et al., 1966). Since the carbonate coatings preferentially form on clasts, studies of gravelly soils with stage I-II development are disproportionally affected by the exclusion of >2 mm material. As carbonate precipitates over a greater portion of the soil material and fills pore space, the relative importance of gravel SIC diminishes slightly.
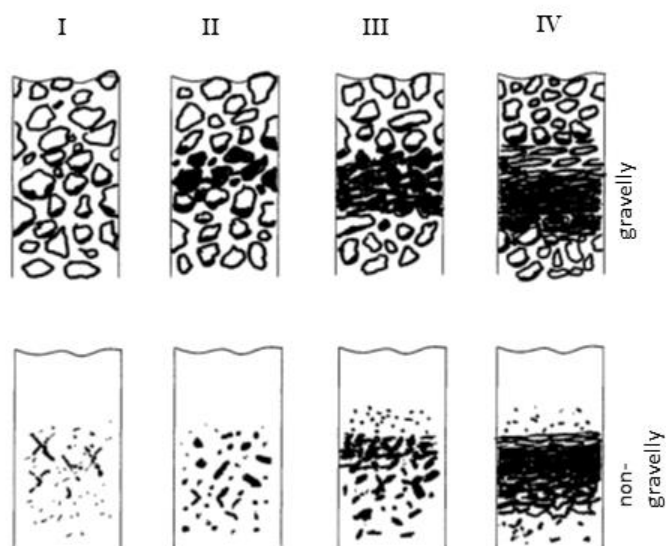
Figure 1.2 Conceptual sketch of the diagnostic morphology of the stages of carbonate development in gravelly and non-gravelly parent materials (modified from Gile et al., 1966). This sketch highlights the differences in SIC accumulation between gravelly and non-gravelly soils. The highest level of carbonate development from this study was stage III.

1.1.2. Gravel SIC in previous studies:

In a survey of 4353 soil profiles from the World Inventory of Soil Emission Potentials (WISE) database, Batjes (1996) found that 79% of the profiles had no data on soil gravel at all. Although previous studies measure the SIC content of the combined fine and gravel fractions (Schlesinger, 1985; Reheis et al., 1992; Grinand et al., 2012) and do ultimately account for the amount of carbonate stored on gravels, other studies that do not measure the gravel SIC concentration (Sobecki and Wilding, 1983; Slate et al., 1991; Vincent et al., 1994; Treadwell-Steitz and McFadden, 2000; Rasmussen, 2006; Kunkel et al., 2011; Ramnarine et al., 2012; Washbourne et al., 2012; Austreng, 2012) may be under-estimating soil carbonate storage. One study (Hirmas et al., 2010) measured both the fine and gravel SIC fractions and combined the measurements into a single value with

no separate examination of the different pools. Other studies do not specify their methods used to process and quantify SIC on gravel (Drees and Nordt, 2001). A number of studies have addressed the amount of SIC on gravels through other methods. Vincent et al. (1994) measured clast coatings to develop a soil chronosequence. Treadwell-Steitz and McFadden (2000) measured the thickness of coatings to understand the relationship between clast size, parent material, and the amount of carbonate present. Pustovoytov (2003) used similar methods to measure growth rates of carbonate coatings. Reheis et al. (1992) used a method of visual inspection to determine the approximate amount of carbonate present in samples with limestone parent material. Our study uses a quantitative method of measuring SIC on gravel clasts to determine its importance in carbon storage in semi-arid soils.

1.2. Study Area:

1.2.1. Site description:

The Reynolds Creek Experimental Watershed has an area of 238 km^2 and is located approximately 60 km southwest of Boise, Idaho in the Owyhee Mountain range (Figure 1.1). Elevations range from ~1100 m to 2245 m, and precipitation closely follows the elevation gradient, with the driest location receiving ~240 mm annually and the higher elevations receiving over 1170 mm annually (Hanson, 2001). State and federal government owns ~75% of the land in the watershed, with the remainder privately owned and utilized primarily for cattle grazing.

2. Methods:

<u>2.1. Field methods:</u>

At each of the 26 sites, we excavated a pit to a depth of ~1 m or refusal due to bedrock. The sites were excavated by hand, but at three Agricultural Research Station study locations (sites 10, 11, and 14) we excavated to depths of ~ 2 m using a backhoe. We collected field observations of soil structure, color, gravel content, root density, and horizon characteristics following protocol outlined in Birkeland et al., (1991). A solution of 10% hydrochloric acid (HCl) was used to qualitatively measure the concentration of SIC present based on the strength of reaction along the soil profile. To determine color and field textures of the <2 mm fraction, we collected small samples at each horizon.

In compliance with the Reynolds Creek Critical Zone Observatory soil sampling protocol (McCorkle, 2015), we collected samples at depth increments of 0-5 cm, 5-10 cm, 10-20 cm and every 10 cm to the bottom of the pit on the center pit face. Although we recognize that sampling based on horizon boundaries could better reflect SIC accumulation processes, this protocol is designed to ensure uniformity among a variety of studies. We removed a volume of approximately 0.2 m^3 for each sample and collected all rock present within this volume. In cases where a particularly large clast extended beyond our collected volume, we left the clast in the profile. Additional profiles were collected from different pit faces at 12 of the sites in order to assess pit-scale variability.

<u>2.2. Lab methods:</u>

The collected samples were first dried overnight at room temperature, then sieved to separate the gravel fraction (>2 mm) and the roots. The <2 mm fraction of soil was split into portions of 40-100 g for inorganic carbon analysis and the remainder was

archived. For replicate analysis, we split four sub-samples from every sample collected at

site #23 and archived the remainder of the sample. We further separated the gravel

fraction using an 8 mm sieve. The largest material not passing the 8 mm sieve was

crushed using a sledge and sledge plate, and the smaller pieces were crushed using a

small rock crusher until all material could pass through the 8 mm sieve. We recombined

the material with the smaller gravel fraction and split out a ~25 g sub-sample. The split

inorganic carbon samples were dried in an oven at 105 ^{o}C overnight to remove moisture.

2.2.1. Inorganic carbon content:

The inorganic carbon samples were powdered using a SPEX SamplePrep 8000M

mill. We weighed 1.00g of each sample (or 0.50g for samples with estimated inorganic

carbon content greater than 1.8%) into 20mL glass bottles and stored in a desiccator. We

added 2mL of a 6M HCl solution with 3% $FeCl_2$ by weight to a 0.5-dram vial which was

placed into each bottle. We capped the bottles with a rubber stopper and aluminum cap

that was crimped closed. Each bottle was agitated by hand to ensure the acid reacted with

the entire sample and left to sit for approximately 10 hours (Sherrod et al., 2002).

A modified pressure calcimeter (Sherrod et al., 2002) measured air pressure as a

voltage that was converted to a percent carbonate through a calibration curve. We created

the curve using known standards with carbonate ($CaCO_3$) contents of 0.14%, 0.24%,

0.6%, 1.2%, 1.8%, 3.6%, 6.0%, 12.0%, and 18.0%. Using the same acid solution, we

converted the standards from a measured voltage to percent carbonate. Along with the

standards, several vials containing no samples were run to ensure consistent readings

throughout the process, and establish the zero concentration point. We measured the

ambient air pressure and subtracted it from the pressure inside the bottle. We measured

the interior pressure by piercing the top of the rubber stopper with a syringe connected by tubing to the transducer sensor. We converted the calculated carbonate value to a percent inorganic carbon by multiplying the percent mass of carbon in carbonate (Eq. 1). A concentration was calculated using the % mass of inorganic carbon (Eq. 2).

$$\%CaCO_3 \times \frac{mass_C}{mass_{CaCO_3}} = \%SIC \tag{1}$$

$$\%SIC \times \rho \times b \times \frac{mass\ of\ fraction\ of\ interest}{total\ mass\ of\ sample} = concentration\ of\ SIC\ (\frac{kg}{m^2}) \tag{2}$$

SIC = soil inorganic carbon

ρ = bulk density (kg/m^3)

b = thickness of profile section (m)

C = concentration (kg/m^2)

2.3. Uncertainty analysis:

We collected samples from 3 different pit faces at 12 of the sites; in addition, we ran replicates of 13 standards and every sample collected for site #23 (Table 1.1). For site #23, we split four sub-samples from every collected sample and processed them separately. The standard replicates confirmed the accuracy of our standards and allowed us to assess the precision of the calcimeter. By determining the uncertainty introduced by our methods, we were then able to measure the soil's natural variability in SIC at the pedon-scale.

3. Results:

3.1. Soil inorganic carbon storage within the gravel fraction of soils:

Within the watershed, there is a general trend of increasing soil inorganic carbon (SIC) storage on gravels as the total SIC content decreases (Figure 1.3). Although the fine fraction of soils is the largest pool of SIC (~87%), gravel clast coatings represent an

average of 13% of the total inorganic carbon for the 26 sites in this study (Table 1.1).

Gravel-poor study sites inherently have less SIC storage on gravels.

Plot: x-axis "Total SIC in profile (kg/m2)" ranging 0 to 30; y-axis "Proportion of profile's SIC on gravel" ranging 0 to 0.5.

$$y = -0.0026x + 0.1311$$
$$R^2 = 0.0244$$
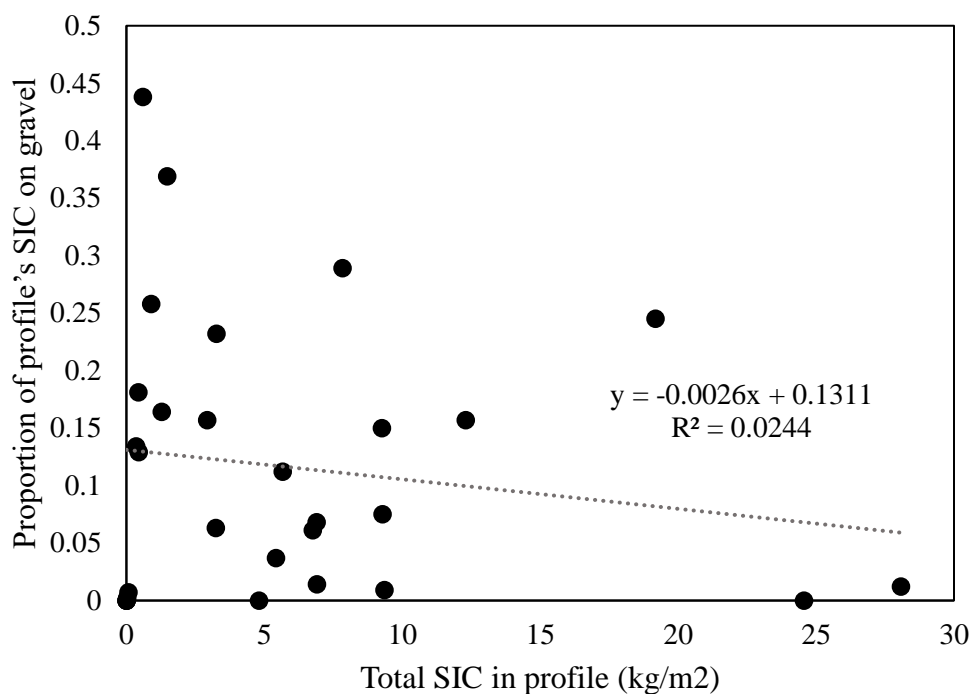
Figure 1.3 As the total amount of SIC in a soil profile decreases, the gravels within the profile store proportionally more SIC. This trend highlights the importance of measuring SIC on gravel coats in stage I to stage II soils.

Site #13 is one of the highest elevation sites studied, receives 370 mm of precipitation annually, and has a welded tuff parent material. Although the SIC concentration is relatively low, this site has the highest amount of SIC in the coarse fraction with an average of 44% of the total soil SIC stored on the exterior of gravels (Table 1.1, Figure 1.4). The presence of gravels and a high clay content from the weathering of the tuff characterize this site. We observed that the exterior of clay peds have patchy coatings of SIC, but when broken apart had no visible accumulations of SIC on the interior of the peds.
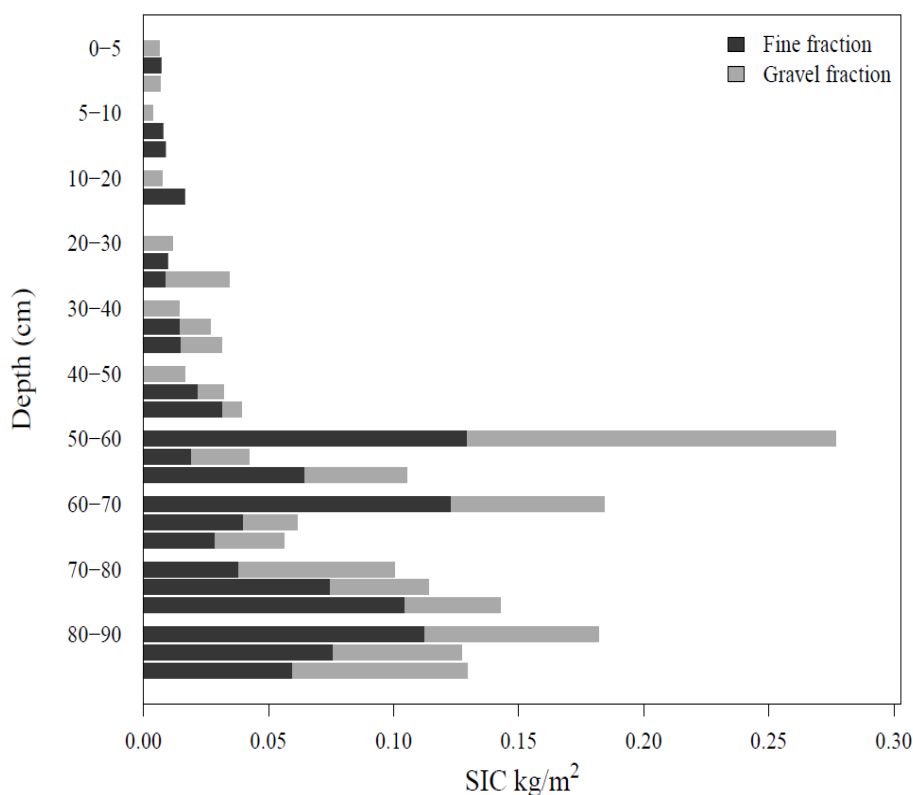
Figure 1.4 Depth profile from site # 13 showing a large portion of total SIC stored as carbonate coats on gravels. Approximately 44% of the total SIC at this site is stored as coatings. Each of the three bars at a depth show the values for a sampled profile within the soil pit.

3.2. Analysis of variability:

Initial lab analysis of site samples showed that there were large variations in SIC values for a given depth between the different soil profiles (Figure 1.5). To determine whether these differences were due to natural variability at the pedon-scale or uncertainty associated with analytical methods, we ran replicates of site #23 samples and of several standards. As seen in Figure 1.5, SIC values may be similar between two of the three pit faces, but it is rare to find comparable SIC values among all three pit faces. Additionally, we calculated the coefficient of variation (CV) for both the fine-grained and gravel samples to describe the variation in measurements relative to the mean (Figure 1.6). The

two fractions have similar median values of CV (0.41 for fines and 0.54 for gravels), but

the gravels have a wider range of values.
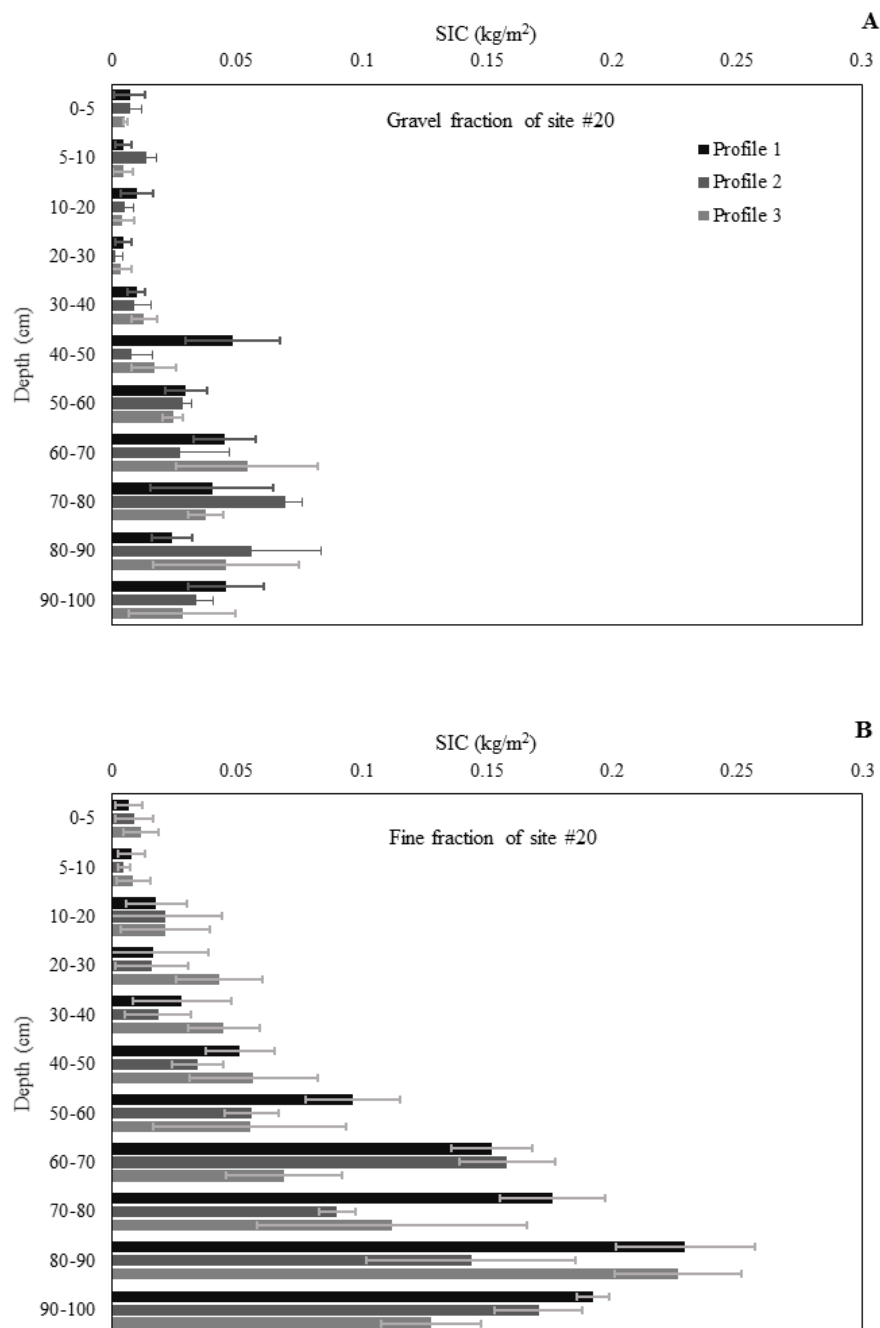
Figure 1.5 Analysis of lab uncertainty for the measurements of both the gravel (A) and fine (B) fractions at site #23. We collected the three profiles from three walls within the same soil pit. The bars at each depth show the values for mean SIC along with their standard deviations as determined from the four measured replicates.

There is considerable uncertainty in both fractions, but the relative uncertainty in the gravel fraction is larger.
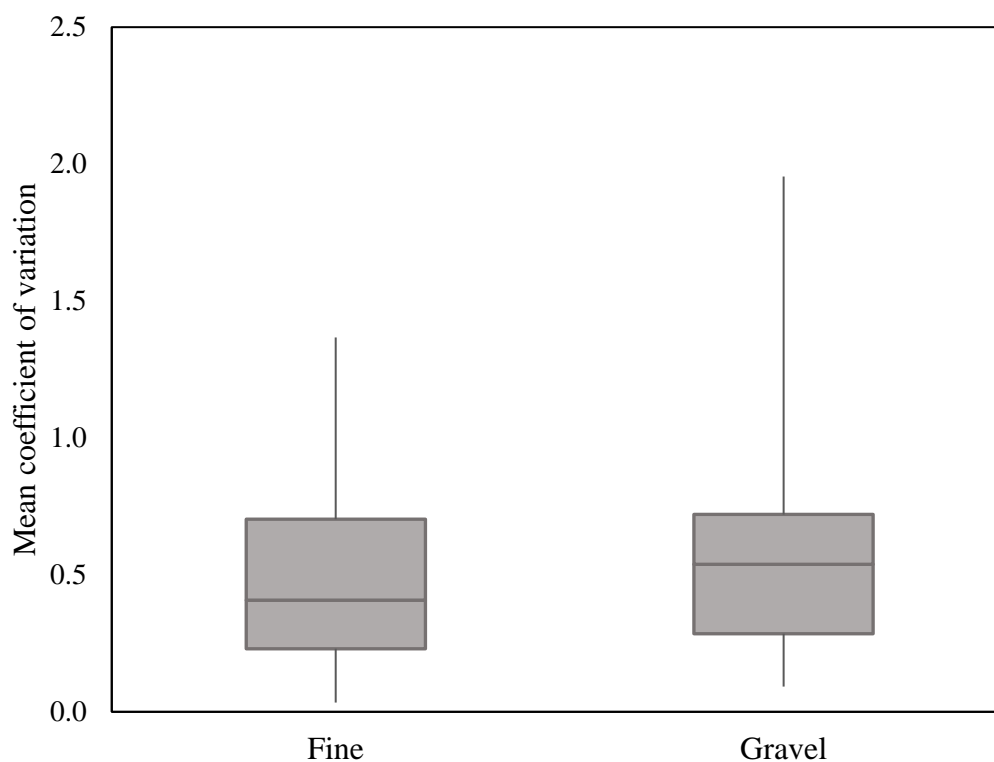
Figure 1.6 Comparison of coefficient of variation (CV) between the measured SIC from fine-grained samples and gravel samples. CV describes the variation in the samples relative to the mean value. The CV is similar between the two fractions, but shows a great deal of variance overall with the widest range found in the gravel fraction.

Replicates of standards showed the instrument introduced little uncertainty in the measured SIC values (Figure 1.7). Measurements of the standards were consistent down to values of 0.016 % SIC. For standards below 0.1% SIC, the average standard deviation is 0.003%. Above 0.1%, the average standard deviation is 0.006%. When we compared both the absolute and relative magnitude of these standard uncertainties to lab measurements of the field samples, we found the uncertainties are negligible relative to

the field variability (Figure 1.5). We assume that naturally occurring heterogeneities in

the soil profile create the large majority of variation in the results.
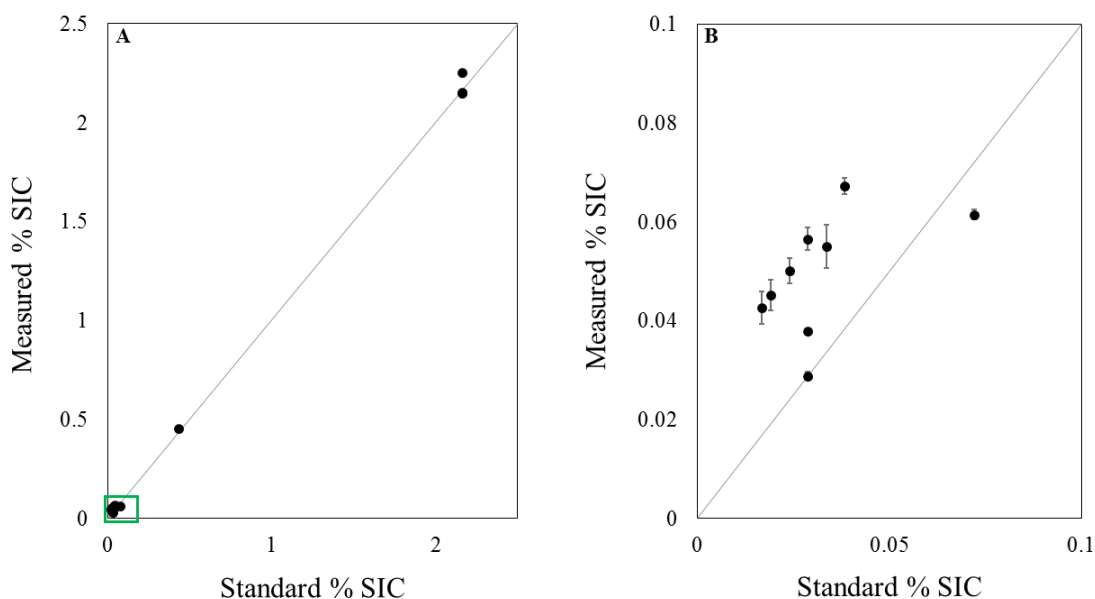
Figure 1.7 Results of known standard replicate analysis with each standard having at least five replicates. A) The image shows the full range of analysis with error bars for each standard. Due to the relatively small amount of error, however, the bars are not visible. B) The image shows the same data for the low concentration samples. As can be seen in both figures, the uncertainty in the measurements was relatively small and the results were highly reproducible.

Table 1.1: Summary of results of analysis.

Site ID	Easting* (m)	Northing (m)	Elevation (m)	Total SIC (kg/m²)	Gravel proportion by mass	Proportion of SIC on gravel by mass	Gravel SIC (kg/m²)
30	520369	4784469	1147	3.24	0.101	0.063	0.20
11	521097	4788320	1148	6.76	0.081	0.061	0.41
5	520581	4786904	1166	0.35	0.100	0.134	0.05
29	519653	4785144	1168	24.56	0.000	0.000	0.00
28	519587	4785291	1171	9.29	0.322	0.075	0.70
6	520583	4786227	1178	0.08	0.044	0.007	0.00
10	521920	4788163	1178	9.35	0.055	0.009	0.08
31	520522	4783679	1193	5.42	0.204	0.037	0.20
38	517874	4788707	1194	6.91	0.112	0.014	0.10
24	520258	4783645	1204	28.08	0.111	0.012	0.34
25	520280	4783627	1207	9.26	0.280	0.150	1.39
22	521311	4783134	1223	4.81	0.000	0.000	0.00
2	521543	4784127	1233	2.93	0.360	0.157	0.46

Site ID	Easting* (m)	Northing (m)	Elevation (m)	Total SIC (kg/m²)	Gravel proportion by mass	Proportion of SIC on gravel by mass	Gravel SIC (kg/m²)
3	521075	4783608	1235	19.18	0.292	0.245	4.70
1	517124	4789664	1247	6.89	0.389	0.068	0.47
20	523913	4788905	1288	5.67	0.168	0.112	0.64
19	523801	4787956	1302	0.44	0.284	0.129	0.06

17	519594	4779068	1310	0.89	0.264	0.258	0.23
16	519792	4778913	1329	1.48	0.320	0.369	0.55
23	522924	4782230	1345	1.28	0.347	0.164	0.21
8	515436	4791916	1375	3.26	0.216	0.232	0.76
18	523312	4779456	1433	7.84	0.253	0.289	2.27
7	524529	4778012	1583	0.43	0.302	0.181	0.08
13	521506	4776829	1626	0.60	0.509	0.438	0.26
4	523628	4777568	1631	12.30	0.403	0.157	1.93
9	522286	4775021	1813	0.03	0.401	0.002	0.00

[1] UTM zone 11

4. Discussion:

<u>4.1. Gravel inorganic carbon:</u>

Our analysis of soil inorganic carbon (SIC) stored in gravel coats has implications for global estimates of soil carbon storage. Although several studies have quantified SIC, their measurements are likely underestimations due to the exclusion of gravels from chemical analysis (Sobecki and Wilding, 1983; Slate et al., 1991; Rasmussen, 2006; Kunkel et al., 2011; Washbourne et al., 2012, Austreng, 2012). In a meta-analysis of collected carbon data, Batjes (1996) found that in the top meter of soil there is 695-748 Pg of carbon in carbonate minerals globally. In Reynolds Creek, approximately 13% of SIC is stored on gravels. Making the (admittedly large) assumption that this amount of SIC storage on gravels is representative of soils globally, approximately 90-97 Pg of carbon could be unaccounted for in these surveys.

Obtaining data on the amount of inorganic carbon stored on gravels is resource intensive, and can be prohibitive depending on the goals of a given study. It is possible to process a few sites in order to establish a relationship between the proportion of gravel and amount of SIC, but the greater the range of soil conditions in a study location, the less feasible this approach. In non-gravelly soils, this concern is obviously not an issue. However, in gravelly soils, inorganic carbon accumulates preferentially on clasts. Following the stages of carbonate development (Gile et al., 1966; Machette, 1985), this carbon accumulates first on the undersides of clasts as surface tension holds water to the bottom. This water evaporates promoting the precipitation of carbonate minerals. As carbonate accumulates on the clasts and the surrounding finer material, it then begins to fill pore space and cover the remainder of the clasts. For gravelly soils with low amounts

of SIC (stage I-II+), only quantifying the <2 mm fraction of carbonate would ignore a large portion of carbon stored in the soil profile.

Estimating SIC storage in areas characterized by the dissolution and re-precipitation of carbonate from lithogenic sources is problematic for estimates of carbon storage in soils vs. rock (Reheis et al., 1992; Ryskov et al., 2008). It is difficult to distinguish the pedogenic and lithogenic pools, but it is possible through isotopic analysis (Ryskov et al., 2008).

4.2. Pedon-scale variability:

In our initial observations, we noted a large degree of variability between the three different profiles within a pit. Replicates of known standards show that our methods introduced little uncertainty for both lower and higher concentration standards (Figure 1.7). The field data also show that there is considerable variability in both the fine and gravel fractions of SIC, making it difficult to distinguish the three profiles from each other. We compared the coefficients of variation (CV) between the fine-grained and gravel SIC fractions (Figure 1.6). While the two fractions have similar median values, the variance in gravel is greater. This greater variance is likely due to the patchy nature of the SIC gravel coatings, compared with more diffuse and uniform distribution of SIC in the soil matrix. These factors, combined with the relatively low total concentration of carbon, likely lead to the larger variation in the gravel samples. We are confident that the variability seen in our measurements of SIC results from natural heterogeneities in soil properties that influence accumulation of pedogenic carbonates.

The low amount of analytical uncertainty confirms that the initial observations of significant pedon-scale variability are naturally occurring. Site #10, for example, has SIC

concentrations of 5.8, 9.14, and 13 kg/m^2 for its three profiles. Therefore, a single measured profile could vary by as much as 7.2 kg/ m^2 of SIC depending on the location sampled. We considered that different amounts of large clasts between profiles at site #10 could be responsible for this variability. However, both site #10 and nearby site #11 have similarly low gravel contents (<1%) whereas site #2 has, in contrast, some of the lowest variability in the watershed with the 3 profiles containing 6.56, 6.76, and 6.96 kg/m^2 of carbon. The soil at site #4 is 40% gravel by mass and has a relatively narrow range of SIC values as well (11.3, 12.3, and 13.2 kg/m^2). Therefore, the amount of gravel within a given site does not correspond with intra-site variability.

Variation in a soil's hydrologic properties likely create these heterogeneities in SIC concentrations. Patchy ground cover, macropores and respiration from roots, differences in dust accumulation, amount and size of gravel, and depth to bedrock can all influence SIC accumulation (Jenny, 1941). The diversity of soil conditions within a given study area determines the degree to which this natural variability should be examined. The RCEW is a relatively varied location with a range of parent materials, climates, relief, and soil. Similarly, studies over relatively large and/or diverse regions will need to examine the range of heterogeneity by collecting enough data to represent the different environments. Smaller scale studies with homogenous conditions may only require sampling a few soil sites to quantify variability.

5. Conclusions:

This work contributes to the field of soil science by 1) examining variability in soil carbonate storage at the pedon-scale, 2) quantifying analytical and measurement error in soil carbonate measurements, and 3) defining the amount of carbonate stored in

gravelly vs. non-gravelly soils. Our sample replication and quantification of variability shows that while analytical and measurement error is low, considerable variation exists at the pedon-scale. Our results show that drawing conclusions from a single measurement at a site can lead to considerable over- or underestimation of carbon at a location. Carbonate coatings on gravel comprise a significant portion of total soil inorganic carbon in the Reynolds Creek Experimental Watershed. Carbonate coats on clasts account for an average of 13% of SIC storage in the RCEW study area; some sites contained >40% of the total SIC as coats on gravels.

Future studies providing measurements of SIC storage will need to account for gravel carbonate coatings and address the inherent soil variability. However, the resources required to process and measure SIC on gravels can be prohibitive. The results of this study, along with other future work, can be used to establish relationships between gravel percentages and the portion of SIC stored on gravels. Future examination of the amount and controls on variability of SIC accumulation at the pedon-scale would provide better insight as to how this information should be integrated in other studies.

CHAPTER TWO: CONTROLS ON THE PRESENCE AND CONCENTRATION OF

SOIL INORGANIC CARBON IN A SEMI-ARID WATERSHED

1. Introduction:

Soil is the world's third largest reservoir of carbon (Lal, 2004). Arid and semi-arid soils store approximately 40% of soil carbon in inorganic minerals (Batjes, 1996; Eswaran, 2000). This pedogenic inorganic carbon pool is comprised of carbonate minerals, predominately calcium carbonate, which precipitate from the soil solution as it evaporates (Dixon et al., 1989). Sufficiently large amounts of rainfall can prevent the formation of soil inorganic carbon (SIC) entirely, but the hierarchy of soil development controls within areas of SIC accumulation is complex (Jenny, 1941). The need to quantify the storage and flux of this carbon pool is becoming more apparent as climate continues to change. Between 1750 and 2011, atmospheric concentrations of carbon dioxide (CO_2) increased 40% globally (Ciais, 2013). Climate projections show that soils in xeric climates such as the Reynolds Creek Experimental Watershed (RCEW) in southwestern Idaho (Figure 2.1) will be more heavily impacted by the changing climate (Settele, 2014); however, the magnitude and even the direction of soil carbon flux are highly variable and frequently unknown (Ciais, 2013). Many studies have examined the *organic* soil carbon pool and its fluxes; however, less work has been devoted to understanding the *inorganic* portion of the stored soil carbon. Total global SIC reservoirs contain from 695 Pg (Batjes, 1996) to 1,738 Pg (Eswaran et al., 1995) of carbon. With estimations of total soil carbon, both organic and inorganic, equaling almost 2,500 Pg of

carbon (Batjes, 1996), better quantification of the amount of soil carbon storage is increasingly important for global climate studies.
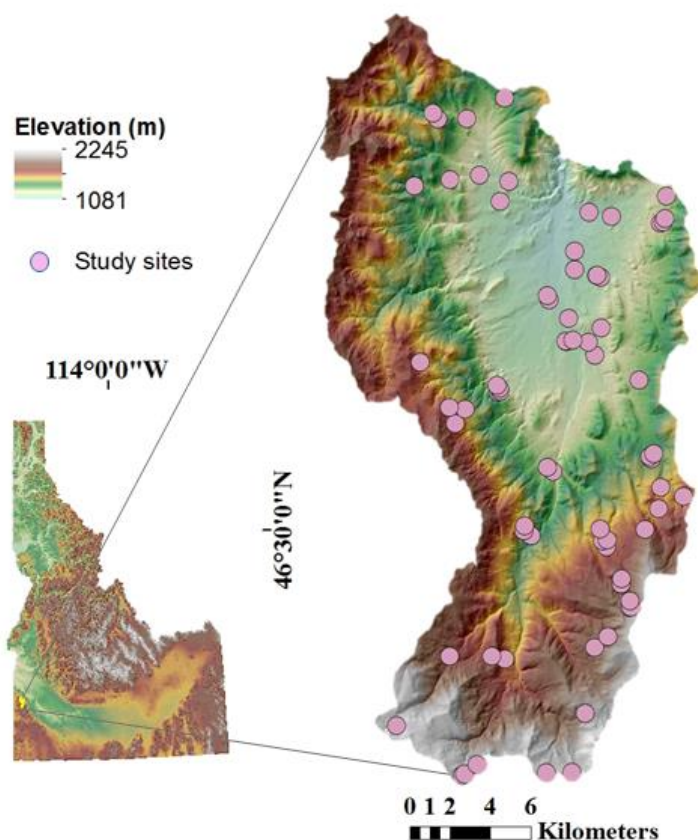
Figure 2.1 Reynolds Creek Experimental Watershed is located in southwestern Idaho.

This study defines the boundaries and hierarchies of controls on SIC accumulation within a sage-steppe dominated experimental watershed. Intensive field-based measurements of soil characteristics show the threshold of SIC accumulation in Reynolds Creek is at ~500 mm of precipitation. Within this zone of SIC accumulation (< 500 mm of precipitation), the parent material of the soil is the next most important predictor of SIC concentration. The threshold of SIC accumulation at 500 mm precipitation matches prior studies in the western USA (Malde, 1955; Birkeland et al.,

1996; Royer, 1999; Retallack, 2005; Zamanian et al., 2016) which show the boundary of carbonate bearing soils and carbonate leached soils (pedocals and pedalfers respectively) ranges from 460-650 mm of precipitation.

1.1. Background:

1.1.1. Inorganic carbon formation:

Calcic soils store SIC through precipitation of secondary carbonate minerals ($CaCO_3$ and $MgCO_3$). Evaporative processes are significant drivers in the formation of these carbonate minerals in arid and semi-arid soils as dissolved species (Ca^{2+}, Mg^{2+}, and carbonate (CO_3^{2-}) ions) are concentrated within the soil pore water (Birkeland, 1999). However, previous work by Dixon et al. (1989) established that there is considerably less $MgCO_3$ than $CaCO_3$ in pedogenic carbonates so we assume that the concentration of $MgCO_3$ is negligible in our analyses. The dissolved CO_2 concentration is one of the largest controls on SIC precipitation (Mayer et al., 1988; McFadden et al., 1998; Retallack, 2005; McFadden, 2013; Zamanian et al., 2016), but sufficiently high amounts of water prevents the formation of carbonate minerals entirely (Jenny, 1941; Malde, 1955; Arkley, 1963; Birkeland, 1999; Royer, 1999; Retallack, 2005). High precipitation and low evapotranspiration flush the dissolved ions (Ca^{+2}, Mg^{+2}) from the soil profile with infiltrating water. Pedogenic carbonate formation is highly correlated with a soil pH greater than 8.0 (Birkeland, 1999). Naturally occurring acids within the soil and low pH rainwater hinder the formation of SIC. Limestones and other carbonate-rich parent materials, in contrast, will obviously promote the formation of secondary calcic deposits with a soil due to the dissolution and re-precipitation of carbonate minerals.

Researchers Gile et al. (1966) and Machette (1985) sought to better understand the development of SIC in arid soils. They found that the carbonate minerals have distinct levels of development and that these characteristics, along with the amount of accumulated SIC, are dependent on the age of the soil and the input of Ca^{2+} ions (Gile et al., 1966; Machette, 1985). The stages of carbonate development (Gile et al., 1966; Machette, 1985) provide widely-used indicators of soil development and soil age in semi-arid and arid environments. Prior to advances in radiometric dating techniques, stages of carbonate development were a field indicator used for chronosequences and dating of geomorphic surfaces (e.g. Pierce and Scott, 1982; Reheis et al., 1992; Vincent et al., 1994; Birkeland et al., 1996). Gravelly soils and non-gravelly soils accumulate SIC differently, since carbonate precipitates and accumulates on the bottom of gravel clasts preferentially (e.g. Gile et al., 1966; Machette, 1985).

Researchers have presented a number of different models of carbonate formation: *per descensum, per ascensum, in situ,* and biogenic (Monger, 2002). *Per ascensum* describes the formation of SIC through the capillary rise of moisture from the water table upward through the soil profile. SIC precipitates as the soil solution evaporates with the greatest accumulations occurring in the upper parts of the profile (Sobecki, 1983; Monger, 2002). For this model of formation to work, the groundwater must be sufficiently close to the surface and contain high concentrations of Ca^{2+}. Additionally, there must be a texture regime that can support this movement of moisture (Machette, 1985). We do not consider *per ascensum, in situ,* and biogenic models to be the dominant processes of SIC accumulation in the RCEW though it is likely they play a small role in

carbonate formation. *Per ascensum* conditions occur in a small portion of the watershed where there are near-surface springs.

In situ formation involves the weathering and re-precipitation of calcareous parent material (Rabenhorst, 1986; Monger, 2002). This model most often involves *in situ* weathering of marine carbonates. It can also involve rocks with high concentrations of other calcium rich minerals such as plagioclase. No limestones or dolostones are present in RCEW. Although there are basaltic rocks in the watershed with higher concentrations of calcium rich minerals (McIntyre, 1972), the concentrations are unlikely to be high enough to explain all of the SIC present. Additionally, these rocks weather more slowly in arid conditions due to lower amounts of moisture (Machette, 1985; Birkeland, 1999). Biogenic formation of SIC occurs through the processes of microscopic organisms. SIC accumulates as organisms create mucilaginous sheaths composed of carbonates, which amass in the profile after the organisms' death (Monger et al., 1991). We assumed that this process accounts for a negligible portion of SIC in our study area.

The *per descensum* model is the most widely accepted view for the development of SIC (Machette, 1985). This model describes the downward movement of water as carrying the necessary components for the formation of carbonates. As the moisture evaporates, the minerals accumulate within the soil profile. By incorporating the input of meteorological sources of Ca^{2+} into the soil profile, this model has successfully accounted for the concentrations of SIC measured at locations where calcareous parent material is less abundant or absent (Machette, 1985).

<u>1.1.2. Soil inorganic carbon in arid and semi-arid soils:</u>

Arid and semi-arid soils contain approximately 92% of all inorganic carbon (Eswaran et al., 2000). However, there is considerable uncertainty in quantifying the amounts of SIC as they are the result of heterogeneous processes and soil characteristics on small pedon-scales that are difficult to scale up to landscapes (Eswaran et al., 1995). There have been efforts to map SIC concentrations over scales ranging from small watersheds to thousands of square kilometers. Even when precipitation is the main predictor for the SIC distribution models, there is recognition that other soil variables can play a large role in SIC accumulation. Rasmussen (2006) used the dominant biome/vegetation type as a proxy for SIC. The use of biomes alone limited his results and he specified the importance of incorporating soil taxonomy data in future work. Hirmas et al. (2010) used data on hydrologic and geomorphic characteristics of a watershed related to runoff to create a process-based model. They state their results could be improved by incorporating the effects of carbonate accumulation on water holding capacity and the effects of roughness and vegetation on dust accumulation. Grinand, et al. (2012) examined a relationship between SIC and mid-infrared reflectance spectroscopy to predict SIC concentrations throughout France. However, the study is of limited applicability to many arid and semi-arid regions as it was only able to predict inorganic carbon in the top 30 cm and the peak accumulations frequently occur at greater depths. Early work in arid and semi-arid soils focused on understanding soil development and the role of dust in soil formation. Traditionally, researchers described soil development as a 'bottom up' process where rock weathers into regolith and finally the mineral component of soil. Arid soils frequently have characteristics that do not match this model of soil

development. Instead, researchers proposed that these soils also formed from the 'top down' as dust was deposited on the surface. This inflationary model describes soils in semiarid climates growing from the input of a new parent material, wind-blown dust (McFadden, 2013). The characteristics of the soil are influenced by the composition and rate of dust input. Gile et al. (1966) noted that all soils in their study area, regardless of underlying geology, have calcareous parent material due to the high influx of dust.

1.2. Study Area:

1.2.1. Site description:

Reynolds Creek Experimental Watershed is located in the Owyhee Mountains southwest of Boise, Idaho and has an area of 238 km^2 (Figure 2.1). The elevation within the watershed ranges from approximately 1100 m to 2240 m. About 25% of the land is privately owned and utilized for cattle ranching; state and federal governments own the remainder. The Agricultural Research Service (ARS) of the United States Department of Agriculture (USDA) has an established research station in the watershed with over 50 years of data collection. The ARS has developed large sets of hydrological and meteorological data during this time (Watershed, 2016).

Mean annual precipitation (MAP) ranges from ~240 mm at lower elevations to 1170 mm at higher elevations (Hanson, 2001). The RCEW receives the majority of its precipitation between November and May in this xeric precipitation regime, with most precipitation (76%) falling as snow at high elevations and mixed rain and snow (20%) at lower elevations (Hanson, 2001). The study area has a mean annual temperature ranging from 4.7 °C to 11 °C and both precipitation and temperature closely follow the elevation gradient (Seyfried et al., 2011). Potential evaporation exceeds precipitation throughout

the watershed except at the highest elevations; this deficit is partially offset by the strong seasonality of precipitation in the RCEW (Seyfried, et al. 2011).

Mixed sagebrush (*Artemisia tridentate* subsp. *wyomingensis*) and greasewood (*Sarcobatus vermiculatus*) dominate landscapes in the low elevations. At high elevations, mixed grasses, low sagebrush (*Artemisia arbuscula*), and bitterbrush (*Purshia tridentate*) become more common and eventually give way to mountain big sagebrush (*Artemisia tridentate* subsp. *vaseyana*), Douglas fir (*Pseudotsuga menziesii*), and aspen (*Populus tremuloides*; Seyfried et al., 2011). Locations in mid-to-high elevations exhibit aspect driven differences in vegetation type and abundance as well. Cooler northeastern facing sites have larger amounts of vegetation which increase the thickness of both the A-horizon and the total soil profile.

Approximately 85% of soils in the RCEW are classified as Mollisols (Stephenson, n.d.). Aridisols comprise ~13% of soils in RCEW, and are found exclusively in the lowest elevations of the watershed receiving < 350 mm of precipitation. Vertisols, Entisols, and Inceptisols comprise about 2% of the remaining soils.

Cretaceous granite from the Idaho Batholith underlies Reynolds Creek and is exposed as rounded corestones throughout the watershed. Miocene volcanism deposited basalts and andesites over the batholith, followed by additional episodes of late Miocene/early Pliocene volcanism, which deposited basalts, latites, and welded tuffs over large portions of the southern watershed (McIntyre, 1972). Soils developed over volcanic parent material within the watershed are typically thin, poorly developed, and rocky. Four alluvial terraces parallel Reynolds Creek in its northern reaches, which provide a basic chronosequence of relative surface ages. Numerous fine-grained sedimentary

arkosic units, comprised primarily of sands and gravels, and one gravel pit exposure

showing a Gilbert delta sequence are visible along the eastern portion of the RCEW.

Most of this material is sourced locally from granite exposures, but it is suggested that

some of the material is external to the watershed (McIntyre, 1972). These deposits

indicate a lake was at one time present in the Reynolds basin. The age, origin and extent

of this lake are not known.

Soils in the low elevations of the study area have thin A-horizons (less than 10

cm) underlain by Bw, Bt and/or Bk-horizons. The B-horizon varies in thickness

considerably depending on the degree of weathering and site stability. Bedrock may be

present <30 cm below the surface.

2. Methods:

2.1. Field methods:

We selected the sampling sites to represent a range of soil forming factors. These

locations captured changes in the soil conditions, particularly precipitation, vegetation,

and parent material. However, we had limited or no access to certain locations due to lack

of roads and privately owned property.

We excavated a soil pit at each site to approximately 1 m or refusal. We obtained

permission to use a backhoe to excavate three sites (#3, #24, and #25) to a depth of about

2 m. We described the vegetation, geomorphic surface, soil structure, color, gravel

content, root density, horizon boundaries, and stage of carbonate development, following

field methods outlined in Birkeland et al. (1991). We used a solution of 10% hydrochloric

acid (HCl) to measure qualitatively the concentration of soil inorganic carbon (SIC) in

the field and noted the reaction strength (none, weak, moderate, or strong). Color and

field textures were determined using small samples of the fine fraction taken from the profile.

Starting at 0-5 cm, 5-10 cm, 10-20 cm and every 10 cm after, we collected samples from the center face of the pit (McCorkle, 2015). This protocol is designed to ensure uniformity among a variety of studies, but we recognize that sampling based on horizon boundaries could better reflect SIC accumulation processes. We described and sampled the left, right, and center faces of soils pits from the first 15 sites to help assess pedon-scale variability. We collected additional observations at ten sites to determine the simple absence or presence of SIC. We excavated a soil profile to a depth of 1 m or rejection, and the 10% HCl acid solution was applied down the profile to qualitatively assess SIC concentration.

2.2. Lab methods:

All samples from this project have been archived at the Boise State sample storage site and labeled according to the RCEW Critical Zone Observatory protocol (McCorkle, 2015).

Samples were dried at room temperature then sieved to separate out the coarse fraction (>2 mm) and roots. The fine fraction (<2 mm) was split into two portions of 40-100 g each for measuring both inorganic carbon concentration and grain size distribution. Clasts not passing through the 2 mm sieve were separated using an 8 mm sieve. The largest pieces were crushed using a sledge until small enough to be run through a small rock crusher. We combined the crushed pieces with the medium sized gravels (~15 mm) to run through the small crusher until all material could pass through the 8 mm sieve. The

material was recombined with the smallest gravels to be split into 20-30 g of sample for analysis. The split samples were dried at 105 $^{\circ}$C in an oven overnight.

2.2.1. Inorganic carbon content:

The inorganic carbon samples were powdered in a ball mill. After powdering, 1.00 g of each sample (or 0.50 g of any sample estimated to contain >1.8% inorganic carbon by mass), was placed in 20 mL glass bottles and kept in a desiccator. A 0.5 dram vial containing 2 mL of a 6 M HCl solution with 3% $FeCl_2$ was added to each sample bottle. A rubber stopper sealed the bottle and an aluminum cap was crimped over the stopper. To ensure the acid reacted with the entire sample, each bottle was agitated by hand and allowed to react for approximately 10 hours (Sherrod, 2002).

We used a modified pressure calcimeter (Sherrod, 2002) to measure air pressure inside the bottle as a voltage. We converted this voltage to a percent carbonate using a calibration curve created by measuring the voltage of known $CaCO_3$ standards (0.14%, 0.24%, 0.6%, 1.2%, 1.8%, 3.6%, 6.0%, 12.0%, and 18.0%). Additionally, we ran several blank samples of the acid solution to monitor for errors in measurements and establish the zero concentration point. The air pressure in the lab was measured and subtracted from the pressure inside the sample bottles. The interior pressure measurements were taken by piercing the top of the rubber stopper with a syringe connected with tubing to the transducer sensor. To obtain the percent inorganic carbon, the calculated carbonate value was multiplied by the percent mass of carbon in the carbonate molecule (Eq. 1). A concentration was calculated using the percent mass of inorganic carbon, soil density, thickness of sampled section, and fraction of gravel or fines depending on the fraction being measured (Eq. 2).

$$\%CaCO_3 \times \frac{mass_C}{mass_{CaCO_3}} = \%SIC \tag{1}$$

$$\%SIC \times \rho \times b \times \frac{mass\ of\ fraction\ of\ interest}{total\ mass\ of\ sample} = C_{SIC} \tag{2}$$

SIC = soil inorganic carbon

ρ = bulk density (kg/m^3)

b = thickness of profile section (m)

C_{SIC} = SIC concentration (kg/m^2)

2.2.2. Texture analysis:

We measured the grain size distribution of 163 site samples from the major horizons within 26 soil profiles (McCorkle, 2015). Some samples had soil grains cemented together by carbonate minerals, which makes the measured texture appear coarser. To remove this cementation, we dissolved the carbonate minerals overnight in a solution containing 10 mL of 1M sodium acetate (CH$_3$COONa) and 100 mL of DI water in an oven at 60 $^\circ$C. The supernatant solution was pipetted off the sample the next day, 100 mL of DI water were added, and the sample was left overnight at 60 $^\circ$C. Finally, the DI water was removed and all texture samples were mixed with 100 mL of a 50 g/L solution of sodium hexametaphosphate to disaggregate soil particles and placed on a shaker table for several hours. The sample was emptied into a 1000 mL graduated cylinder and room temperature DI water was added until there was 1 liter of solution. The soil solutions were agitated with a stir rod to distribute material throughout the cylinder and allowed to settle for 7 hours. After this time, hydrometer density measurements were taken along with the solutions' temperature. The same measurements were taken with a blank cylinder containing 100 mL of the hexametaphosphate solution and 900 mL of DI water to account for the solution's density.

Clay and silt sized particles were removed from the sample by wet-sieving with a 53 µm sieve after the 7-hour measurement. The remaining sand fraction was dried overnight in an oven at 105° C. This dried sand was weighed and placed in a muffle furnace at 450° C for 8 hours to remove organic material. This final ashed weight was recorded and provided both the weight of sand and a correction to the total sample weight after removal of organic material.

The 7 hour reading provided the density of the soil solution when all soil particles larger than clay sized had settled out of suspension. The blank reading is subtracted from the sample reading after corrections for temperature had been applied. This corrected value was the mass of clay in the sample. The silt fraction was determined by subtracting the clay mass and the sand mass from the total sample mass.

2.3. GIS and data analysis:

To supplement our analyses, we incorporated data from two soil studies in the RCEW (Will and Benner, unpublished results; Seyfried, personal communication). Site locations, elevations, parent materials and soil carbonate data from 31 additional soil pits augmented our 40 sites to increase the efficacy of our models and improve prediction.

We used ArcMap software to integrate our data with previously created spatial coverages for the RCEW including the following: digital elevation models (DEMs,), normalized difference vegetation index (NDVI), precipitation, percent ground cover, metrics of vegetation height, and mapped vegetation and geologic unit for the sites. Insolation values were calculated using the area solar radiation tool in ArcMap and the DEM for the watershed.

We established the relative importance and quantitative relationships between the different environmental controls and SIC through the use of random forest analysis and multiple linear regression (MLR). The random forest analysis used precipitation, insolation, different vegetation metrics, aspect, slope, northness (Eq. 3), elevation, and geologic unit.

$$Northness = \cos(aspect) * \sin(slope) \tag{3}$$

We used random forest analyses to examine the importance of different environmental controls on the presence, absence, and amount of SIC. The model creates a series of decision trees where each of the nodes on the tree tests the effectiveness of a predictor variable. A portion of the data are withheld from each run and tested against the tree to determine its accuracy. This process is repeated hundreds of times until the most powerful predictors are established.

2.4. Dust collection and analysis:

We collected dust deposited in cavities > 2 m above the ground surface within exposed basalt, granite, and rhyolite. We assumed that the material was transported by wind (e.g. Reynolds et al., 2006). These samples, along with 10 soil samples, were analyzed with inductively coupled plasma mass spectrometry (ICPMS) to determine the concentrations of major elements within the samples. Additionally, we measured the $CaCO_3$ concentration for one of the dust collection sites with the pressure calcimeter.

3. Results:

3.1. Variation in Soil Inorganic Carbon with Precipitation:

Variations in precipitation govern the presence or absence of soil inorganic

carbon (SIC) within the Reynolds Creek Experimental Watershed (RCEW). Mean annual

precipitation (MAP) determines whether or not SIC is able to precipitate, but the

interactions of other soil forming factors are complex making it difficult to establish a

relationship and a hierarchy of controls. We analyzed 710 samples for inorganic carbon

content in both the fine and gravel fractions (Table 2.1). Soils at high elevations with

higher MAP generally do not contain any SIC; low elevation soils contain variable

amounts of SIC. These lower elevation sites have SIC accumulations ranging from trace

amounts to a high of 28.08 kg/m^2 (Table 2.1). The large majority of sites have less than

13 kg/m^2 of SIC. Soils from areas receiving > 500 mm of precipitation do not contain

calcic horizons, whereas soils below this 500 mm threshold do accumulate carbonate

minerals.

Table 2.1 Summary of site data.

Site ID	Easting[1] (m)	Northing (m)	Elev. (m)	SIC (kg/m^2)	MAP[2] (mm)	Vegetation	Geologic unit
1	517124	4789664	1247	6.89	342	Wyoming Sagebrush	Boston Ranch unit - bedded silicic tuff, diatomite and lignite
2	521543	4784127	1233	2.93	275	Wyoming Sagebrush	Gravel capped pediment remnants, higher level
3	521075	4783608	1235	19.18	282	Wyoming Sagebrush	Gravel capped pediment remnants, higher level
4	523628	4777568	1631	12.3	388	Low Sagebrush	Toll Gate olivine basalt including underlying basalt tuff
5	520581	4786904	1166	0.351	252	Wyoming Sagebrush	Granitic rock, quartz monzonite in part
6	520583	4786227	1178	0.079	250	Wyoming Sagebrush	Arkosic sand, granitic gravel and silty clay
7	524529	4778012	1583	0.432	379	Low Sagebrush	Hoot Nanny olivine basalt
8	515436	4791916	1375	3.26	486	Wyoming Sagebrush	Salmon Creek basalt - andesite unit
9	522286	4775021	1813	0.03	458	Mountain Sagebrush-Snowberry	Tuff associated with upper latite unit

Site ID	Easting[1] (m)	Northing (m)	Elev. (m)	SIC (kg/m^2)	MAP[2] (mm)	Vegetation	Geologic unit
10	521920	4788163	1178	9.35	260	Wyoming Sagebrush	Granitic rock, quartz monzonite in part
11	521097	4788320	1148	6.76	261	Greasewood	Arkosic sand, granitic gravel and silty clay

Site ID	Easting[1] (m)	Northing (m)	Elev. (m)	SIC (kg/m^2)	MAP[2] (mm)	Vegetation	Geologic unit
12	520965	4770146	1943	0	716	Low Sagebrush	Granitic rock, quartz monzonite in part
13	521506	4776829	1626	0.601	372	Low Sagebrush	Rhyolitic welded tuff, Black Mt. unit
14	514764	4789264	1385	0	522	Wyoming Sagebrush	Salmon Creek basalt - andesite unit
15	516059	4789497	1296	0	414	Wyoming Sagebrush	Salmon Creek basalt - andesite unit
16	519792	4778913	1329	1.48	413	Wyoming Sagebrush	Boston Ranch unit - bedded silicic tuff, diatomite and lignite
17	519594	4779068	1310	0.893	414	Wyoming Sagebrush	Boston Ranch unit - bedded silicic tuff, diatomite and lignite
18	523312	4779456	1433	7.84	314	Wyoming Sagebrush	Hoot Nanny olivine basalt
19	523801	4787956	1302	0.443	263	Wyoming Sagebrush	Hoot Nanny olivine basalt
20	523913	4788905	1288	5.67	264	Wyoming Sagebrush	Granitic rock, quartz

Site ID	Easting[1] (m)	Northing (m)	Elev. (m)	SIC (kg/m²)	MAP[2] (mm)	Vegetation	Geologic unit
							monzonite in part
21	523701	4778341	1558	0	363	Low Sagebrush	Hoot Nanny olivine basalt
22	521311	4783134	1229	4.81	281	Wyoming Sagebrush	Boston Ranch unit - bedded silicic tuff, diatomite and lignite
23	522924	4782230	1345	1.28	276	Wyoming Sagebrush	Hoot Nanny olivine basalt
24	520258	4783645	1204	28.08	286	Wyoming Sagebrush	Gravel capped pediment remnants, lower level
25	520280	4783627	1207	9.26	286	Wyoming Sagebrush	Gravel capped pediment remnants, lower level
26	522275	4774835	1808	0	472	Mountain Sagebrush-Snowberry	Hoot Nanny olivine basalt
27	523138	4776818	1716	0	401	Low Sagebrush	Hoot Nanny olivine basalt

Site ID	Easting[1] (m)	Northing (m)	Elev. (m)	SIC (kg/m²)	MAP[2] (mm)	Vegetation	Geologic unit
28	519587	4785291	1171	9.29	294	Wyoming Sagebrush	Arkosic sand, granitic gravel and silty clay
29	519653	4785144	1168	24.56	292	Greasewood	Floodplain alluvium
30	520369	4784469	1147	3.24	277	Cultivated	Floodplain alluvium
31	520522	4783679	1193	5.42	286	Wyoming Sagebrush	Floodplain alluvium

32	519003	4776592	1460	0	488	Wyoming Sagebrush	Granitic rock, quartz monzonite in part
33	516668	4791703	1306	0	405	Wyoming Sagebrush	Tuff associated with lower latite unit
34	517760	4782044	1315	0	360	Wyoming Sagebrush-Bitterbrush	Granitic rock, quartz monzonite in part
35	517801	4781795	1341	0	377	Wyoming Sagebrush-Bitterbrush	Granitic rock, quartz monzonite in part
36	517877	4781830	1313	0	364	Wyoming Sagebrush-Bitterbrush	Granitic rock, quartz monzonite in part
37	517853	4781926	1313	0	359	Wyoming Sagebrush-Bitterbrush	Granitic rock, quartz monzonite in part
38	517874	4788707	1194	6.91	315	Wyoming Sagebrush	Boston Ranch unit - bedded silicic tuff, diatomite and lignite
39	518736	4776764	1513	0	506	Wyoming Sagebrush-Bitterbrush	Granitic rock, quartz monzonite in part
40	516609	4781178	1528	0	525	Wyoming Sagebrush-Bitterbrush	Granitic rock, quartz monzonite in part

[1]UTM zone 11
[2]Mean annual precipitation

3.2. Using random forest analysis to determine primary controls on SIC

When creating a classification tree model that solely focused on presence or absence of SIC, we found that precipitation was the strongest determinate followed by geologic unit, elevation, and slope. The model was very effective at predicting the absence of SIC with an overall success rate of 89%, and had similar but lesser success with predicting its presence correctly 82% of the time (Table 2.2). We also used random forest analyses to predict SIC accumulation classes (none, low, medium, high, and very high) and actual amounts. Each model was respectively less successful in its ability to predict, but they provided similar results and highlighted the complexity of SIC accumulations below 500 mm of MAP. The accumulation class model was particularly successful in predicting locations with no (74% accuracy) and very high SIC (67%), but low (23%), medium (33%), and high (28%) sites were more difficult. The regression analysis model established a correlation between the predictors and SIC with an R^2 of 0.25. Precipitation was the top predictor in all random forest analyses, and parent material, along with site elevation, ranked highly in both the presence/absence and accumulation class model (Table 2.2). These models also selected slope and percent ground cover, respectively, as their final predictors. In the regression model for predicting SIC amounts, max vegetation height and range were the only two predictors along with precipitation to be selected. However, these measures of vegetation height have much lower predictive ability relative to precipitation.

Table 2.2 Output of predictive success with the random forest models

Model target	Overall success rate	Top predictors
Presence/absence		Precipitation
	84.50%	Elevation
		Geology
		Slope
Concentration category (none, low, medium, high, very high)	52.10%	Precipitation
		Geology
		Elevation
		% ground cover
Concentration (kg/m^2)	$R^2 = 0.25$	Precipitation
		Max vegetation height
		Range of vegetation height

We used the results from the random forest analysis along with the predictors and site data to model distributions of SIC throughout the watershed (Figure 2.2). The regions predicted to contain SIC are predominately in the center of the RCEW, which also correspond to the areas receiving the least precipitation. These low-lying areas are also characterized by stable, dry terrace surfaces vegetated primarily by Wyoming sagebrush (Figure 2.3). We observe that the greatest concentration of areas with mixed presence and absence are found just below the 500 mm precipitation threshold.
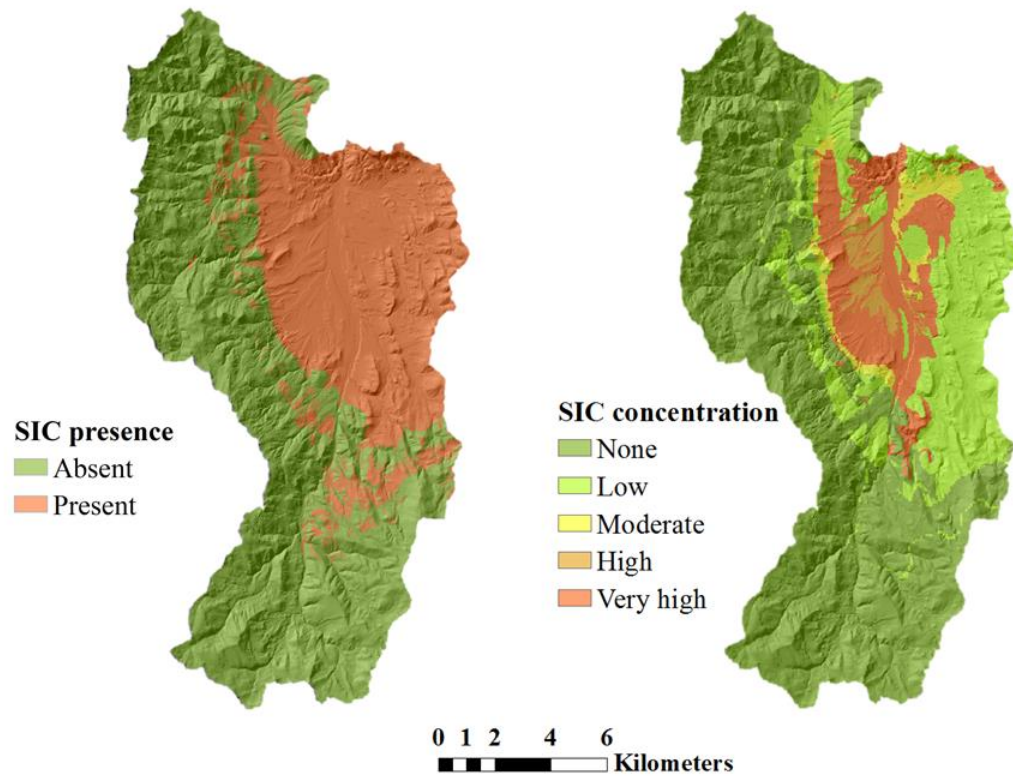
Figure 2.2 Map of modeled SIC distributions throughout the watershed. The figure on the left is the result of modeling the presence or absence of SIC. We grouped the sites into categories of SIC accumulation (none, low, moderate, and high) for the modeled map on the right.
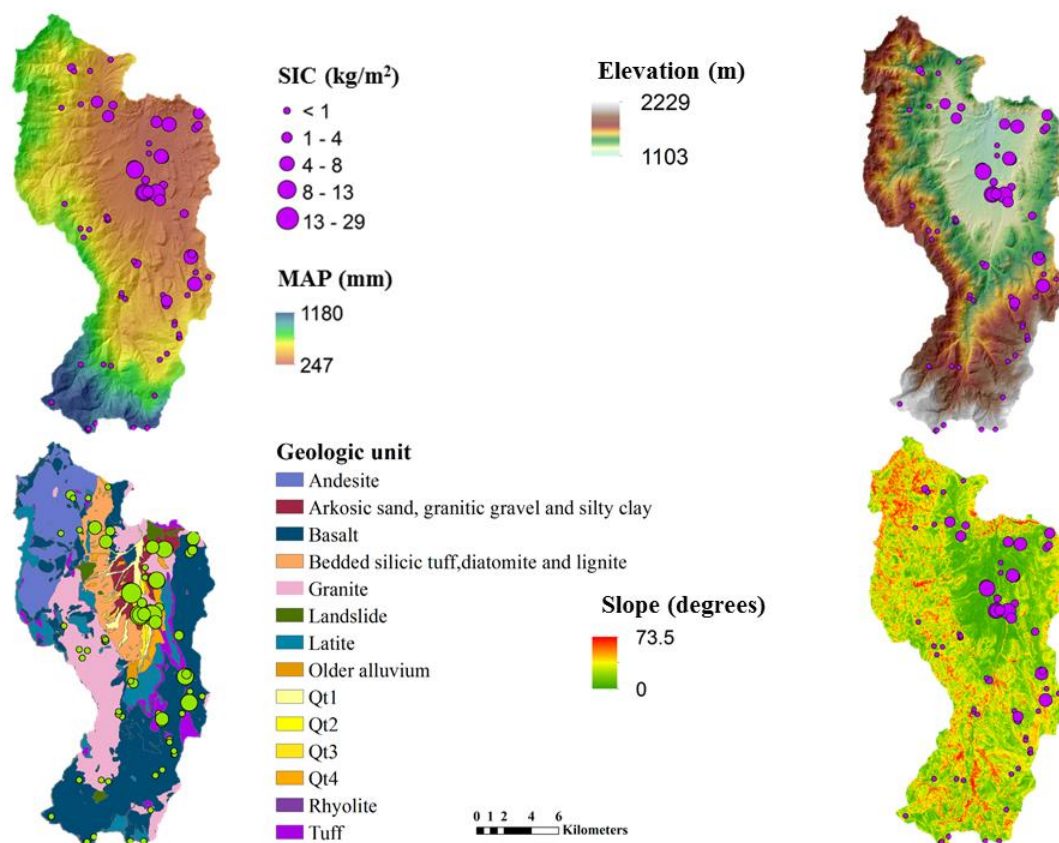
Figure 2.3 Maps showing distribution of SIC and related predictors. SIC rich sites are generally concentrated in areas with low precipitation, low elevation, and low slope.

3.3. Predicting soil inorganic carbon using statistical analysis of possible environmental factors:

We used linear regression as an additional method to investigate controls on SIC presence and accumulation. Initially through simple linear regression, we found that elevation and precipitation were the top two predictors of SIC. Our results from this analysis indicate that the threshold of SIC formation is ~500 mm MAP (Figure 2.4). Multiple linear regression (MLR) showed that elevation, slope, and certain parent materials and vegetation type were important predictors. Although many of the variables presented the expected trend with SIC accumulation in MLR (e.g. negative relationship

between SIC and precipitation), the correlations were relatively weak. In contrast to the

random forest analysis, precipitation performed poorly when grouped with other

variables in MLR. Slope behaved in the opposite fashion, being an ineffective predictor

by itself but being one of the most important during MLR. These inconsistent results

between the linear regression methods made it difficult to disentangle the importance and

significance of auto-correlated factors.
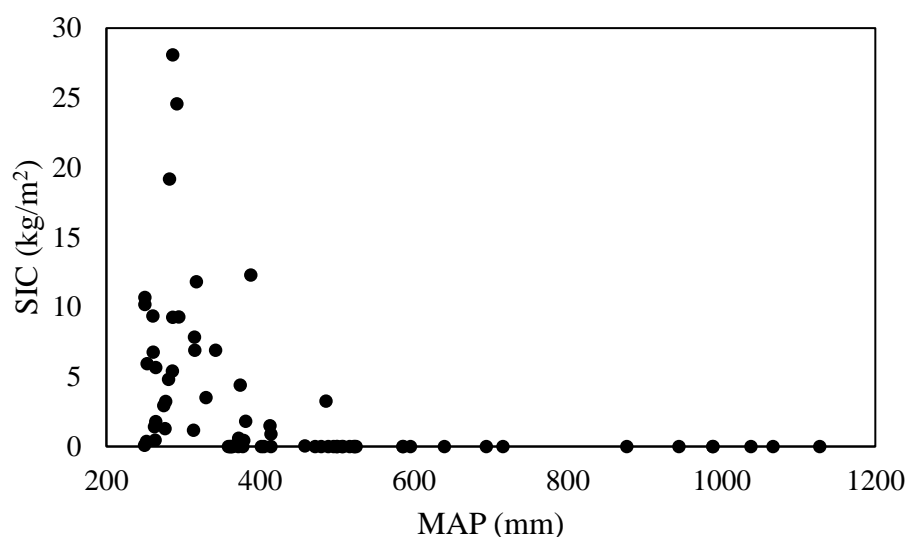
Figure 2.4 Mean annual precipitation for each site with measured SIC concentrations. Although precipitation does not have a strong correlation with concentration, there is a boundary at about 500 mm of rainfall where SIC accumulation stops.

To further explore the relationship between parent material and SIC

accumulation, we examined the mean values of SIC in three of the most prevalent,

mapped parent materials: basalt, granite and alluvium. Alluvium had by far the largest

amount of SIC and granite had the least (Figure 2.5). However, precipitation co-varies

with parent material, since terraces are formed and preserved along the lower reaches of

Reynolds Creek (Figure 2.3).
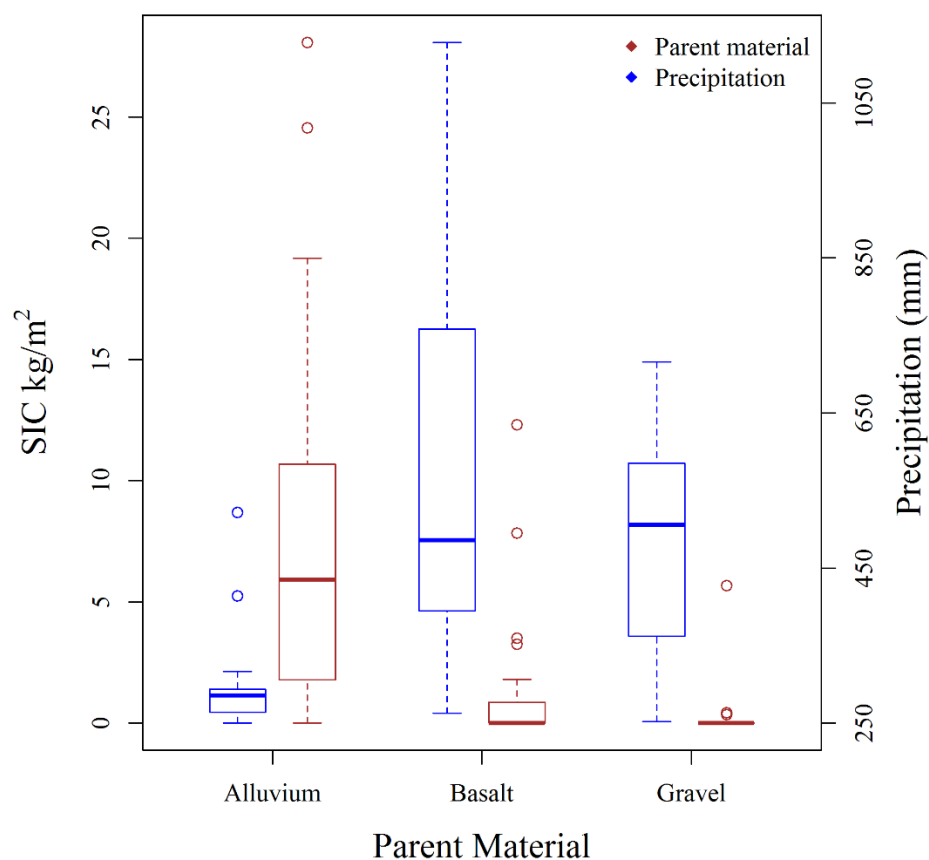
Figure 2.5 Comparison of measured values of SIC in the three most common parent materials. The red boxes show SIC concentration and the blue boxes show precipitation.

3.4. Changes in carbon storage with soil depth

Soils in the RCEW typically have thin A-horizons from 1-10 cm thick. Bw or Bt-horizons follow the A-horizon and are ~10 cm to over 40 cm thick. SIC accumulation occurs primarily in the Bk-horizon, which typically begins 40 cm or more below the surface. The highest peaks in SIC accumulations often appear below 50 cm as can be seen at sites #2 and #24 (Figure 2.6). At site #24, we also observed a second larger peak in SIC around 170 cm. This observation implies that there are potentially considerable stores of SIC below the depths sampled at many of the sites. As bedrock impeded

excavation at several of the sites, however, it is difficult to ascertain how accurate this

assumption is in the watershed.
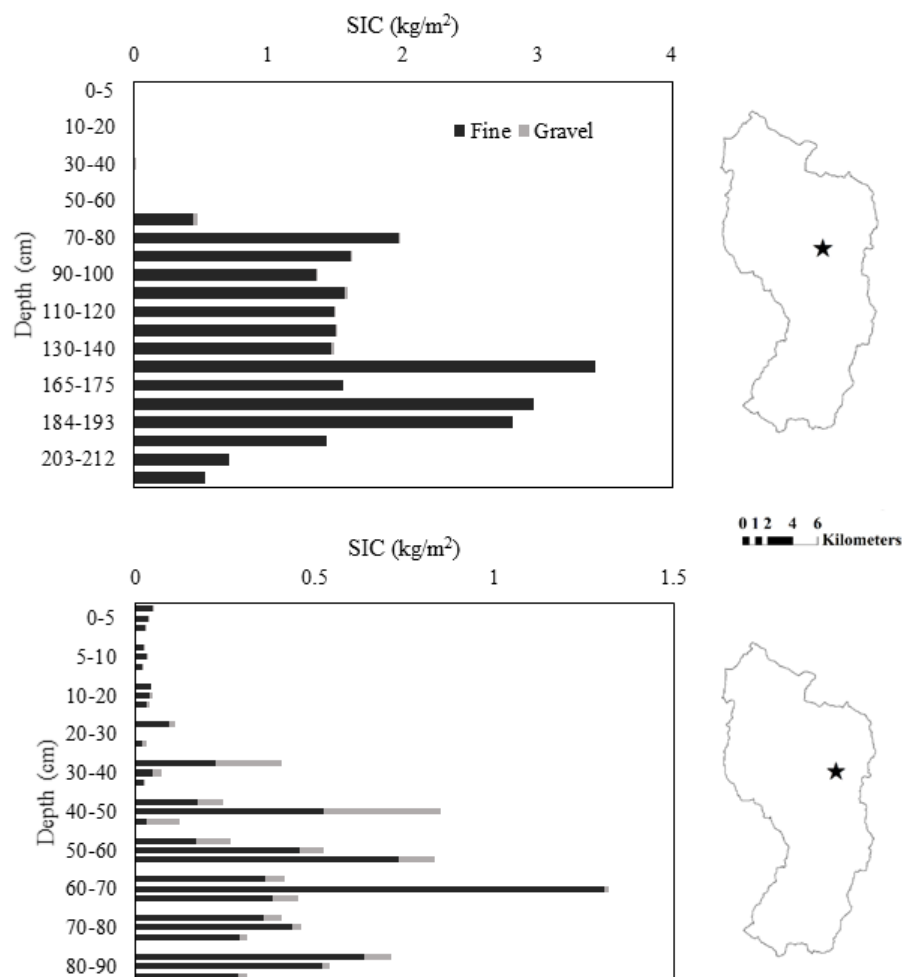
Figure 2.6 SIC profiles of site #24 (top) and #2 (bottom). Note the large increase in SIC at depth for both sites and the range of variability at the pedon-scale for site #2. Site #24 also highlights the large amounts of carbon stored at depths most pits did not reach.

We found through lab analysis of the samples that many of the sites had large

differences in SIC values at a given depth between the different soil profiles (Figure 2.6).

To determine whether these differences were due to natural variability at the pedon-scale

or uncertainty associated with analysis methods, we ran replicates of each sample

collected at site #23 and ran several replicates of standards. We found that our analytical

methods introduce very little uncertainty (0.001-0.014% SIC), but the observed

variability between soil profiles was up to 220% (Stanbery et al., *in review*).

Additionally, we compared the field measurement of maximum carbonate stage

(Gile et al., 1966; Machette, 1985) at a site to the actual measured concentration (Figure

2.7). The field method proved to be mostly reliable with there being a general increase in

SIC with higher, observed stages of development. However, there were some issues with

sites containing a maximum stage of II+, which had the highest SIC concentration of all

stages. Two of the sites in this category have almost continuous accumulations of

carbonate throughout the profile creating very high concentrations even though the

carbonate is less well developed (Stanbery et al., *in review*).
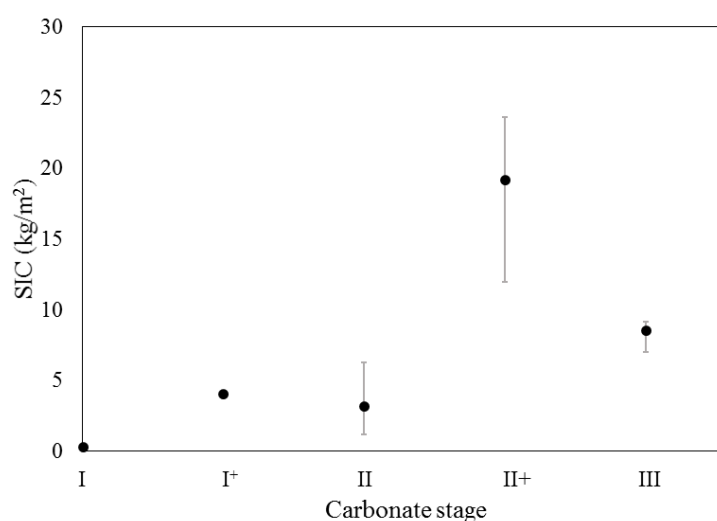
Figure 2.7 Comparison of field measurements of the stage of carbonate development and values measured in lab analysis. There are sites in the stage II+ category with exceptionally high concentrations due to SIC accumulation throughout the profile but no stage III characteristics.

3.5. Soil texture and soil inorganic carbon storage within the gravel fraction of soils:

Silt and sand dominate the grain size distribution within the RCEW soils, with little clay at most sites (Figure 2.8). Wind-blown dust is likely an important component of many soils in this semi-arid watershed. Many of the more stable soil profiles studied, particularly sites # 24, 28, and 29, have relatively large amounts of silt-sized particles in the upper portions of the profiles. However, there are no clear correlations among texture, elevation, and carbonate content in soils. There are varying amounts of SIC on gravels in the soils studied but clast coatings represent, on average, about 13% of the total inorganic carbon at a site. Site #13 has the highest amount of SIC in the gravel-sized fraction with over 40% of the carbonates forming on the exterior of rocks and hard clay-rich peds (Stanbery et al., *in review*). This analysis highlights the importance of including carbonate coats on gravels when estimating total SIC content in soils, especially when working in gravelly soils.
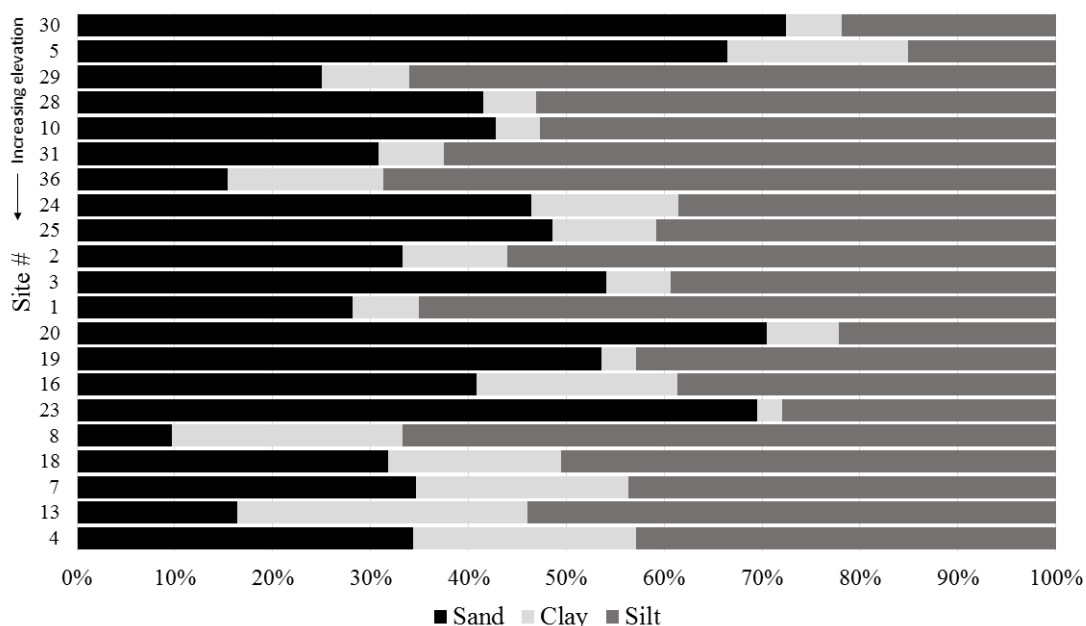
Figure 2.8 Grain size distribution for several of the study sites. The sites are listed in order of increasing elevation.

3.6. Chemical analysis of dust:

We collected dust deposited in natural cavities > 2 m above the ground surface within exposed basalt, granite, and rhyolite, and assumed that the fine-grained material we collected from these vugs was primarily wind-blown (Reynolds et al., 2006). The dust from the three different rock exposures (granite, basalt, and rhyolite) have very similar compositions with CaO ranging from 2.3-3.2% by mass (Figure 2.9). Most of the soil samples showed similar concentrations as well. However, soil samples from site #23 showed much higher concentrations (11.3-12.1%). We also found the dust sample from the rhyolite site to contain 5.6% carbonate by mass.
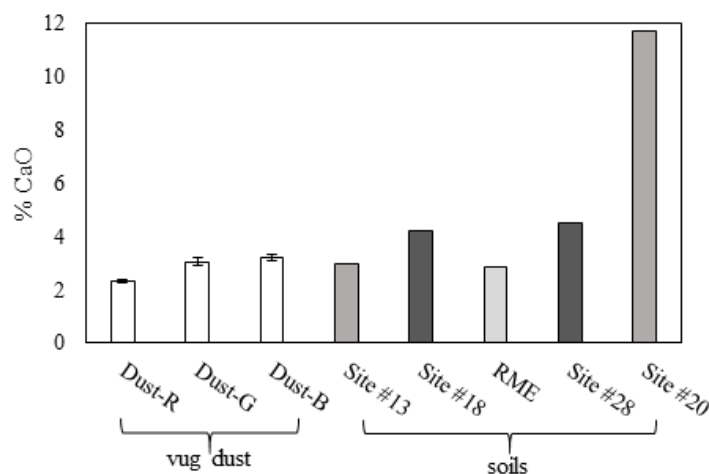
Figure 2.9 Measured CaO values from the collected dust samples and soil samples. We collected dust samples from vugs or concavities in rhyolite (R), granite (G) and basalt (B). The dust and soil composition are similar with the exception of samples from site #23. This particular site contains relatively large amounts of basalt clasts in varying stages of weathering which might account for the elevated levels of CaO. For the soil samples, darker bars indicate greater concentrations of SIC.

4. Discussion:

Soil scientists have long recognized that precipitation is a first order control on soil inorganic carbon (SIC) accumulation (Marbut, 1935; Baldwin, et al., 1938; Jenny, 1941; Arkley, 1963; Gile et al., 1966; Machette, 1985; Royer, 1999; Retallack, 2005; Hirmas et al., 2010). We confirmed this observation for the Reynolds Creek Experimental Watershed (RCEW) by demonstrating that precipitation was the top ranked predictor in all random forest analyses (Table 2.2). Our investigations into the expected relationship between SIC and precipitation provided two key insights: First, SIC does not form in the top 1 m of sites receiving more than 500 mm of rainfall, and amounts of SIC in the top 1 m rapidly drop as this threshold is approached (Figure 2.4). Second, within the zone of SIC accumulation, SIC storage does not linearly increase with decreasing precipitation, highlighting the influence of other soil forming factors.

Early work by American soil scientist Curtis Marbut (1935), classified soils at their highest level into two great groups: the 'pedocals' and the 'pedalfers.' Pedocals are distinguished by the accumulation of calcium and magnesium carbonates throughout all or a part of the soil profile, while pedalfers are distinguished by the absence of carbonate accumulation and usually by an accumulation of iron and aluminum compounds (Baldwin et al., 1938). Marbut recognized the relationship of these great soil groups to the climatic zones, where pedocals typified the subhumid, semiarid, and arid regions, while pedalfers typified the humid regions (Baldwin et al., 1938).

Earlier work in soils found that the boundary between pedocals and pedalfers is a function of an area's precipitation (Marbut, 1935; Baldwin et al., 1938; Jenny, 1941; Malde 1955). Machette (1985) described the pedocal and pedalfer boundary not only as a function of the amount of precipitation but also the input of Ca^{2+}.

Our study builds on this prior work by Marbut (1935) and Jenny (1941) by precisely quantifying not only the precipitation threshold for carbonate, but the amount of carbonate present within the upper meter of soil within the zone of carbonate precipitation. In an extensive study of soils from Colorado to Missouri, Jenny found the depth to carbonate bearing horizons can vary up to 1 m for a given rainfall value (Figure 2.10). Carbonate accumulation begins at 1 m or deeper in soils receiving 500-800 mm of precipitation, which matches well with our results. However, since the RCEW soils are on the drier end of this spectrum, we hypothesize that SIC formation is limited by Ca^{2+} input. Arkley (1963) discovered that data on the soil's water holding capacity helped to improve prediction of depth to carbonate. Based on rainfall alone, however, he determined that ~630 mm will push calcic horizons below 1 m. Although we do not have

data on the sources and amounts of Ca^{2+} in the RCEW, we were able to use data on

rainfall to determine the precipitation threshold between calcic and non-calcic soils.
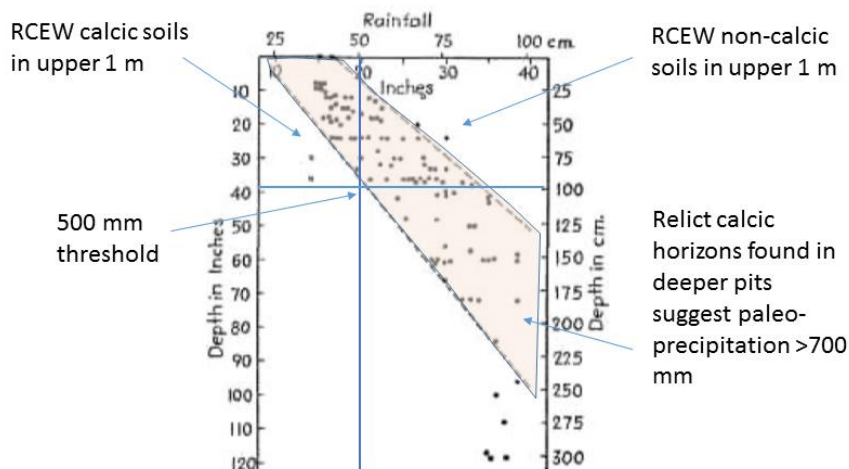
Figure 2.10 Hans Jenny's (1941) plot of depth to the calcic horizon as a function of precipitation. At a given amount of rainfall, there is a wide range of depths to carbonate accumulations. The soils in RCEW are on the driest end of the depth spectrum with our calcic horizons forming at 1 m or deeper at 500 mm of precipitation. This boundary implies that carbonate formation is limited by the amount of Ca^{2+}. Additionally, large amounts of SIC were found below 1 m at the deepest sites (#3, #24, and #25). These deep accumulations of SIC are likely relict horizons formed during glacial periods with increased precipitation.

Royer (1999) examined NRCS data along with those from previous studies to

establish a relationship between the depth to the top of the carbonate horizon and annual

rainfall. After incorporating 1482 soil profiles into the analysis, Royer found the

correlation between the two was weak ($R^2 = 0.31$) but that there is a strong relationship

between areas receiving less than 760 mm of rainfall and the accumulation of SIC.

Additionally, the relationship Royer established predicted a depth of 1 m to the carbonate

horizon in areas receiving ~535 mm of precipitation. As most of our sites were excavated

to a depth of approximately 1 m, Royer's results agree with our work showing no SIC in

soils receiving more than 500 mm of rain. Malde (1955) found the pedocal/pedalfer

boundary in Rocky Flats, Colorado to be at 460 mm and Zamanian et al. (2016) found

that the majority of SIC accumulation occurs when precipitation is <500 mm. Retallack

(2005) conducted a similar study with 675 soils describing the relationship between depth

to carbonate and precipitation. With Retallack's results, SIC accumulating more than 1 m

from the surface occurs in areas receiving >650 mm. Differences in our results could be

attributed to Retallack's efforts to reduce the effects of competing environmental factors

and the limited number of soil profiles studied in our work. Our study continues the work

of linking precipitation to SIC accumulation. However, our work relates rainfall to the

amount of SIC accumulated in a profile instead of depth to the calcic horizon, which

could be incorporated into future work.

4.1. The role of elevation, slope and vegetation in SIC accumulation

Elevation is one of the higher-ranking predictors of SIC in our analyses (Table

2.2). This result is not surprising as elevation, precipitation, and vegetation type are

strongly correlated within the RCEW (Figure 2.3). Establishing whether elevation was

important due to its relationship with precipitation and vegetation or as a result of another

environmental factor (e.g. differential dust deposition, temperature) requires further

work. We found that as slope increases there is a general trend of decreasing SIC.

Pedogenic carbonate's relationship to slope is somewhat complex. Increasing slope tends

to decrease the residence time of water within the soil, effectively making it drier and

promoting SIC accumulation. However, high erosion rates on steep slopes can decrease

soil stability and inhibit SIC formation (Birkeland, 1999).

Although vegetation characteristics (e.g. ground cover, vegetation height) never

ranked as a top predictor of SIC in our analyses, some measure of vegetation was present

in two of the three random forest models (Table 2.2). Vegetation can directly influence SIC precipitation by impacting the amount of water in the soil, its flow path, the concentration of dissolved CO_2, and the soil solution's pH (McFadden, 2013; Zamanian et al., 2016). The pH of the soil solution is a strong control on SIC and plants play an important role in determining the solution's acidity. As roots respire, they release CO_2 and increase the partial pressure of CO_2 (pCO_2). Larger pCO_2 values increase the concentration of carbonic acid (H_2CO_3) and lower the soil solution's pH. (Birkeland, 1999; Appelo, 2010). Vegetation removes soil water through transpiration, which increases the relative level of carbonate saturation in the soil solution and promotes carbonate mineral precipitation. Plant roots can also create preferential flow paths, allowing water to flow through a profile more quickly and limiting evapotranspiration (Dingman, 2008). The presence of SIC is correlated with the presence of Wyoming sagebrush, but it is a plant that resides almost exclusively in low precipitation areas.

4.2. The importance of parent material in soil development

We did find agreement with previous work that parent material (Gile et al, 1966; Machette, 1985; McFadden and Tinsley, 1985; Reheis et al., 1992; Birkeland, 1999) and measures of relief (Hirmas, 2010) are important factors in SIC accumulation as well. Parent material plays a significant role in SIC accumulation (Table 2.2). Alluvial terraces contain the highest amounts of SIC in their soils, although the high terrace surfaces are also old, stable, and dry (Figure 2.3). The soils' parent material can impact the accumulation of SIC through its influence on soil particle size distributions and availability of Ca^{2+} after weathering. Soil particle size is a control on the movement of water through soils with coarser grained soils promoting rapid movement of soil water

and clay-rich soils inhibiting the flow (Jenny, 1941; Dingman, 2008). Although there is no carbonate bearing bedrock in the watershed, some of the rocks within the RCEW contain calcium-rich minerals and are a potential source of Ca^{2+} cations for the formation of SIC (Figure 2.3). There are limited data on the chemical composition of the bedrock in the area. McIntyre (1972) performed mineral counts on several rocks throughout the watershed and obtained the chemical composition of a single basalt sample. He found that the groundmass of the andesite and basalt samples is 50-70% plagioclase by mass. The Ca-rich endmember anorthite is the predominant phase of plagioclase in these samples. Chemical analysis of the one basalt sample showed a composition of 10.0% CaO, 7.1% Ca, by mass.

It is likely that dust provides much of the Ca^{2+} in arid soils (Machette, 1985; McFadden and Tinsley, 1985). As seen in our elemental analysis of the dust samples, the dust and soil have very similar Ca^{2+} compositions (Figure 2.9). We infer that these results show the dust is well mixed within the profiles and is indeed a significant parent material within the watershed. However, the elevated Ca^{2+} concentrations at site #23 warrant further investigation. This site is on basalt and the profile contains considerable amounts of partially weathered basalt clasts. So it is possible that the weathering of the parent material produces the CaO.

The dust collected from the rhyolite vugs is 5.6% carbonate by mass whereas soil samples contain up to 25% carbonate by mass. These elevated levels of carbonate in soils relative to dust (Figure 2.9) show a concentration of carbonate and Ca^{2+} in the deeper parts of soil profiles, suggesting the importance of time needed for the concentration of carbonate and the development of calcic horizons. Although both dust and weathered

bedrock are likely sources of Ca^{2+}, we are unable to differentiate the relative contribution from these two sources.

We anticipated there would be a strong correlation between SIC amounts and the grain size distribution of a site. Although we did see a positive trend in SIC accumulation with finer textured soils (Figure 2.11) and a negative one with sandier soils, the correlations were very weak. We anticipate that more data on the source of this fine grained material and the ability to distinguish between wind-blown dust and *in situ* silt sized material will be of great use. We could use these data to better relate dust presence to SIC accumulation.
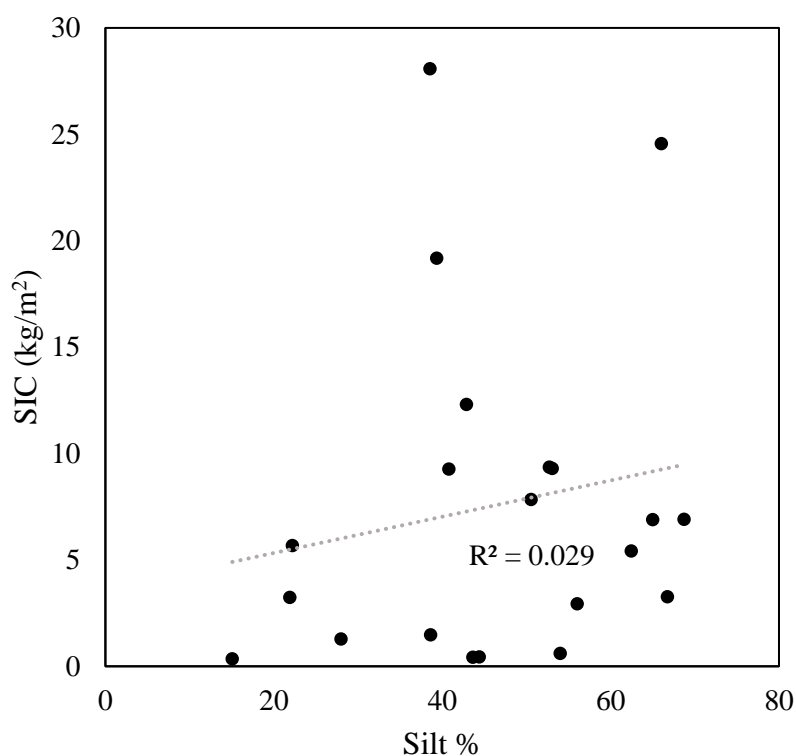
Figure 2.11 Comparison of SIC concentration with the amount of silt sized particles in the soil. There is a positive correlation between the two, but silt does not appear to have a strong impact on SIC accumulation.

4.3. The role of time in soil development

The importance of time in the development of calcic horizons is well established by the substantial body of work on carbonate stages and chronosequences from the southwestern USA (e.g. Gile et al., 1966; Machette, 1985). Site #4 has a large amount of SIC and it receives approximately 390 mm of rainfall making it one of the wettest sites with significant SIC accumulation (Figure 2.12). The profile is well-developed with distinct horizons, suggesting an old soil developed on this stable surface. Interestingly, site #4 has not only the highest SIC amount in the immediate area but has one of the highest amounts of SIC throughout the watershed with 12.27 kg/m^2 of SIC. In this particular case, the elevated amounts of SIC are likely the result of the site having ample time to develop (Figure 2.12).
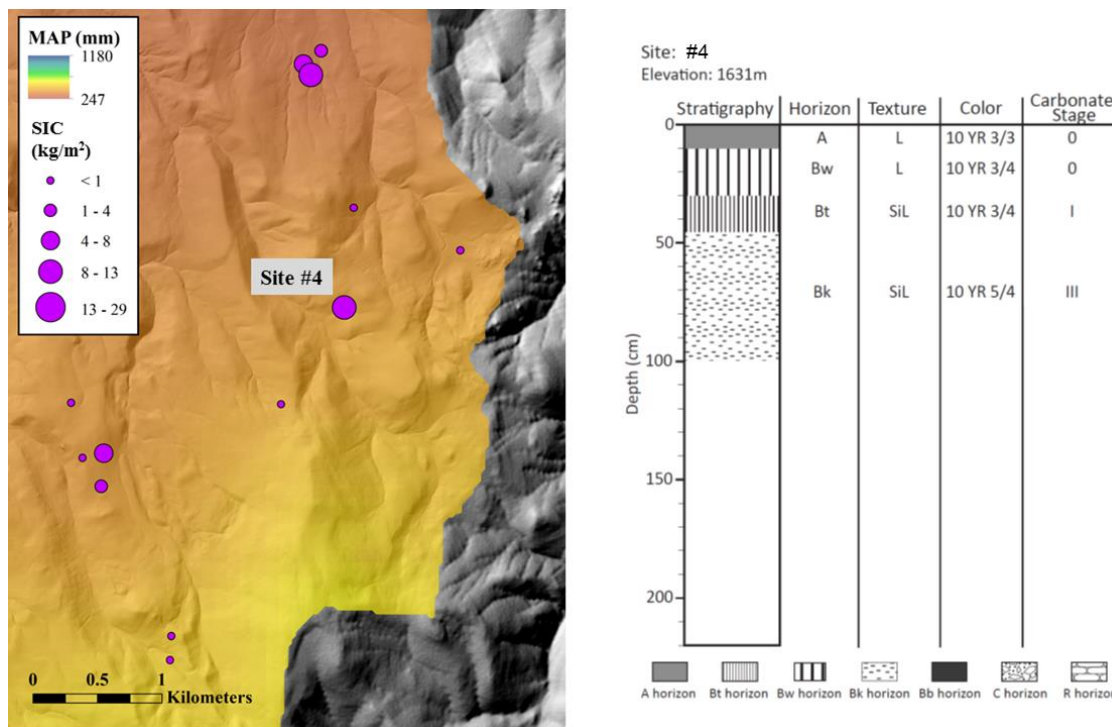
Figure 2.12 The image on the left shows a portion of the southeastern portion of the RCEW highlighting the degree of variability present in SIC concentrations. Site #4 has a high concentration of SIC but also receives a relatively large amount of precipitation. An illustration of the soil profile at site #4 (Dryden Creek) can be seen

on the right. The site is characterized by a distinct and relatively well-developed Bk-horizon and comparatively large amount of precipitation (390mm) which implies that the soil has had ample time to develop.

We also collected several samples along a soil chronosequence consisting of the abandoned terraces of Reynolds Creek. Changes in Reynolds Creek's base level as climate has fluctuated over interglacial timescales, have likely lead to stream incision and the creation of these terraces. During interglacial periods over the past 225 ka, relatively warm, dry conditions characterized the area of southern Idaho and northern Utah (Jiménez-Moreno et al., 2007). For Pleistocene-aged and older soils, carbonate minerals accumulate over glacial/interglacial timescales. In the Pacific Northwest, glacial periods were cooler and effectively wetter, while interglacial times are marked by more arid conditions and greater amounts of dust accumulation, which increases the influx of Ca^{2+} to the soil (McFadden et al., 1986; Chadwick et al., 1995). The increased supply of Ca^{2+} will in turn increase SIC accumulation rates. Wetter conditions and increased vegetation characterize glacial periods. These conditions can negatively affect SIC accumulation rates, or cause carbonate to be precipitated lower in the soil profile. Additionally, in areas that are sufficiently dry, increased precipitation can promote carbonate formation through the dissolution of the necessary components (Machette, 1985). In the RCEW, increased precipitation would likely push the threshold of formation down in elevation and push the carbonate boundary lower in the soils profile. Glacial climates could also potentially enhance SIC accumulation rates in the lowest, driest locations.

The soil pit at site #24 may provide evidence of the influence of glacial climates on carbonate precipitation. This 2.2 m pit, one of 3 sites reveals extensive carbonate precipitation with peaks in SIC at 80 cm, 160 cm, and 180 cm (Figure 2.6). A well-

developed argillic B-horizon with excellent prismatic structure also characterizes this site, suggesting the soil formed on this terrace (~12 m above current Reynolds Creek) is quite old. From Jenny's (1941) relationships between depth of carbonate accumulation and rainfall (Figure 2.10), significant carbonate precipitation in excess of 1.5 meters corresponds with rainfall values between 750-1000 mm. As the current rainfall at this site is 285 mm, the site profile suggests this deeper carbonate horizon may have formed during glacial intervals characterized by greater effective precipitation.

Although there were insufficient samples collected in this study to establish strong statistical relationships between soil development and soil age, there is a general trend in increasing amounts of SIC as the relative age of surface increases. However, we see the opposite relationship when comparing sites #28 and #29 as they are on two different terraces within 200 m of each other (Figure 2.13). The vegetation community and climate are the same, but there is a considerably larger amount of SIC in the pit excavated on the *younger* surface. A possible reason for this difference could be that the carbonates were weathered and transported from the older, higher terrace into the younger, lower surface.
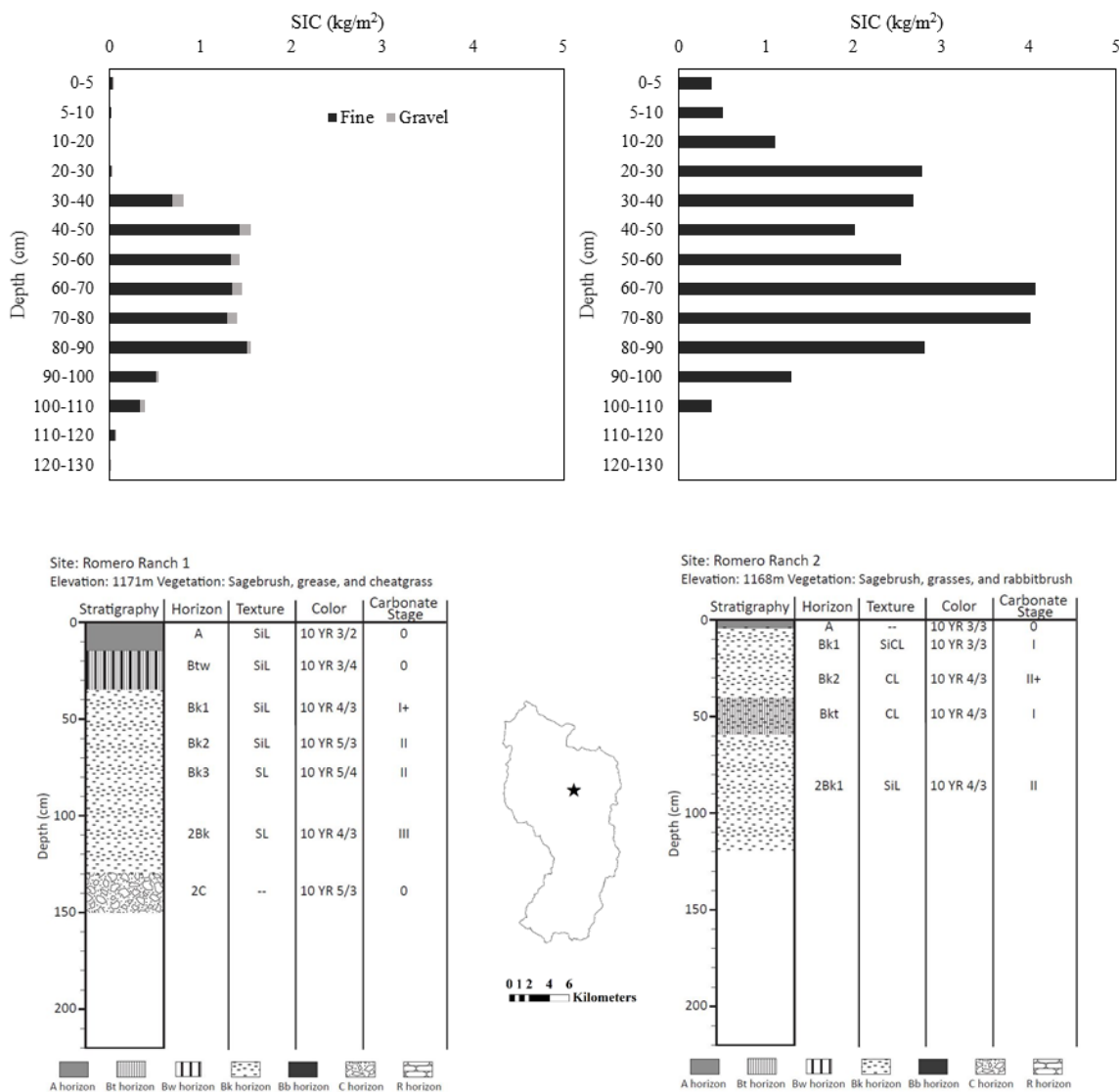
Figure 2.13 Comparison of SIC concentrations of different terraces. Site #28 (on the left) is located within a short distance of sites #29 (right most figure) but on the next youngest terrace surface.

5. Conclusions:

We find soil inorganic carbon is governed largely by rainfall; no SIC is found in areas receiving more than 500 mm of precipitation. Within the zone of SIC accumulation, the amounts of SIC reflect the complex influence of other controls on soil development, including parent material, time, and relief. These results support early soil classification

work by Marbut (1935) and Jenny (1941). They found within the continental USA, the pedocal/pedalfer boundary for the upper 1 meter of soil is found in areas receiving between ~450-750 mm of precipitation.

The soil carbon pool is a critical component of the carbon cycle. Our study provides analyses that illuminate the relationships between soil forming factors affecting the SIC pool. These analyses provide useful insight on where SIC forms and the controls on its accumulation. Here we show that precipitation is the best predictor of the presence of SIC within the Reynolds Creek Experimental Watershed (RCEW). Sites located in areas that receive over 500 mm of precipitation annually are unlikely to have SIC accumulate within the top 1 m. Areas receiving less rainfall, however, see great variation in the concentrations present due to the complex interactions of factors controlling the balance of Ca^{2+} and water within the soil column.

We found that parent material is an important predictor for the presence of SIC in the RCEW, but the nature of this control was not well constrained in our study (Table 2.2). Likely, the material's impact on soil hydrology and Ca^{2+} levels provide the greatest controls on SIC. Additional work to better understand the meteorological flux of Ca^{2+} into the soils is needed, as the amount of dust accumulated is likely a large control on the amounts of SIC. The elevation and slope of the site are important as well as they impact the development of soil and its secondary characteristics. Future work that investigates the impact of vegetation on CO_2 concentrations within the soil solution, and the role of surface age and time of soil development in SIC accumulation would improve understanding of the role of soil forming factors in SIC accumulation. As more site-specific data are collected, we can refine these analyses in order to improve our ability to

predict the amount of SIC at a site. Other workers can use this information to help create

estimates of SIC concentrations throughout a watershed and better inform future models

of the global carbon cycle.

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