

Reactive Silica in Loess-Derived Soils of Central North America

By

Paul Eric Reyerson

A dissertation submitted in partial fulfillment of
the requirements for the degree of

Doctor of Philosophy
(Geography)

at the

UNIVERSITY OF WISCONSIN-MADISON

2012

Date of final oral examination: 11/30/12

The dissertation is approved by the following members of the Final Oral Committee:

Joseph Mason, Professor, Geography
John Williams, Professor, Geography
Erika Marin-Spiotta, Assistant Professor, Geography
James Burt, Professor, Geography
Sara Hotchkiss, Professor, Botany

© Copyright by Paul E. Reyerson 2012
All Rights Reserved

ACKNOWLEDGMENTS

The completion of the research described in the dissertation could not have been accomplished without the help, advice, and most importantly patience from many people. I owe a particular debt of gratitude to my advisor, Joe Mason, for his assistance in countless ways. His help with this dissertation was always forthcoming. Joe supplied necessary funding, equipment, and lab space. In addition, Joe was generous enough to allow me to borrow equipment for extended periods of time as I finished my research in Minnesota. Along with other collaborators, Joe collected several soil cores used in this dissertation. I would also like to thank Joe for providing feedback in other areas, such as grant writing and letters of recommendation.

I would also like to thank my other committee members for advice and encouragement. As a paleoecologist, Jack Williams supplied many useful concepts, especially in Chapter 4. Jack was kind enough to allow me to use his lab and equipment from time to time. He also allowed me to attend his weekly lab meetings while I was living in Madison. Jim Burt was instrumental behind many of the statistical approaches used throughout the dissertation. Erika Marin-Spiotta provided useful advice regarding biogeochemical cycles. Sara Hotchkiss has been a supportive faculty member from Botany. I must particularly thank Sara for first hiring me as a researcher and then for her patience while I finished my Ph.D.

I feel I owe a great debt of gratitude to my wife Karla, for her patience while I struggled through my Ph.D. career. Our first years of marriage were spent apart, while I finished my classwork and much of my research. Karla was always supportive despite research delays, an empty bank account, and even strange smells originating from the basement “lab”. Without her love I don’t think I could have persevered.

Henry Loope was always willing to lend a hand, both in the lab and the field. I am especially grateful for his help when digging soil pits. Richard Donohue, Colin Belby, and many other graduate students made Madison life much more enjoyable. Over the years Jim Knox provided advice from time to time, and I will miss chatting with him by the water fountain. Many landowners in Houston County were cooperative in my field efforts. Loredana Saccone and Erica Koning offered practical advice for chemical extraction techniques. Erica deserves special recognition for processing a few samples using her Si/Al automated method.

This research was supported by a National Science Foundation grant awarded to J. Mason, the Geological Society of America Charles A. and June R.P. Ross research award, and the University of Wisconsin-Madison, Department of Geography Luna Leopold geomorphology award. Travel to conferences was supported by two Geological Society of America travel grants, and the University of Wisconsin-Madison Graduate School Vilas travel grant.

.

TABLE OF CONTENTS

Acknowledgements	i
Table of Contents	iii
List of Figures	vi
List of Tables	vii
Abstract	viii
1. Introduction	1
2. A refined method for the determination of reactive silica in soils	8
2.1 Introduction	8
2.2 Methods	15
2.2.1 Establishment of minimum solubility	15
2.2.2 Soil Samples	17
2.2.2.1 Soil 1	18
2.2.2.2 Soil 2	21
2.2.2.3 Soil 3	22
2.2.3 Sample dissolution and measurement of silica concentration	23
2.2.4 Precision and accuracy	28
2.2.5 Determination of constraints for LE	29
2.2.6 Linear Extrapolation	32
2.3 Results	33
2.3.1 Sequential leaching of sediment samples	33
2.3.2 Sequential leaching of soil samples	36
2.3.3 Breakpoint identification (RSi depletion)	36
2.3.4 Comparison of predictive models	39
2.3.6 Analysis of depth profiles	41
2.3.6.1 Soil 1	42
2.3.6.2 Soil 2	45
2.3.6.3 Soil 3	45
2.3.6.4 Further comments on depth profiles	46
2.4 Conclusions	47
3. Reactive silica in loess-derived soils of central North America	50
3.1 Introduction	50
3.2 Study Region and Methods	53
3.2.1 Study soils	53
3.2.1.1 Nebraska soils	54
3.2.1.2 Minnesota soils	58
3.2.1.3 Wisconsin and Illinois soils	60
3.2.2 Analytical methods	62
3.2.2.1 Total RSi (alkali-extractable)	62
3.2.2.2 RSi greater than 10 μm (floatation-extractable)	63
3.2.2.3 RSi smaller than 10 μm (alkali extractable minus floatation-extractable)	65

	3.2.2.4 Pedogenic/shard RSi (oxalate-extractable)	66
	3.2.2.5 Particle size, organic C, and pH	68
3.3	Results	69
	3.3.1 RSi _{Tot} (alkali-extractable)	70
	3.3.2 RSi _{<10} (alkali extractable minus floatation-extractable)	74
	3.3.3 RSi _{>10} (floatation-extractable)	74
	3.3.4 RSi _{Ox} (oxalate-extractable)	76
3.4	Discussion	77
	3.4.1 RSi _{Tot}	77
	3.4.2 RSi _{<10}	84
	3.4.3 RSi _{>10}	87
	3.4.4 RSi _{Ox}	89
	3.4.5 Implications and Future Questions	91
3.5	Conclusions	92
4.	Forms and quantities of reactive silica across a prairie-forest ecotone in southeastern Minnesota, USA	94
4.1	Introduction	94
4.2	Methods	97
	4.2.1 Study area	97
	4.2.2 Study used for the study	104
	4.2.3 Analytical methods	106
4.3	Results	108
	4.3.1 RSi _{Tot}	109
	4.3.2 RSi _{<10}	109
	4.3.3 RSi _{>10} , BSi, NSi	112
	4.3.4 RSi _{Ox}	113
	4.3.5 Clay content	113
	4.3.6 Organic C	114
4.4	Discussion	114
	4.4.1 Comparison of soil orders	114
	4.4.2 Implications	119
4.5	Conclusions	120
5.	References	122
Appendix 1	Chapter 2 sediment sample sequential leaching data	152
Appendix 2	Chapter 2 soil sample [R _{rem}] _t data	153
Appendix 3	Chapter 2 soil sample RSi estimates	154
Appendix 4	Chapter 2 data point experiment results	155
Appendix 5	Chapter 3 soil descriptions	156
a.	8G00	157

b.	5G00	158
c.	3G00	159
d.	AL2	160
e.	KO1	161
f.	KA	162
g.	TQ	163
Appendix 6	Chapter 3 data sets	164
a.	8G00	164
b.	5G00	165
c.	3G00	166
d.	AL2	167
e.	KO1	168
f.	KA	169
g.	TQ	170
Appendix 7	Chapter 4 soil descriptions	171
a.	KL1	172
b.	KL3	173
c.	KO1	174
d.	NL	175
e.	AL2	176
f.	CA	177
g.	CAR	178
h.	OR	179
Appendix 8	Chapter 4 data sets	180
a.	KL1	180
b.	KL3	181
c.	KO1	182
d.	NL	183
e.	AL2	184
f.	CA	185
g.	CAR	186
h.	OR	187

LIST OF FIGURES

2.1	Dissolution curves	14
2.2	Volcanic glass content of nearby soil profile	21
2.3	Depiction of slight nonlinearity throughout dissolution curve	32
2.4	Sediment sample dissolution curves	33
2.5	Study soil dissolution curves	37
2.6	Estimates of cv_{Rep} for replicate samples	39
2.7	Soil profile RSi estimates	40
2.8	Repeatability of surface soil samples	41
2.9	Typical pattern of BSi content with depth	42
2.10	Comparison of RSi measurements	47
3.1	Maps of study soil locations	54
3.2	Soil profile data, absolute amounts	71
3.3	Soil profile data, relative amounts	73
3.4	Scatterplot of clay particle and $RSi_{<10}$ content	85
3.5	Scatterplot of clay particle and RSi_{Ox} content	90
3.6	Scatterplot of pH and RSi_{Ox}	91
4.1	Maps of study soils, soil orders, and pre-settlement vegetation	98
4.2	Soil order data	110
4.3	Scatterplot of clay particle versus RSi_{Tot} and $RSi_{<10}$ content	117
4.4	Scatterplot of clay particle versus RSi_{Ox} content	119

LIST OF TABLES

2.1	Sediment sample details	17
2.2	Study soil details	18
2.3	Study soil descriptions and particle size data	19
2.4	Soil sampling depths	20
2.5	Sediment sample LE data	35
2.6	Soil sample predictive model parameters and breakpoint times	38
3.1	Study soil characteristics	55
3.2	List of data gathered by other researchers	68
3.3	Soil profile RSi averages	69
3.4	RSi content of some common clay minerals	86
3.5	Predicted amounts of clay mineral-associated RSi	86
4.1	Soil order averages and t-test data	111

REACTIVE SILICA IN LOESS-DERIVED SOILS OF CENTRAL NORTH AMERICA

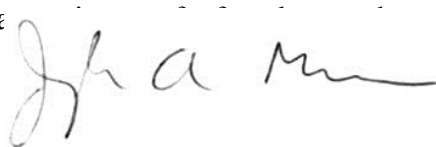
Paul E. Reyerson

Under the supervision of Professor Joseph Mason

At the University of Wisconsin-Madison

This dissertation explores the nature and occurrence of reactive silica (RSi) in soils. RSi is defined as any form of silica which exhibits solubilities greater than silicate minerals, and therefore is more susceptible to chemical breakdown and cycling in the soil weathering environment. To quantify soil RSi, a sequential leaching method was refined which allows for complete RSi extraction. Mineral silica contributions were subtracted from the RSi estimate by linear regression of data points following RSi depletion (breakpoint time). The use of six data points at 30 minute intervals from 150 to 300 minutes was found to produce results comparable to power models (which use points throughout the entire dissolution curve). Along with other methods which target certain RSi fractions, SLLE was then employed to investigate RSi forms and quantities in loess-derived soils of central North America. These methods revealed the presence of many forms including inherited, biogenic, and pedogenic RSi. In all soils studied, clay-sized RSi was the dominant form present, indicating a need for silica researchers to consider this neglected component. Clay-sized RSi was concentrated in illuvial horizons, suggesting a pedogenic origin for this fraction. Silt-sized RSi grains were common in surface horizons, typically as biogenic silica (BSi). If an inherited component was present, nonbiogenic, silt-sized RSi particles were most common in C horizons, suggesting losses due to weathering in upper horizons. These same methods were then used to explore differences in soils formed under forest

and prairie vegetation in southeastern Minnesota. Most differences were observed in eluvial horizons, possibly due to a shared early and mid Holocene vegetation history. Eluvial to illuvial horizon contrasts were more pronounced in Alfisols for clay content and total, clay-sized, and oxalate-extractable RSi, possibly due to less intense biocycling of silica under forest. In contrast, Mollisols contained slightly more total RSi as well as silt-sized RSi, although the variation within this soil order was greater. These results demonstrate that soil RSi is modified by vegetation, and that this modification can occur within a



CHAPTER 1. INTRODUCTION

Silica is a major component of most soil minerals, composing 28.8% on average (Wedepohl 1995). At the global scale, chemical weathering of terrestrial rocks and soils results in 5.6 ± 0.6 teramoles of silicon per year exported by rivers to the world oceans (Tréuger et al 1995). The main drivers of these exports from soils are weathering processes, both biotic (Derry et al 2005; Kidder & Gierlowski-Kordesch 2005) and abiotic (White & Blum 1995; Stonestrom et al 1998). Silica weathering has important implications for global climate, because chemical weathering of silicates and subsequent export to oceans leads to a net drawdown of atmospheric CO_2 over geologic time (Berner 1990; Street-Perrot & Barker 2008), and could potentially mitigate the effects of anthropogenic greenhouse gas emissions as a warmer global climate drives more rapid weathering (Lenton & Britton 2006).

Many forms of silica exist in soils, ranging from relatively stable primary and secondary crystalline minerals (quartz, feldspars, clay minerals, etc.) to more reactive fractions, which consist of amorphous and poorly ordered species (Sommer et al 2006). While all silica in the surface Earth system is ultimately derived from the weathering of crystalline silicates, primary and secondary minerals release silica into soil water relatively slow rates, and thus these forms can be thought of as a stable pool of silica. On the other hand, forms of silica which exhibit little weathering resistance due to chemical and/or physical properties tend to be quite mobile and modifiable in soils. Working in a Congolese rainforest, Alexandre et al (1997) calculated silica released from phytolith dissolution at approximately $54 - 70 \text{ kg ha}^{-1} \text{ yr}^{-1}$. By comparison, soil minerals released $20 - 22 \text{ kg ha}^{-1} \text{ yr}^{-1}$, despite being approximately 365 times larger than the phytolith pool. These “reactive silica” forms (RSi) supply the bulk of silica available for

biogeochemical cycling. Thus RSi is a very good candidate for study if the goal is to better understand the interplay of silica with the surrounding environment.

As with any biogeochemical cycle, the amounts and forms of RSi present, as well as movement within the pedosphere and biosphere, result from a dynamic interplay between abiotic and biotic processes. RSi, which is defined as forms of silica that exhibit solubilities greater than well-ordered clays and primary minerals, can be products of inheritance (emplacement along with the sediment in which the soil forms) or *in situ* pedogenic and biotic weathering processes. A result of sedimentary deposition, inherited RSi is common in Andisols (Niewenhuyse & van Breemen 1997; Cusack et al 2012; Marin-Spiotta et al 2012) and other soils with parent materials rich in RSi forms such as volcanic glass or cristobalite (Busacca et al 1992; Mason 1992; Mason & Kuzila 2000). Pedogenic and biotic weathering of primary and secondary minerals can produce a variety of forms such as biogenic silica (phytoliths, diatoms, sponge spicules), silica in or adsorbed to Al- and Fe-hydroxides, sesquioxides, and in poorly ordered clays such as allophane and imogolite (Sommer et al 2006; Saccone et al 2007; White et al 2012). Pedogenic weathering can also introduce silica into soil water solution, consisting of monosilicic and polysilicic acids, and complexes with inorganic and organic compounds (McKeague & Cline 1963a; Iler 1979; Tavakkoli et al 2011; Cusack et al 2012). Solubilities of silica forms generally decrease as crystalline ordering and density increase (Iler 1979). The presence of impurities, namely Fe and Al, are known to suppress the rate of dissolution of silica (Iler 1973; Beckwith & Reeve 1964).

Weathering of RSi leads to the buildup of altered forms as well as desilication. Preferential weathering of higher solubility RSi can minimize weathering of primary minerals (Hole & Nielsen 1968; Kelly et al 1998; Cusack et al 2012) as well as act as a buffer to acidity

(Hole & Nielsen 1968; Burke et al 1998; Kelly et al 1998; Sommer et al 2006). Diagenesis of RSi leads to progressively lower solubility forms, including short-range-order clays (such as allophane), secondary minerals, and eventually authigenic quartz formation (Drees et al 1989). Along with several other factors, the presence and quantity of RSi in soils can modify the formation of secondary mineral species formation (Folkoff & Meentemeyer 1987; Michalopoulos & Aller 2004; Barré et al 2009; Cusack et al 2012). Movement of silica within semiarid and arid soils can lead to silicification of horizons, including duripans (Flach et al 1969; Chadwick et al 1987; Chartres 1990; Kendrick & Graham 2004), fragipans (Karathanasis 1989), hard-setting soils (Chartres et al 1990), and even plow pans in certain cases (Brown & Mahler 1987). Chronosequence studies demonstrate silica losses over millennial timescales (Langley-Turnbaugh & Bockheim 1998; Brimhall et al 1991; Ziegler et al 2005), but this can be at least partially offset by intense biologic cycling which acts to move silica upward in the solum (Lucas et al 1993). Desilication has also been documented in Holocene-aged soils (as cited in Sommer et al 2006, Table 1).

The addition of diatomite (a form of RSi) to soils in the laboratory setting has been shown to alter soil physical properties, namely by increasing aggregate stability and plant available water content, as well as decreasing soil penetration resistance (Aksakal et al 2012). In Andic soils, volcanic glass and its weathering byproducts act to increase cation exchange capacity, primary productivity, and soil carbon sequestration (Torn et al 1997; Zehetner 2010; Cusack et al 2012; Marin-Spiotta et al 2012). Indeed, a positive relationship has been documented between short-range-order mineral abundance and soil carbon retention in Hawaiian soils (Torn et al 1997; Cusack et al 2012).

Silica is a beneficial nutrient for many plants (Epstein 1994; Epstein 2001; Ma 2003; Raven 2003). These benefits are many, including structural rigidity, increased photosynthesis rate and resistance to disease and insect herbivory, and minimization of water and nutrient stresses (Menzies et al 1992; Ma et al 2001). Silica fertilization for various crops has been shown to increase productivity, especially in highly weathered, acid soils (Korndörfer & Lepsch 2001; Tavakkoli et al 2011). Plant use of silica varies by species, between 0.1 and 10% of dry weight (Epstein 1999). Monosilicic acid availability is influenced by plant uptake, leaching, and adsorption/desorption reactions in the soil (McKeague & Cline 1963a, b; Beckwith & Reeve 1963, 1964; Tavakkoli et al 2011).

Recent studies have shown the importance of vegetation in soil silica cycling (Alexandre et al 1997; Markewitz & Richter 1998; Blecker et al 2006). In many ecosystems, vegetation can control the rate of silica output to streams (Watteau & Villemin 2001; Derry et al 2005; Farmer et al 2005). Biocycling by plants can act to maintain soil silica at much higher levels than otherwise would be expected when considering purely geochemical processes (Lucas et al 1993; Kelly et al 1998). Plant use of silica can similarly lead to the buildup of biogenic silica (BSi) pools in soils (Meunier et al 1999; Henriot et al 2008). Recent studies have suggested that encapsulation of organic matter within phytoliths during the formation process could serve as a viable means to sequester atmospheric CO₂ (Parr & Sullivan 2005, 2011; Sullivan & Parr 2007; Parr et al 2009; Parr et al 2010). However, other findings suggest that phytolith C is of a nonphotosynthetic origin, thus limiting its usefulness as a sequestration mechanism (Santos et al 2010; Santos et al 2012). At the global scale, the rise of grasslands and subsequent increased biocycling of silica during the Miocene may have led to adjustments to the flux of silica to the world oceans, which has important implications for diatom productivity (Kidder & Gierlowski-

Kordesch 2005). The amount of biogenic silica present in soils is spatially variable, but in general it is a function of the rate of chemical weathering (Alexandre et al 1997), mineral composition (Dahlgren et al 1989; Meunier et al 1999; Henriot et al 2008), plant species, and biologic uptake (Kelly et al 1998). Solubilities of BSi vary depending upon species (Bartoli & Wilding 1980), but in general they are higher than most primary and secondary minerals.

Plants (and microbiota) can increase chemical breakdown and mobility of RSi by altering the chemistry of the rhizosphere, by introducing respired CO₂ as well as organic acids (Drever 1994; Kelly et al 1998), which act to lower overall soil pH and increase desilication (Drever 1994). Humic and fulvic acids, which represent the end product of biomass decomposition, can have similar effects (Ugolini & Sletten 1991). The plant effect on weathering is most important in O and A horizons, as well as the rhizosphere (van Breemen et al 1993), and their influence decreases with depth. Further, removal of nutrient base cations (Mg, Na, Ca) by plant uptake and leaching can also lead to increased acidity and RSi mobility (Richter & Markewitz 2001).

Anthropogenic disturbance also influences the quantities, distribution, and forms of RSi present in soils. Over the course of approximately 50 yr, logging of plots in Hubbard Brook Experimental Forest led to a redistribution of amorphous silica (ASi) to lower horizons, possibly due to a cessation of biocycling (Conley et al 2008; Saccone et al 2008). Despite the significant mobilization of ASi within these soils, whole-profile losses were not observed. Over the course of centuries, continued land use can lead to the depletion of ASi and pedogenic RSi (Clymans et al 2011b).

A fundamental challenge to the understanding of the nature and occurrence of RSi in soils is the lack of a suitable method which can extract and measure all forms of RSi. Chemical extraction methods are preferred over the more traditional floatation technique, since the latter

cannot measure all clay-sized RSi grains and coatings. Several chemical extraction methods exist in the literature, and no one is universally accepted. Of these methods, alkali extraction using 0.1 M Na₂CO₃ is the most popular, but studies show that it cannot fully remove all forms of RSi (Schlüter & Rickert 1998). Other studies have utilized various molarities of NaOH, but this has generally been avoided because this solvent induces mineral silica dissolution to a greater degree. In Chapter 2 of this dissertation I describe a refined chemical extraction technique which uses 0.5 M NaOH and a mineral correction described in DeMaster (1979, 1981). Termed sequential leaching with linear extrapolation (SLLE), I demonstrate that this refined method is able to fully extract all forms of RSi with solubilities greater than or equal to laboratory grade diatomite (a reasonable proxy for lower solubility forms of RSi). I then show that DeMaster's mineral correction approach yields similar RSi estimates as power models used in other studies (Koning et al 2002).

Recent studies have made advances by using elemental ratios and/or stable isotope ratios to yield information regarding fractions (Koning et al 2002; Kurtz et al 2002; Derry et al 2005; Ziegler et al 2005; Cornelis et al 2010a; White et al 2012). A more cost-effective and simple approach is to use lower-technology methods such as SLLE, and each of these has benefits and drawbacks. For example, the traditional floatation technique is ideal for morphological analysis of grains, but as mentioned above it cannot fully extract all sizes of RSi. On the other hand, SLLE is able to extract all sizes of RSi, but it cannot distinguish between forms. Other chemical dissolution techniques utilizing weaker alkalis and acids are thought to specifically target certain RSi fractions, but of course morphological analysis is not possible. To overcome the limitations of any one method, the use of several techniques in tandem can yield valuable information regarding the characteristics of RSi in soils. In Chapters 3 and 4 of this dissertation, I first apply

the SLLE technique to measure total RSi in a series of loess-derived soils. I then use floatation and an acid dissolution technique to identify several fractions, including biogenic silica, inherited, and pedogenic forms. With the use of particle size data, I also describe a simple way to estimate the proportion of total RSi in each particle size class.

While the same methods are applied for both Chapters 3 and 4, the goals are different. The purpose of Chapter 3 is to investigate changes to RSi quantities and forms within and across soils, which has never been attempted. In this chapter I demonstrate that RSi inheritance is an important factor to consider, and that while biogenic silica (phytolith production) is the main component of silt-sized grains, the vast majority of RSi exists in the clay-sized realm. Chapter 4 focuses on the prairie-forest ecotone of southeastern Minnesota to determine how vegetation affects soil RSi. RSi quantities and fractions are measured in soils formed under forest and prairie, and these are compared. The results of Chapter 4 demonstrate that slight differences exist between prairie and forest soils. These differences most likely stem from the young age of the ecotone, which was established within the last 34000 yr. Further, all soils showed nearly identical RSi patterns below 40 cm, which may indicate a legacy effect from the widespread early Holocene deciduous forest which covered the region.

CHAPTER 2. A REFINED METHOD FOR THE DETERMINATION OF REACTIVE SILICA IN SOILS

2.1. Introduction

Given the many ways in which reactive silica (RSi) can influence the biogeosphere (Chapter 1), it is important to measure its quantity in soils. RSi in soils is more soluble than most primary and secondary minerals (Drees et al 1989), and thus it can account for most short-term biogeochemical cycling of silica. Nonbiogenic RSi (NSi) forms arise from *in situ* weathering processes including silica in solution, amorphous precipitates and coatings, short range order clays, and silica adsorbed to metal oxyhydroxide, mineral grain, and organic matter surfaces. NSi can also originate from inheritance (emplacement in sediment in which the soil is formed), and examples include volcanic glass and cristobalite (Drees et al 1989). Biogenic RSi (BSi) is mostly composed of plant-produced phytoliths, but can also include silicified diatom and microorganism exoskeletons (Sommer et al 2006). Particle sizes of RSi can range from clay-sized grains and coatings to several dozens of micrometers. By definition, the solubility of RSi is higher than that of well-ordered primary and secondary minerals. Nevertheless, measured RSi solubilities can vary considerably depending upon particle size, degree of crystallinity and the presence of adsorbed ions (Drees et al 1989).

In this chapter I describe an RSi estimation technique which is a refinement of the DeMaster method (DeMaster 1979; 1981). This chemical extraction method dissolves all forms of RSi and it is measured colorimetrically through time (sequential leaching). Mineral silica contamination is removed from the RSi estimation through the use of a linear regression model.

Several refinements have been made to the dissolution and measurement steps, including the use of 0.5 M NaOH and the more rigorous control of pH during the color development process. The timing and number of data points used in the linear regression model have been adjusted to provide a balance between precision and ease of use. Sequential leaching experiments using various forms of relatively pure silica as well as soil samples have allowed for the characterization of the forms of silica which contribute to RSi.

Using a variety of methods, many forms of RSi have been targeted for measurement in soils, including phytoliths (e.g. Bartoli 1983; Blecker et al 2006), dissolved silica (DSi; Richter & Markewitz 2001; Cornelis et al 2010b), volcanic glass (Yamada & Shoji 1990), pedogenic silica (Kelly et al 1998; Saccone et al 2007), and short range order clays (Wada 1989; Kodama & Ross 1991; Follett et al 1965). Yet it is only recently that researchers have attempted to quantify total RSi in soils (Saccone et al 2007; Cornelis et al 2011). The results of those studies demonstrate that the quantities and composition of RSi can be highly variable across the landscape as factors of soil formation change.

Recent advances in our understanding of the silica cycle have highlighted the need to account for total RSi in soils, yet many of the more popular methods employed were designed to target and extract specific fractions. Quantification of total RSi is especially problematic, in that a single method must be sensitive to the broad physical and chemical properties of RSi, yet be robust enough to filter out contamination from undesired forms.

The floatation technique has been widely used to quantify one or more fractions of soil RSi (Blecker et al 2006; Borelli et al 2010). This method physically separates lower density RSi forms from more heavier crystalline fractions. By mechanically extracting RSi unaltered from the sample, this a good method for identification of specific types of RSi using particle

morphology. However floatation cannot remove RSi particles smaller than 2-20 μm (depending upon the approach used) due to clay mineral interference (Piperno 2006), nor can it account for dissolved silica or RSi coatings on mineral grain surfaces (Saccone et al 2007). Taken together, these fractions can make up a sizeable proportion of the total RSi pool (Jones & Beavers 1964a; Wilding & Drees 1971, 1974; Bartoli & Wilding 1980).

X-ray diffraction is a technique that has lost popularity due to time-consuming procedures (Goldberg 1958; Eisma & van der Gaast 1971). Moreover, x-ray diffraction may overestimate the true RSi fraction in samples, although the exact reason is unknown (Conley 1998).

Infrared spectroscopy has been successfully used to quantify biogenic silica (BSi) in marine and lacustrine sediments (Bailey-Watts 1976; Chester & Elderfield 1968). Further modifications have allowed for BSi measurement even in quartz-rich sediments (Fröhlich 1989), although this technique cannot be used if the ratio of RSi to quartz is less than 3:1 (Leinen 1977). Hence, infrared spectroscopy may not be applicable to soil RSi measurements due to the varying chemical composition of the material. Further, sample particles must be 2 μm or smaller, which requires aggressive grinding. It has been demonstrated that overgrinding of samples can disrupt clay minerals and create new reactive layers, which can potentially lead to an overestimation RSi (Müller & Schneider 1993).

In recent years, Fourier transform infrared spectroscopy (FTIS) has emerged as an advancement of standard infrared spectroscopy (Vogel et al 2008). FTIS offers the advantage of being able to measure multiple sediment or soil constituents at one time with good accuracy. Recent papers have used FTIS to simultaneously measure total organic and inorganic carbon along with BSi in lake sediments (Vogel et al 2008; Rosén et al 2010). Further, FTIS is able to

distinguish subtle characteristics in RSi molecules. Absorption of differing IR wavelengths corresponds to various types of chemical bonds. For example, hydroxyl groups can be detected, which can aid in determining the form of RSi present.

Chemical extraction methods, which dissolve and measure silica concentration in solution (Sauer et al 2006), are able to measure all forms and sizes of RSi of a given solubility (depending on the method used), and they are broadly applicable to most sediments. However, chemical extraction by itself is nonspecific, in that the solvents used can induce dissolution of all silica forms. Thus, if the goal is to selectively measure RSi, then corrective measures must be implemented to minimize the influence of undesirable fractions.

To avoid mineral silica dissolution, some researchers have used weak acids such as oxalic, acetic or dilute hydrochloric, which are thought to leave lower-solubility crystalline forms relatively intact (Beckwith & Reeve 1963; Wada 1989; Kodama & Ross 1991; Kelly et al 1998; Snyder 2001; Sauer et al 2006; Saccone et al 2007; Tavakolli et al 2011). The purpose of acid extractions is to target several pedogenic RSi fractions, including dissolved, exchangeable, and adsorbed silica, sesquioxides, and short-range-order clays. However, these weak acids cannot dissolve particulate amorphous silica forms including BSi, glass, and cristobalite.

Several studies have used alkali solvents instead of acids, based on the knowledge that silica dissolves much more rapidly at pH >9 (e.g. Jones 1969; DeMaster 1981). Sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) are the most popular choices for alkali solvents (Foster 1953; Follett et al 1965). Alkali digestion was developed in the soil sciences as a way to remove amorphous silica and alumina coatings on clay minerals for XRD analysis (Jackson et al 1949; Foster 1953; Whittig 1954; Hashimoto & Jackson 1958; McKyes et al 1974). In turn, alkali dissolution was adapted for the direct measurement of RSi in sediments

(Segalen 1968; Jones 1969). Since these pioneering studies, alkali dissolution has been adapted to a variety of sediments, including terrestrial (Saccone et al 2006; Saccone et al 2007; Saccone et al 2008; Melzer et al 2010; Cornelis et al 2011), lacustrine (Rippey 1983; Flower 1993), and marine (DeMaster 1979, 1981, 1991; Landén et al 1996; Koning et al 1997; Koning et al 2002; and many others).

Visible light spectrophotometry (colorimetry) is widely used to measure silica concentration (Saccone et al 2007; Saccone et al 2008; Melzer et al 2010) as well as inductively coupled plasma spectrometry (Swann 2010; White et al 2012).

Alkali solutions effectively dissolve all forms of RSi; however, these solvents also induce mineral silica dissolution. This problem has been solved via two very different approaches. First, similar to acid dissolution techniques, single-extraction methods tailor alkali solvent molarities (and thus pH) to avoid mineral silica dissolution (Mortlock & Froelich 1989). The assumption is made that higher solubility forms will undergo dissolution in the presence of a weak alkali solvent, while mineral silica dissolution is minimized. However, solvent molarity, temperature, and digestion time must be carefully tailored to avoid mineral silica dissolution, which requires precise knowledge of the mineralogical content of the sample. In many cases the single extraction technique can lead to an overestimation of the true RSi fraction (Gehlen & van Raaphorst 1993). Indeed, single extraction techniques may not be suitable to soils due to the complex variety of RSi forms they contain.

The second approach, sequential leaching (SL), differentiates RSi from mineral fractions by focusing on the rate of silica dissolution through time (Follet et al 1965; Segalen 1968; McKyes 1974; DeMaster 1979, 1981). A critical assumption is that easily dissolvable RSi will be quickly depleted early in the procedure. Because the rate of silica released into solution is

directly proportional to the remaining solid mass of RSi, rapid depletion will produce distinct nonlinearity in plots of cumulative silica dissolution vs. extraction time. In contrast, low-solubility mineral silica (MSi) will dissolve slowly, without appreciably depleting the remaining mass of mineral silica, producing an apparently linear trend in silica released over time. Thus, cumulative silica dissolution (dissolution curve, Fig. 2.1a) can then be parsed into nonlinear (RSi) and linear (mineral silica or MSi) fractions through the use of a predictive model.

Many versions of SL employ weak alkali media, such as 0.1 M Na_2CO_3 (pH = 11.2). This solvent is used primarily to target higher solubility RSi forms such as phytoliths and diatoms while minimizing MSi release (DeMaster 1981; Saccone et al 2007; Saccone et al 2008). However, the use of such a weak base cannot fully dissolve lower-solubility forms such as adsorbed silica, nor can it fully avoid at least some mineral silica contamination (Hashimoto & Jackson 1958; Eggimann et al 1980; Gehlen & van Raaphorst 1993; Schlüter & Rickert 1998; Kamatani & Oku 2000; Saccone et al 2008). Therefore, it is not an appropriate solvent if the goal is to fully measure total RSi. Stronger bases have been used in the soil sciences to fully remove lower solubility RSi, of which 0.5 M NaOH (pH = 13.7) is the most popular (Hashimoto & Jackson 1960; Follett et al 1965; Jones 1969; Saccone et al 2007). Müller & Schneider (1993) found that 0.5 M NaOH was able to remove lower solubility RSi forms completely. Hence, the use of 0.5 M NaOH is the preferred solvent to dissolve all forms of RSi.

Two predictive models have been implemented to remove MSi interference when using SL. Linear extrapolation (LE) predicts RSi content by using least-squares regression to fit a straight line to the linear portion of the dissolution, representing mineral forms of silica. This line is then extrapolated back to time 0, where the offset from zero silica indicates the RSi amount (Fig. 2.1b). In other words, the y-intercept (b_0) represents the offset of the MSi curve generated by RSi. LE benefits from its ease of use, since data points are only needed from the linear portion

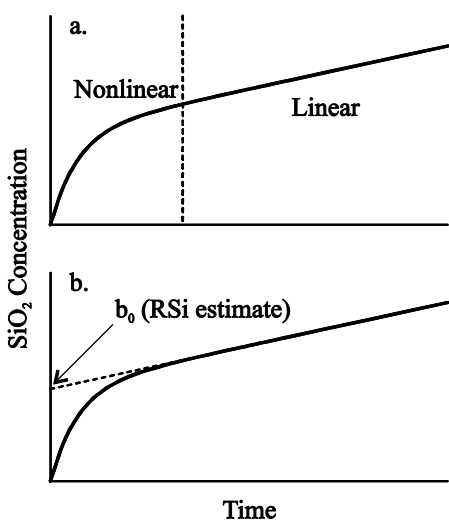


Figure 2.1. Dissolution curves, depicting cumulative silica concentration through time. Nonlinear and linear portions are shown in a. Linear extrapolation determination of the RSi estimate (b.)

of the curve. This model has been applied successfully to marine sediments (e.g. DeMaster 1981) as well as soils to a much more limited extent (Saccone et al 2007; Saccone et al 2008). Power models (PM) have also been utilized successfully to predict RSi (Koning et al 1997; Koning et al 2002; Saccone et al 2007). PM fits models representing the kinetics of RSi and various clay minerals to data obtained throughout the entire dissolution procedure. In theory, this approach should yield the most accurate estimate of RSi, but it requires either detailed knowledge of clay mineral dissolution kinetics for a particular type

of sample, or simplifying assumptions which may reduce the advantages of this approach. PM is typically used with automated systems which gather hundreds to thousands of data points for each dissolution procedure. I will demonstrate below that this model can be applied successfully to far fewer data points gathered using manual techniques, but this is still not practical for routine analysis. A strictly comparative study of LE and PM has not been attempted to date.

SL has been refined for use with manual and automated systems. In the case of automated systems, aliquots are drawn off at short intervals over the course of the procedure (Müller & Schnieder 1993; Koning et al 1997; Koning et al 2002), which makes them ideal for PM. Due to a large number of data points gathered, automated SL allows for greater precision (Müller & Schnieder 1993). On the other hand, manual SL, which typically uses LE, utilizes only a handful of points over the course of several hours. However, the precision of manual SL remains largely unexplored.

Hence, manual SL using 0.5 M NaOH and linear extrapolation (hereafter referred to as SLLE) may offer the most efficient and cost effective option to accurately and precisely measure RSi in soils. However, no study has applied this method for the express purpose of measuring RSi in whole-soil samples. The primary goal of this paper, therefore, is to describe a refined SLLE for use in soils.

2.2 Methods

2.2.1 Establishment of Minimum RSi Solubility

SLLE relies on the assumption that the early, nonlinear portion of the dissolution curve is dominated by RSi dissolution. That is, all forms of RSi are soluble enough that they rapidly deplete during the early part of the dissolution procedure, so the quantity dissolved per unit time decreases and leads to a nonlinear dissolution curve. Given the myriad of silica forms and solubilities in nature (Follett et al 1965; Drees et al 1989; Sauer et al 2006), it is difficult to determine which forms of silica actually exhibit such behavior. However, if a given form of

silica displays nonlinearity, then all forms with equal or greater solubility should also display nonlinearity. The establishment a minimum solubility at which nonlinearity occurs is then possible, allowing for inferences to be made regarding the most likely forms which contribute to the RSi estimate for a given sample.

Establishment of minimum solubility was accomplished experimentally by dissolving various forms of relatively pure forms of silica in 0.5 M NaOH (Table 2.1), and observing the degree of nonlinearity and the time at which nonlinearity ceased. Both of these variables are linked to solubility. One sample in each of the five sediment types was processed except for diatomite, for which three samples were analyzed. These sediment types were chosen to serve as analogs for forms of RSi commonly found in soils. Reagent grade silica gel 60 was used as an analog for very high solubility amorphous coatings and gels formed in soils (Table 2.1). Given that the silica gel is nearly pure, this sample also allows testing of the efficacy of the SL technique. That is, the amount of silica extracted and measured should equal the weight of the silica gel sample. The diatomite sample consists mostly of crushed diatom frustules and a cementing amorphous silica matrix. Diatomite forms in marine sediments, but because it consists almost entirely of biogenic silica, it can serve as reasonable substitute for biogenic silica (BSi) in soils. The next type was taken from an outcrop of the White River Group in western Nebraska, consisting mostly of fine-grained Oligocene-aged volcanoclastic silts and rhyolitic to andesitic ash (Swinehart et al 1985). Thus, the White River Group (WRG) sample is intended to represent inherited forms of RSi in soils such as volcanic glass. An illitic clay was also procured from the upper member of the Decorah Shale formation in east-central Minnesota. The sample is composed largely of illite, although carbonate fossils are common (Ludvigson et al 1996). Finally, a sample of fine- to medium-grained quartz sand derived from Ordovician-aged St. Peter

Sandstone was collected from east-central Minnesota. The sand is composed almost entirely of quartz (>99%; Thiel 1935). The illite and quartz sand samples act as analogs for secondary and primary minerals in soils, respectively.

Table 2.1. Sediment sample details.

Silica Form	Characteristics of Source	Location
Silica gel	Alfa Aesar, 19-37 μm	-
Diatomite	MP Biomedicals, acid washed, <100 μm , 92.5% silica	-
Volcaniclastic sediment	White River Group: Volcaniclastic siltstone and ash, fine grained ¹	41.30°N, 102.12°W
Illite Clay	Decorah Shale Formation: Illite clay with some carbonates ²	44.92°N, 93.11°W
Quartz Sand	St. Peter Sandstone Formation: Sand, fine to medium grained, 99.44% quartz ³	44.92°N, 93.11°W

¹Swinehart et al (1985); ²Ludvigson et al (1996); ³Thiel (1935).

2.2.2 Soil Samples

Although the sediment samples described above should represent the dissolution characteristics of individual silica forms, soils may display different patterns given that they combine multiple composites of a variety of silica fractions. Soil samples were next procured to determine their dissolution characteristics and to determine the constraints necessary for linear extrapolation. Three soils formed in loess were analyzed (Table 2.2). These soils were selected primarily based upon expected RSi amounts, but vegetation type and degree of weathering were important factors as well. Each soil is briefly described here, focusing on important factors which may influence RSi including inherited forms from parent material, dominant natural vegetation, and degree of pedogenic development. All three soils were formed in stable upland settings with <2% slopes. The three soils were sampled either by hydraulic push core (1 and 2) or outcrop (3). Soils were described by genetic horizon (Table 2.3) using standard soil survey methods (Soil

Survey Staff 1993). Four samples were collected for each soil to approximately 50 cm, at depths generally corresponding to soil horizons (Table 2.4). Samples represent a composite of material collected within 5 cm of the sampling depth. Three replicates of each of the surface samples were processed in order to gauge precision. Due to their thickness, the A horizons for Soils 1 and 2 were split into two samples.

Table 2.2. Location, climatic, and vegetation data for study soils.

Soil	Location	Precipitation, mm ¹			Temperature, °C ¹			Dominant Vegetation ²
		<i>Annual</i>	<i>January</i>	<i>July</i>	<i>Annual</i>	<i>January</i>	<i>July</i>	
1	41.51°N, 99.45°W	585	10.9	91.9	8.2	-6.2	22.6	Mixed grass prairie
2	43.56°N, 92.21°W	888.8	24.9	119.6	8.8	-4.2	22.8	Tall grass prairie
3	39.53°N, 92.51°W	906.5	40.6	85.6	11.2	-3.9	24.4	Deciduous broadleaf forest

¹Normalized 1971-2001. Climate data from NOAA Staff 2002. ²Vegetation data from Gröger (1973); Marschner (1974); and Zawacki & Hausfater (1969) for Soils 1, 2, and 3, respectively.

2.2.2.1 Soil 1

Soil 1 is a Mesic Pachic Argiustoll from central Nebraska, immediately east of the Sand Hills. The upper 50 cm consists of the uppermost Brady Soil, a paleosol which formed in late Pleistocene-aged Peoria Loess (Schultz & Stout 1945; Johnson & Willey 2000), and the modern soil, which formed in Holocene-aged Bignell Loess (Mason et al 2003). Sediments for both the Peoria and Bignell Loess originated from the nonglaciogenic erosion of the Oligocene-aged White River Group and other rocks and sediments to the west and northwest of the sampling site (Aleinikoff et al 1998; Mason 2001). Sediments in the White River Group contain an average of 53% rhyolitic/andesitic volcanic glass (Swinehart et al 1985). After deflation from their source to the west, these sediments were temporarily trapped in dunes and then remobilized and deposited

Table 2.3. Descriptions and particle size data for soils used in this study. Horizon designation and descriptive terminology is based on Soil Survey Staff (1993). The soil descriptions use the following format: "Color, texture, structure, moist consistence, lower boundary, effervescence. Other features." A glossary of the abbreviations used is listed below this table. Descriptions and particle size data are from J. Mason, unpublished data (soil 1), Mason (1992) (soil 2), Mason & Jacobs (1998) (soil 3).

	Soil (Horizon depth, cm)	Depth (cm)	Particle Size %	
			Clay	Silt/Sand
Soil 1	A 1 (0-24)	7.5YR 3/1, sil, 1 f _{sbk} ptg. to 1 f _{gr} , ns, c, eo.	22.81	77.20
	A 2 (24-45)	7.5YR 3/1, sil, 1 f _{sbk} ptg. to 2 f _{gr} , ns, c, eo.	29.09	70.91
	A 1b (45-55)	7.5YR 2/1, s _{icl} , 2 f _{sbk} , ns, c, eo.	33.03	66.97
Soil 2	Ap (0-21)	10YR 2/1, sil-s _{icl} , 1 m _{sbk} ptg. to 1 f _{sbk} - 1 f _{gr} , fr, a, eo.	27.12	72.88
	AB (21-39)	10YR 3/2-4/2, s _{icl} , 1 m _{sbk} ptg. to 1 f _{sbk} , fr, c, eo. Some distinct areas of 10YR 4/4-4/3.	29.69	70.31
	Bt1 (39-58)	10YR 5/3, s _{icl} , 2 m _{sbk} , fr, g, eo. Many thin continuous 10YR 4/2 coatings on ped faces. Few very thin very patchy silans on ped faces.	29.85	70.15
Soil 3	A (0-13)	10YR 4/2-3/2, sil, 1 f _{sbk} ptg. to 1 v _{fgr} , v _{fr} , a.	15.55	84.45
	E (13-20)	10YR 5/3, sil, 2 f _{&m_{sbk}} , fr, c.	18.39	81.61
	BE (20-28)	9YR 5/4, sil, 2 f _{&m_{sbk}} , fr, c. 10YR 5/3 silans.	23.51	76.49
	Bt1 (28-50)	10YR 4/4, s _{icl} , 3 m _{&f_{sbk}} , fi, g. Many thin continuous 10YR 4/4 on ped faces.	38.54	61.46

Abbreviations Used:

<i>Texture</i>		<i>Moist Consistence</i>	
s _{icl}	silty clay	f _i	firm
	loam	f _r	friable
sil	silt loam	ns	not specified
		v	very
<i>Structure</i>		<i>Lower Boundary</i>	
1	weak	a	abrupt
2	moderate	c	clear
3	strong	g	gradual
f	fine		
m	medium		
gr	granular	<i>Effervescence</i>	
s _{bk}	subangular	eo	none
	blocky		

as loess further downwind during subsequent times of dune activity (Mason 2001; Mason et al 2003). Volcanic glass content varies with depth in Soil 1 due to changes in loess provenance through time. Sand- and silt-sized volcanic glass peaks in the deep Peoria Loess, followed by a decrease throughout the Brady Soil, and finally increases again into the Bignell Loess (Fig. 2.2; Jacobs & Mason 2007). It was not possible to identify clay-sized glass shards, but the amount present presumably correlates to the patterns observed in the sand and silt fractions.

Table 2.4. Soil sample depths in cm and genetic horizons (in parentheses). Two horizons are listed if sampling crossed horizon boundaries. Three replicates each of the surface samples were processed.

Sample	Soil 1	Soil 2	Soil 3
1	0-10 (A1)	0-10 (Ap)	0-13 (A)
2	10-20 (A1)	10-22 (Ap)	13-20 (E)
3	20-30 (A1/A2)	22-35 (AB)	20-28 (BE)
4	40-50 (A2/A1b)	44-58 (Bt1)	28-50 (Bt1)

Brady Soil formation is documented to have occurred between about 14 and 11 cal yr BP (Johnson & Willey 2000; Mason et al 2003; Miao et al 2007; Mason et al 2008; Muhs et al 2008) followed by

episodic burial by Holocene-aged Bignell Loess (Mason et al 2003). Illuvial clay coatings found within and beneath the Brady Soil at some sites indicate that pedogenic processes were active at that time due to a wetter climate. No illuvial coatings have been documented at this site in the modern soil, presumably due to a shift to a drier climate in the early Holocene (Jacobs & Mason 2007).

Paleoecological records are scarce for the region surrounding Soil 1, but regional reconstructions show that open aspen and spruce parkland was present throughout the central Great Plains for most of the late Pleistocene and even into the earliest Holocene (Fredlund 1985; Rousseau & Kukla 1994; Johnson & Willey 2000). Warmer and drier conditions of the Holocene favored grassland which has persisted to modern times (Grüger 1973). Extensive use of silica by grassland vegetation has probably transformed a significant amount of inherited RSi into phytoliths. Soil 1 has never been cultivated, according to the long-time landowner.

2.2.2.2 Soil 2

Soil 2 is a Mesic Typic Hapludoll located in southeastern Minnesota. Loess deposited at this site originated mostly from the region immediately to the west (Mason 1992; Mason & Nater 1994; Mason et al 1994), which includes pre-Illinoian till of the Iowan Erosion Surface (Ruhe 1969), and late Pleistocene Wisconsinan till from the Des Moines Lobe (Mason 1992). A large component of Des Moines Lobe sediments originated from the northern Great Plains, which contains material reworked from the Cretaceous Pierre Shale (Gill & Cobban 1973; Jones & Blatt 1984; Lusardi et al 2011). Beds within the Pierre Shale on the northern Great Plains contain large amounts of cristobalite in the silt fraction (up to 70%), and probably significant amounts of clay-size grains as well (Jones & Blatt 1984). Cristobalite is a poorly crystallized form of silica, which tends to exhibit solubilities between amorphous silica and quartz (Drees et al 1989). Glacial erosion and transport, combined with subsequent eolian deflation and sorting may have produced even smaller cristobalite grains in Soil 2. These grains probably exhibit large surface area to volume ratios, thus making them possible RSi sources. Cristobalite has been identified in

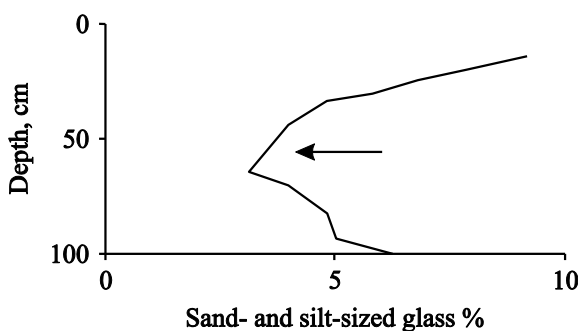


Figure 2.2. Sand- and silt-sized volcanic glass content of a soil sampled nearby to Soil 1. Arrow denotes the top of the Brady Soil at this site. The Brady Soil was encountered at a depth of 45 cm for Soil 1. Data are from Jacobs & Mason (2007).

the loess deposits that form the parent material of Soil 2, but its abundance is not known (Mason 1992).

Just prior to Euro-American settlement, vegetation at Soil 2 was mixed prairie and oak savanna (Marschner 1974; Minnesota DNR Staff 2009). The site is near the prairie-forest ecotone which was constantly shifting

throughout the Holocene (Grimm 1983, 1984; Baker et al 2002); therefore, vegetation ranging from prairie to closed forest may have affected development of this soil. Soil 2 is currently cultivated and probably has been since the nineteenth century.

2.2.2.3 Soil 3

Soil 3 is a Mesic Typic Hapludalf from west-central Illinois. This soil was formed in calcareous Peoria Loess, which was deposited mostly between 28,000 and 12,000 cal. yr B.P. (Hansel & Johnson 1996). The loess originated mostly from valley-train deposits from the Illinois River Valley (Frye et al 1968; Grimley et al 1996), and loess deposition coincided with the westward advancement of the Lake Michigan and Lake Erie lobes (Frye et al 1968). Lake Michigan lobe glacial till is composed primarily of Devonian and Mississippian shales and to a lesser extent Silurian dolomite (Willman & Frye 1970). Similarly, Peoria Loess deposited on the Illinois River bluffs is high in illite content, reflecting the sedimentary origin (Frye et al 1968). Thus, the inherited RSi component from local dust sources in this soil was expected to be small.

On the other hand, evidence for far-travelled, fine dust has been documented in this soil (Mason & Jacobs 1998). This fine dust is thought to originate from regions as far west as the Great Plains, and therefore it may contain significant amounts of RSi, similar to Soil 1. The timing of deposition of this fine dust may have occurred throughout the final phase of loess aggradation, or later in the Holocene. As will be shown in Chapter 3, very little RSi was found within the C horizon of this soil, below the depths where Mason and Jacobs (1998) found evidence of fine dust addition.

Vegetation consists of hardwood forest (Zawacki & Hausfater 1969), and the preservation of a thin A horizon over a light-colored E horizon indicates the site has not been plowed (Mason & Jacobs 1998).

2.2.3 Sample Dissolution and Measurement of Silica Concentration

Samples were dried in an oven at 50°C, and then crushed and homogenized using a mortar and rubber pestle. Flower (1993) found that oven drying above 50°C introduced severe fragmentation of diatoms in sediment samples. Of course, fragmentation of RSi is not a main concern since it will be dissolved regardless. However, fragmentation of crystalline forms and the creation of high reactivity surfaces is a possibility, which in turn could lead to overestimation of RSi (Müller & Schneider 1993).

Previous studies have tested the validity of pretreatment with dilute HCl (Mortlock & Froelich 1989; Landén et al 1996), which increases the surface area of RSi available for alkali attack by removing adsorbed metal, organic, and carbonate ions (Stumm & Morgan 1970; Saccone et al 2007), thereby increasing the overall dissolution rate (Hurd 1973). Chemical pretreatment also removes loosely bound silica from Al and Fe (Koning et al 2007), which are known to retard silica dissolution (Bickmore 2006). Further, pretreatment offers a way to release silica bound in sesquioxides, which are unreactive with alkali solvents (Jones & Handreck 1963; Follett et al 1965; Wada & Greenland 1970). Many studies have reported higher silica values when HCl pretreatment is used prior to alkali dissolution (Hurd 1973; Mortlock & Froelich 1989; Landén et al 1996; Michalopoulos & Aller 2004; Saccone et al 2006), although one did not (Saccone et al 2007).

On the other hand, chemical pretreatment can remove octahedral layers in clay minerals, thereby exposing silica in tetrahedral layers (Foster 1953; Eggimann et al 1980; Landén et al 1996). Chemical pretreatment can release silica which would otherwise be shielded from chemical attack, thereby overestimating the true RSi pool. Therefore chemical pretreatment was not used.

Samples of 12 to 20 mg were immersed in 500 ml alkali solvent which yielded solid-solution ratios of 0.024 to 0.04 mg ml⁻¹. These ratios are considerably lower than the ranges recommended by other studies (Gehlen & van Raaphorst 1993; Loassachan & Tada 2008; Clymans et al 2011a). Those studies, along with others, found that silica dissolution rates were suppressed when higher solid-solution ratios were used (Hashimoto & Jackson 1958; Flower 1993; Gehlen & van Raaphorst 1993; Landén et al 1996). This may be due to metal ion interference, which can suppress silica dissolution (Bickmore et al 2006; Iler 1973). Hence, there appears to be a negative relationship between Al and Fe concentrations in solution and the rate of silica dissolution. However, this relationship is not linear: greater concentrations of these ions inhibit silica dissolution in an exponential fashion (Bickmore 2006).

On the other hand, increasing silica concentrations may retard dissolution as well. Gehlen & van Raaphorst (1993) prepared artificial samples by mixing varying proportions of kaolinite clay and silica gel. Sample weights remained similar, and the solid-solution ratio was held constant at 0.67 mg ml⁻¹. Samples were then processed using 0.1 M Na₂CO₃ and silica concentrations were measured colorimetrically. The authors found that the recovery rate of silica decreased exponentially as the proportion of silica gel increased. Interfering ions from the kaolinite can be ruled out, since this would cause greater dissolution suppression as the proportion of clay increased. These results were confirmed by another study which used similar

methods (Loassachan & Tada 2008). The reagents used to develop color used in these studies are similar to the ones used here, and it is known that these reagents cannot measure silica polymers (Jones & Handreck 1963). Hence it is unclear if the recovery rate of silica is due to increased polymerization or dissolution suppression. In any case, high solid-solution ratios should be avoided.

Experiments conducted for the present study revealed that dissolution suppression and/or polymerization may be significant when using solid-solution ratios above 0.1 mg ml^{-1} . In order to minimize any problems, it was decided to use the smallest solid-solution ratio that was practical.

In the literature, low solid-solution ratios were similarly found to be problematic, by either introducing precision errors due to sample heterogeneity (Clymans et al 2011a) or inducing supposed clay mineral dissolution (Loassachan & Tada 2008). However, I have observed that precision of replicate subsamples is not adversely affected when using solid-solution ratios of 0.024 to 0.04 mg ml^{-1} , as long as the samples were thoroughly mixed.

Furthermore, the studies which analyzed ASi dissolution under a variety of solid-solution ratios each recommend different ranges (Gehlen & van Raaphorst 1993; Loassachan & Tada 2008; Clymans et al 2011a). These discrepancies suggest that more work is required to better understand the factors which influence ASi dissolution rates. As noted in Clymans et al (2011a), until this phenomenon is better understood, a constant solid-solution ratio should be used throughout all samples.

The solution used for this study was 0.5 M NaOH (pH 13.7). Schlüter & Rickert (1998) recommended that solvents should be above pH 12.5 to completely dissolve all forms of RSi. Prior to sample immersion, the NaOH solution was preheated to 85°C in order to avoid a

sigmoidal dissolution curve that may result from raising the temperature after immersion (Koning et al 2002).

During the dissolution procedure, samples were mixed using magnetic stir bars at approximately 100 rpm. Aliquots were drawn off at prescribed intervals using an Eppendorf Research Pro digital pipettor (at 2.5 ml, accuracy $\pm 1.2\%$; precision $\leq 0.25\%$). A replacement aliquot of fresh, preheated 0.5 M NaOH was then added to the sample bottle, in order to maintain a constant solid-solution ratio throughout the dissolution procedure. Based upon previous observations, I determined that an aliquot volume of 2 ml yielded silica concentrations that were within the analytical limits throughout the entire dissolution procedure.

The silica aliquots were then aspirated into 30 ml opaque HDPE bottles, followed by a 2 ml water aliquot (in order to rinse the pipette tip of any residual dissolved silica). Bottles were used in lieu of volumetric flasks because all reagents were added using bottletop dispensers (BrandTech Dispensette III; at all volumes, accuracy $\leq 0.5\%$; precision $\leq 0.1\%$).

For spectrophotometric analysis of dissolved silica concentrations, color was developed using a modified molybdate blue method of Jones & Dreher (1996). This method can measure silica concentrations from 0.08 to 0.4 $\mu\text{g ml}^{-1}$ (Strickland & Parsons 1968; Jones & Dreher 1996). The molybdate reagent can take two forms, β and α , with the former occurring between a pH of 1.1 to 1.8, and the latter forming at higher pH (Truesdale & Smith 1975). β -molybdate exhibits a higher spectrophotometric absorbance for a given dissolved silica concentration, and is thus the preferred form. Any deviation of pH above 1.8 will rapidly transform a portion of β - to α -molybdate, thereby causing absorbance and measurement errors.

Silica aliquots (along with the water rinse) were acidified using 2 ml 1 M H_2SO_4 , swirled to mix, and allowed to cool for 0.5 hr. Following this, 5 ml 43.7 nM ammonium molybdate

tetrahydrate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, was added, swirled, and allowed to sit for approximately 4 minutes. Due to the sensitivity of the molybdate reagent to changes in acidity (Truesdale & Smith 1975), the pH of the mixture prior to molybdate addition was held constant from bottle to bottle. Care was taken to ensure precise aliquot and reagent volumes were used, since changes in volume can alter H_2SO_4 molarity and thus pH. With the addition of the molybdate reagent, the pH was measured as 1.33.

Ammonium molybdate will only combine with monomeric silica (Jones & Handreck 1963). Silica polymerization is common in alkali media (Iler 1979), but acidification prior to molybdate reagent addition can at least partially mitigate this problem (Bickmore 2006). The degree to which polymerization affects accuracy is not known, and it most likely varies depending upon individual sample properties. This problem could be assessed by comparing silica measurements made colorimetrically using ammonium molybdate to those made by inductively coupled plasma spectrometry (which is not hindered by polymerization). However, this assessment was not attempted here.

Next 5 ml 0.667 M tartaric acid, $\text{C}_4\text{H}_6\text{O}_6$, was added to the bottle, followed immediately by 9 ml reducing solution (25 g sodium bisulfite, 2 g sodium sulfite, and 0.4 g 1-amino-2-naphthol-4-sulfonic acid dissolved into 2.25 L H_2O). The bottles were then capped and mixed thoroughly. The bottles were then allowed to sit for one hour. Color development varies as a function of time, and so absorbances should be measured after a consistent waiting time. Dissolved silica concentrations were measured spectrophotometrically at 810 nm using a Milton Roy Spectronic 21 spectrophotometer.

Silica concentrations were then calculated using standard curves prepared daily. In order to mimic sample dissolution conditions, silica standards were prepared using 0.5 M NaOH, and 2

ml aliquots were used. Variation caused by the colorimetric measurement technique was approximately 1% of the mean value, based on replicate experiments using silica standards and soil leachates.

For all processed samples (described below), data points were gathered at thirty minute intervals out to 300 minutes after sample immersion ($n = 11$); this is considerably more points than would be needed for routine analysis (typically 5 to 6). This was done to gauge the pattern of dissolution (the degree of nonlinearity in the dissolution curve) well beyond the expected time of RSi depletion.

Throughout this paper, silica measurements are expressed as mg SiO₂ per g dry soil weight.

2.2.4 Precision and Accuracy

Precision was determined by estimating the variation of a given measurement across the sample replicates (repeatability). This was accomplished by calculating mean (μ_{Rep}) and standard deviation (σ_{Rep}) for each of the replicate sets. As a reminder, three replicates each of the surface soil samples were processed. Coefficient of variation percentages ($\text{CV}_{\text{Rep}} = \mu_{\text{Rep}}/\sigma_{\text{Rep}} * 100$) were then calculated. This analysis of replicates enables accounting for all sources of imprecision throughout the entire dissolution and measurement procedure.

Absolute accuracy of any RSi measurement method is difficult to ascertain due to the fact that no standards exist for soils (Saccone et al 2007). In fact, no study to date has attempted to constrain the accuracy of SLLE using independent methods. This task is especially daunting given the complexity of soils. Nevertheless, RSi measurements utilizing the chemical extraction

method used here should act as an upper limit to soil RSi estimates. Other methods which are known to underestimate RSi, such as floatation, can similarly act as a lower estimate.

Nevertheless, previous researchers have verified accuracy by using pure samples, such as silica gel. Sequential leaching of pure silica gel using 0.5 M NaOH on an automated system yielded >95% recovery (Koning et al 2002), indicating good extraction and measurement. Using the silica gel replicates from section 2.1, I determined recovery here as well.

However, as mentioned in Section 2.3, several factors can affect accuracy within soil samples. Some factors, such as solid-solution ratios, can be controlled. Other factors such as interfering metal ions and polymerization can be minimized but not entirely eliminated. It is worth noting again that great care was taken during sample preparation, dissolution, and measurement to process all samples as similarly as possible. This ensures consistent accuracy across all samples, despite that fact that accuracy itself cannot be constrained.

2.2.5 Determination of constraints for LE

Following data point acquisition, tests were performed to determine breakpoint identification, of the timing of the end of nonlinear depletion, which marks the first data point used for linear extrapolation (LE). The timing of the last data point used for LE was set at 300 minutes for all samples. While somewhat arbitrary, most previous versions of SLLE use this end time (e.g. DeMaster 1981). Further, the wide temporal spread from the first data point to the last was expected to be sufficiently large so as to minimize variance in the LE calculation.

A breakpoint was defined as the point on the dissolution curve where nearly all nonlinearity ceased. Simple visual inspection may be sufficient in some cases, but visual

identification can be complicated by noise in the data or when the transition to linearity is gradual. So instead, breakpoints for the samples were determined objectively by fitting a model that represents dissolution of one composite fraction of nonlinear RSi and one of linear MSi. First-order dissolution power models (PM) have been used to describe dissolution curves with the goal of BSi quantification (Kamatani & Riley 1979; Hurd & Birdwistell 1983; Greenwood et al 2001; Koning et al 2002). The increase of silica concentration through time from the dissolution of one RSi fraction can be described by the following equation (Koning et al 2002):

$$R_{aq} = [R_{extr}]_0 * (1 - e^{-kt}) \quad (1)$$

where R_{aq} is dissolved RSi concentration at time t , $[R_{extr}]_0$ is the amount of extractable RSi originally present in the sample, both expressed as $\text{mg SiO}_2 \text{ g}^{-1}$ dry sediment weight, and k is the dissolution constant ($\text{mg g}^{-1} \text{ min}^{-1}$). Hence, when $[R_{extr}]_0 - R_{aq}$ approaches 0, RSi depletion has occurred. This model assumes first-order dissolution of a single RSi fraction, although in reality multiple fractions can exist in soils. However, treating RSi as a single composite fraction is a reasonable approximation, given that multiple fractions cannot be differentiated by the methods used here.

The above equation was modified by Koning et al (2002) to include linear MSi dissolution:

$$\frac{dM}{dt} = -b \quad (2)$$

where M represents mineral silica. Combining equations 1 and 2 and assuming linearity of MSi and constant b (also a reasonable approximation):

$$R_{aq} = [R_{extr}]_0 * (1 - e^{-kt}) + bt \quad (3)$$

Given a set of dissolution observations, parameters for this model can be simultaneously estimated using the Microsoft Excel Solver routine, which arrives at the most likely values based

on a minimization of sums of squares. To summarize, this model compartmentalizes total dissolved silica into two fractions: nonlinear (RSi) and linear (MSi).

Once the parameters for equation 3 are known, it is possible to calculate the time at which RSi has been almost entirely depleted and change in R_{aq} is virtually all due to the term representing mineral dissolution (bt):

$$[R_{rem}]_t = [R_{extr}]_0 - [R_{aq}]_t \quad (4)$$

where $[R_{rem}]_t$ is the amount of undissolved RSi remaining at time t . In this way, RSi depletion was identified when the change in $[R_{rem}]_t$ neared zero. As a reminder, the identification of nonlinear depletion, or breakpoint, sets the timing of the first data point used for linear extrapolation. RSi depletion was defined as the extraction interval when $[R_{rem}]_t$ fell below 1% of $[R_{extr}]_0$. The 1% threshold is arbitrary, but serves as a useful indicator of minimal nonlinearity.

Given the complex nature of soils, it is possible that the estimated parameters will vary in a significant way from sample to sample. Samples which contain RSi forms with higher solubility may translate to higher k -value parameters, and thus earlier breakpoint times. Similarly, samples with low solubility forms of RSi should yield later breakpoint times. While it would be ideal to use the true, estimated breakpoint time for each sample, this would not be convenient for routine analysis as it would require data points from the entire dissolution procedure. Instead, once the range of true breakpoint times was determined, the mean of those times was used as a standard breakpoint time for subsequent analyses.

However, the use of a standard breakpoint time can introduce uncertainty if slight nonlinearity exists in the mineral portion of the dissolution curve. A hypothetical example is shown in Figure 2.3, where RSi has been estimated using the standard and true breakpoint times. The standard breakpoint time underestimated RSi due to a steeper slope facilitated by the use of earlier data points. This underestimation was minimized somewhat because both RSi estimations used 300 minutes as the last data point, but the difference is still sizeable. Unlike LE, which must rely upon a standard breakpoint time out of practicality, PM estimates RSi by using data points

from the entire dissolution procedure.

Therefore PM is not subject to estimation errors if RSi depletion occurs significantly before or after the standard breakpoint time.

The results of LE when using a standard breakpoint were therefore compared to PM results to determine if there is any significant difference between the two.

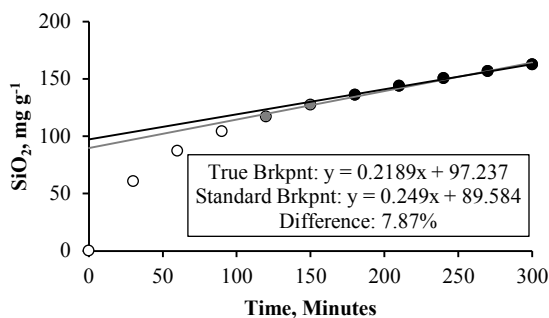


Figure 2.3. Hypothetical depiction of slight nonlinearity throughout the dissolution curve. Black extrapolation line represents RSi estimated using data points after 180 minutes (true breakpoint time), while gray line was generated using points after 120 minutes (standard breakpoint time).

2.2.6 Linear Extrapolation

Once the standard breakpoint was determined, linear regression was employed to estimate the b_0 parameter:

$$b_0 = \bar{y} - \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sum(x_i - \bar{x})^2} * \bar{x} \quad (5)$$

which is also the RSi estimate and is equivalent to $[R_{\text{extr}}]_0$ from equation 3. This traditional approach to linear extrapolation (LE) uses a single regression calculation of the data points. The results from LE and PM are then compared to each other. This was done to determine if the three models yield similar RSi estimates and precision. By comparing the LE results to PM, it is possible to determine the degree to which a standard breakpoint alters the RSi estimations.

2.3. Results

2.3.1 Sequential leaching of sediment samples

Results are shown in Figure 2.4 and Appendix 1, which show cumulative silica concentration through time. Data points for the diatomite sample represent the mean of three replicates, while error bars are one standard deviation. Only one sample was processed for the other samples. The silica gel, which is nearly pure amorphous silica, displayed concentrations of approximately 1000 mg g^{-1} for the entire dissolution procedure, indicating that it was fully

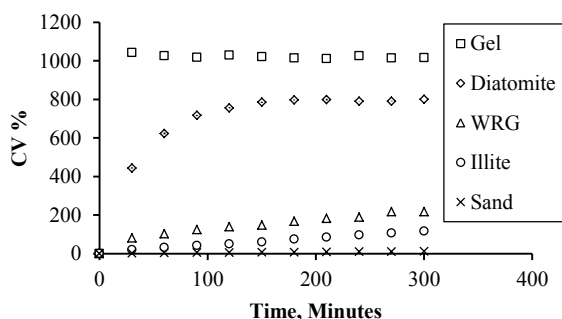


Figure 2.4. Dissolution curves for sediment samples. WRD is White River Group. Error bars on diatomite sample denote one standard deviation of three replicates.

depleted by 30 minutes. This lends confidence to the method: given that the gel is nearly pure amorphous silica, concentrations of 1000 mg SiO_2 per g of dry sample weight confirm that the method is able to fully measure all of the silica released.

Silica concentrations for diatomite increased in a nonlinear fashion until approximately 150 minutes. The diatomite released approximately 800 mg g^{-1} . Repeatability (cv_{Rep}) amongst the diatomite replicates ranged from 1.24% to 4.91% ($\mu=2.93\%$; Appendix 3). The amount of silica released from the diatomite is 20% lower, per unit weight, than silica gel. Post-depositional impurities such as carbonates and metals, as well as partial diagenesis of diatom frustules to less soluble silica forms probably account for the remainder of the sample. As a rough comparison, another study documented silica content of 879 mg g^{-1} for diatoms when using $0.1 \text{ M Na}_2\text{CO}_3$ (Gehlen & van Raaphorst 1993). The status of the diatoms was not specified in that paper, so it is unknown if they were fresh or procured from sediments. Diatoms in a sedimentary environment could have partially crystallized and/or adsorbed ions to their surfaces, thereby lowering overall solubility, which may explain why they did not achieve 100% recovery. However, Gehlen & van Raaphorst (1993) reported that their diatom samples were not fully depleted after five hours, which suggests that their choice of a weaker alkali solvent was insufficient to fully extract all silica.

Silica concentrations in the remaining samples were much lower than the silica gel and diatomite, and these samples continued to release silica throughout the entire dissolution procedure, indicating that some of the forms of silica present were never fully depleted. The sample WRG (White River Group: volcanoclastic sediments) released more silica than illite or quartz due to its volcanic glass content. The amount of silica released from illite clay was similar to that found in another study (Koning et al 2002), while quartz sand was almost negligible. Taken together, the very small amounts of silica released from illite and quartz sand indicate that well-ordered primary and secondary minerals are not significant sources of RSi.

Table 2.5. Breakpoint times and linear extrapolation of linear portions of the dissolution curves for the sediment samples. WRG is White River Group. The diatomite sample is a composite of three replicates.

Sample	Breakpoint, minutes	b_0 , mg g ⁻¹
Silica gel	<30	1033.35
Diatomite	~150	783.08
WRG	<30	79.61
Illite clay	<30	8.38
Quartz sand	<30	1.96

All of the samples exhibited an initial higher rate of dissolution, although this is not visually apparent for illite and quartz sand (Fig. 2.4). The higher rate is most obvious for the diatomite sample, which shows a nonlinear decrease in the rate of silica dissolution until depletion at 150 minutes. The initial higher rate of dissolution can be inferred for the other samples, since the trend of the linear portion of their curves do not cross the y-axis at zero (Table 2.5). This higher rate of dissolution indicates the presence of at least two fractions of silica in the samples: one which displays higher solubility and nonlinear dissolution (as shown in the diatomite curve), and one with lower solubility and a linear rate of dissolution. The transition from nonlinear to linear dissolution, termed the breakpoint, is less than 30 minutes for all of the samples except diatomite (Table 2.5). A breakpoint time of 150 minutes for the diatomite most likely indicates that at least some of the RSi present in this sample is of slightly lower solubility, probably similar to that encountered in many soils. Conversely, the relatively quick depletion times for the remaining samples indicates very high solubilities. Alternatively, the RSi present may exhibit solubilities similar to diatomite, but the very small amount initially present, coupled with a progressive decrease in the dissolution rate, rapidly falls below detectable levels.

If diatomite is used as a proxy for RSi in soils, any silica forms with solubilities equal to or greater than it should be fully depleted at 150 minutes. Likely forms with this behavior are BSi, adsorbed and soluble silica, amorphous inherited forms such as glass and possibly cristobalite.

2.3.2 Sequential leaching of soil samples

Sequential leaching results for the soil samples are reported in Figure 2.5 and Appendix 2. As a reminder, data points were gathered in thirty minute intervals out to 300 minutes. All of the dissolution curves displayed parabolic shapes (Fig. 2.5), with a rapid nonlinear increase of silica concentration initially, after which silica concentrations continued to increase, but at a slower, nearly linear rate. The amount of silica extracted at 300 minutes ranged from 68.49 mg g⁻¹ (Soil 3, 0-13 cm) to 159.19 mg g⁻¹ (Soil 1, 40-50 cm).

Coefficient of variation percentages (cv_{Rep}) for the three replicates from each extraction interval offer a convenient way to elucidate repeatability. As can be seen in Figure 2.6, cv_{Rep} values for all data points are less than 6%. Further, there is no visual temporal trend in cv_{Rep} , indicating that certain parts of the dissolution curve do not display more variability than others.

2.3.3 Breakpoint Identification (RSi Depletion)

Model variables are listed in Table 2.6. As a reminder, $[R_{extr}]_0$ is the predicted nonlinear RSi component total, in mg g⁻¹. The variables k and b (mg g⁻¹ min⁻¹) represent dissolution constants for the nonlinear and linear components, respectively. Estimated breakpoint times (based on the power model) range from 115 to 205 minutes.

Replicate precision for all parameters are generally high (Table 2.6). The parameter $[R_{extr}]_0$ represents the power model's estimate of RSi, and so this yields a comparative benchmark for the linear extrapolation model. $[R_{extr}]_0$ increased with depth for Soils 1 and 3, but remained relatively unchanged for Soil 2. The parameter k , which represents the dissolution

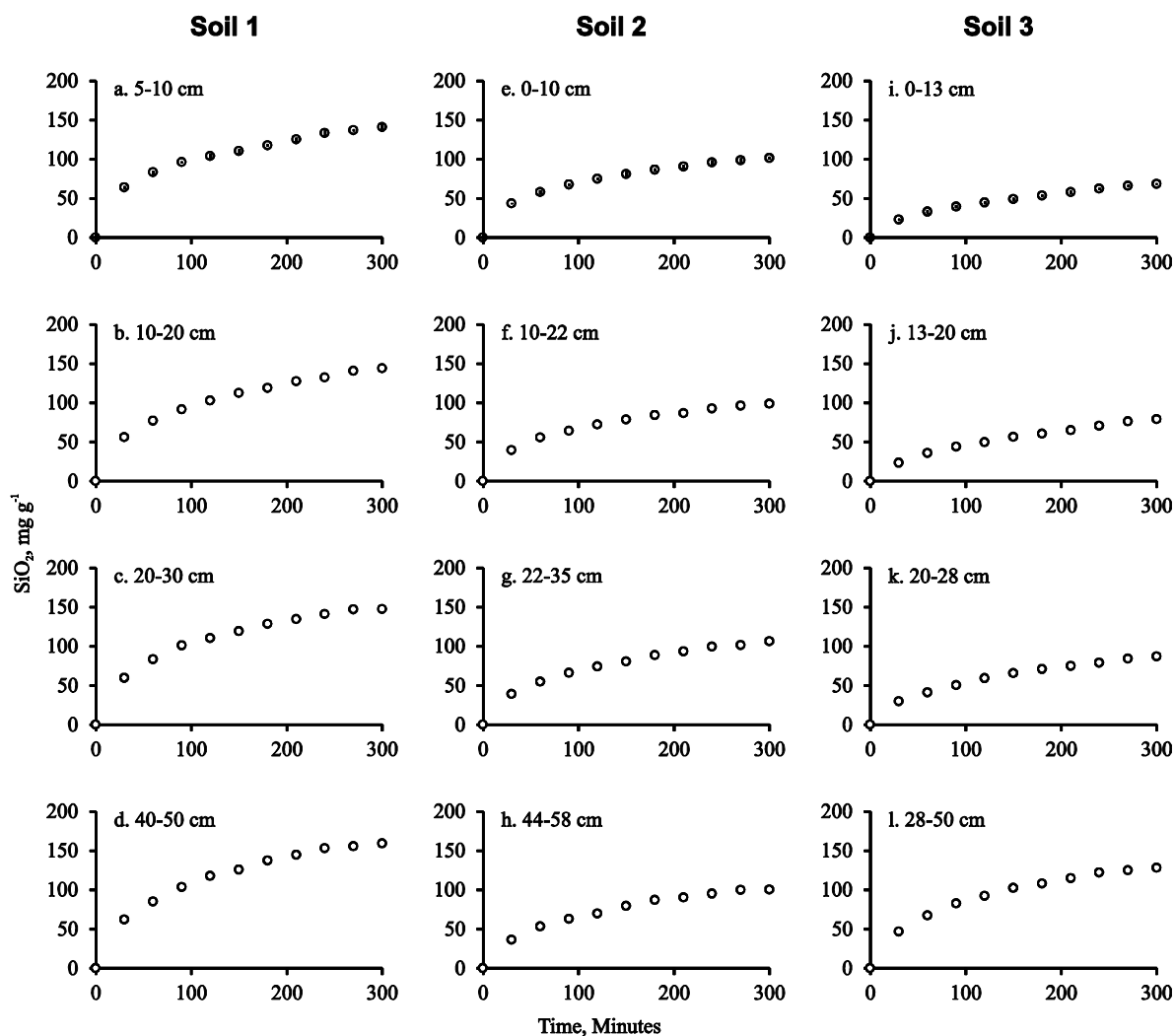


Figure 2.5. Sequential leaching dissolution curves for study soils. Surface samples are means and standard deviations of three replicates each.

constant for nonlinear dissolution, decreased with depth for all soils. This overall change in solubility with depth suggests changes in RSi fractions, with higher solubility forms in the upper layers. The parameter b , representing linear dissolution, did not show any noticeable pattern with depth. However b -values for a given soil are generally similar. These similar b -values suggest that this parameter is controlled by soil parent material (lower solubility primary and secondary minerals), which is relatively invariant across the profiles. At the same time, k -value variation with depth suggests that the power model is sensitive to changes in overall RSi solubility.

Table 2.6. Power model parameters and breakpoint times for soil samples. $[R_{\text{extr}}]_0$ is expressed as $\text{mg SiO}_2 \text{ g}^{-1}$ dry soil weight, while k and b are $\text{mg g}^{-1} \text{ min}^{-1}$. Data are the means of 500 bootstrap iterations. Precision data for surface samples are standard deviations ($\pm$), and coefficients of variation percentages (in parentheses) of three replicates. Breakpoint times are rounded to the nearest minute.

	Depth, cm.	$[R_{\text{extr}}]_0$	$k (1 * 10^{-2})$	b	Breakpoint, Min.
Soil 1	0-5	80.73 $\pm$ 2.96 (3.66)	4.02 $\pm$ 0.11 (2.71)	0.22 $\pm$ 0.02 (9.84)	115 $\pm$ 3 (3)
	10-20	80.03	2.88	0.23	160
	20-30	95.39	2.55	0.19	181
	40-50	100.49	2.41	0.22	191
Soil 2	0-10	59.23 $\pm$ 2.42 (4.08)	3.28 $\pm$ 0.21 (6.39)	0.15 $\pm$ 0.00 (2.98)	141 $\pm$ 9 (6)
	10-22	57.57	2.89	0.14	160
	22-35	57.64	2.71	0.17	170
	44-58	60.62	2.40	0.15	192
Soil 3	0-13	30.84 $\pm$ 2.30 (7.47)	3.05 $\pm$ 0.25 (8.34)	0.13 $\pm$ 0.00 (3.18)	152 $\pm$ 12 (8)
	13-20	33.17	2.73	0.16	169
	20-28	46.26	2.36	0.14	196
	28-50	79.83	2.25	0.17	205

Following the determination of the model parameters, equation 4 was utilized to determine the amount of undissolved, predicted RSi remaining or $[R_{\text{rem}}]_t$ for each extraction interval. RSi depletion was defined as the extraction interval when $[R_{\text{rem}}]_t$ fell below 1% of $[R_{\text{extr}}]_0$, and the time of this interval is defined as the breakpoint (Table 2.6). Sample $[R_{\text{rem}}]_t$ values for all extraction intervals are shown in Appendix 3. As before, error bars represent 1 σ of the replicates.

Breakpoint times increase with depth as a result of lower k -values. This suggests that the same general processes affect RSi with depth for these soils. The average breakpoint time was 169 ± 26 minutes.

The average breakpoint time of 169 ± 26 minutes determined here overlaps two extraction intervals at 150 and 180 minutes. Despite being slightly closer to the average, the 180

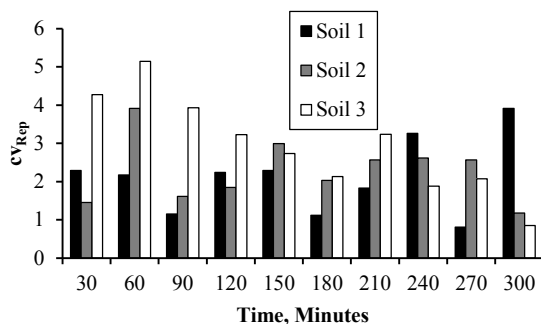


Figure 2.6. Estimates of CV_{Rep} for replicate samples.

minute extraction interval was not used as the standard breakpoint for all samples.

Instead, 150 minutes was chosen for the following reasons. First, the use of data points from 150 to 300 minutes allows for more data points, a longer temporal range, and a shorter extrapolation length,

all of which minimize b_0 uncertainty. Second, this time matches the depletion time of the diatomite sample (Fig. 2.4; Appendix 1).

2.3.4 Comparison of Predictive Models

Following the determination of the standard 150 minute breakpoint time, RSi estimates were generated for the samples using LE. Hence, six data points were used, from 150 to 300 minutes. Results are displayed in Fig. 2.7. As a comparison, RSi estimates generated by PM are also shown. Error bars on the surface samples represent 1 standard deviation of the replicates.

It can be seen that both LE approaches agree well with the power model. The variation of the replicates from the surface samples are all within one standard deviation of one another. This indicates that both LE approaches yield reliable results when compared to the more laborious PM technique. LE slightly underestimates RSi relative to the PM where the true breakpoint occurred later than the standard 150 minutes (Table 2.5). Slight overestimation occurred where the true breakpoint occurred earlier than 150 minutes. Nevertheless, it can be seen that these differences are typically within error.

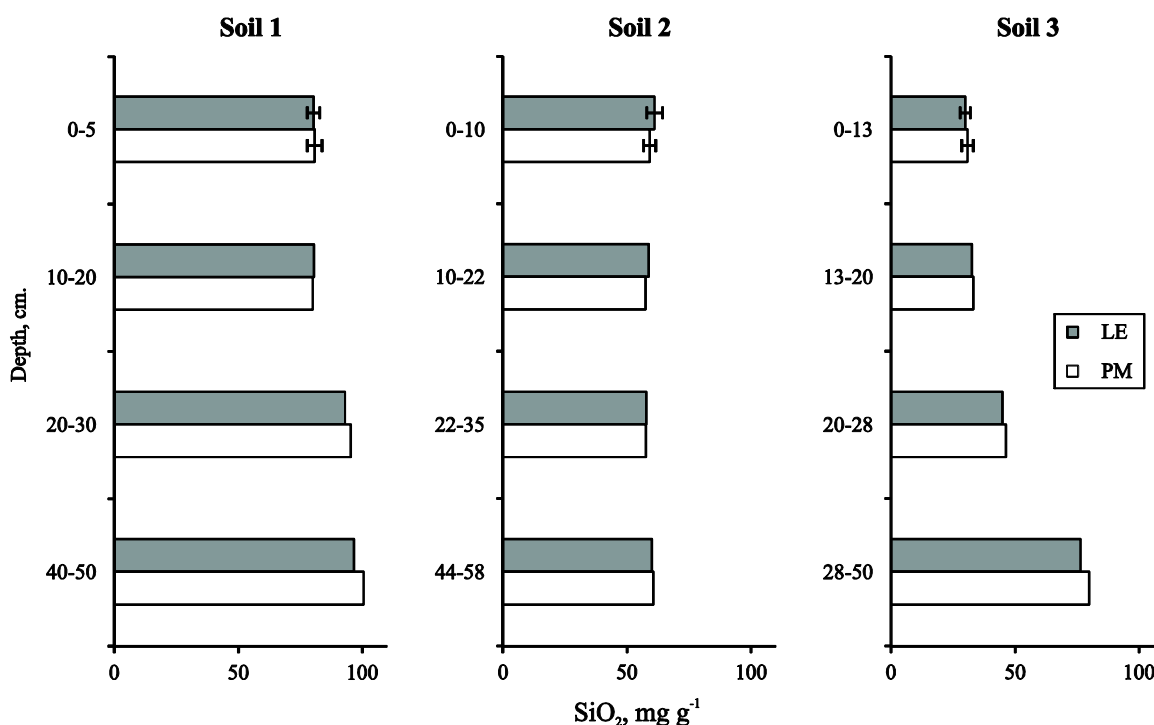


Figure 2.7. RSi estimates for each soil, using LE and PM. Error bars for surface samples denote one standard deviation of three replicates each.

Repeatability of the surface samples, expressed as coefficient of variation percentages (cv_{Rep}), are reported in Figure 2.8a and Appendix 3. Values ranged from 3.14% (Soil 1, LE) to 7.47% (Soil 3, PM). It can be seen that cv_{Rep} for a given sample is very similar for all predictive models. Indeed, precision appears to be more related to the amount of RSi present in the samples. Note that cv_{Rep} is highest for the low-RSi Soil 3 and lowest for Soil 1. Figure 2.8b displays standard deviation data (σ_{Rep}) for the models, and it can be seen that this measure of precision remains fairly constant across the soils. This is an indication that the absolute variation generated by the method (σ_{Rep}) is similar for all samples. The relative effect of σ_{Rep} becomes more influential as RSi values are decreased.

Comparison of the repeatability values reported here to results in the literature is difficult because most studies do not report precision, or they use different methodological approaches. Nevertheless, Saccone et al (2007) reported cv_{Rep} values ranging from 0% to 49% ($\mu=9.77\%$)

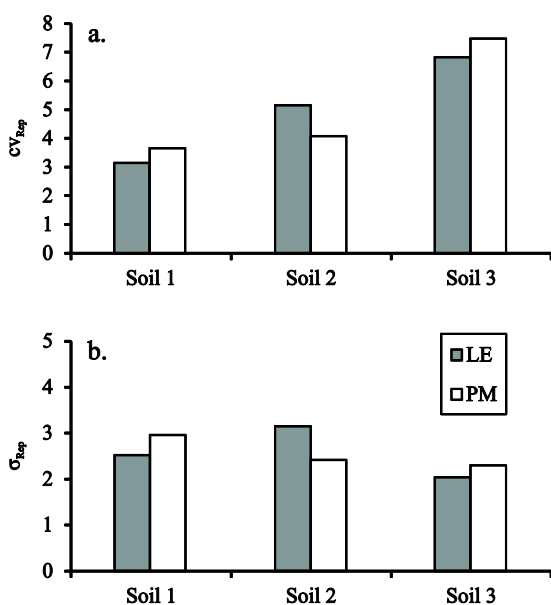


Figure 2.8. Repeatability of surface soil samples, expressed as coefficient of variation percentage (cv_{Rep}) (a.), and standard deviation in $mg\ g^{-1}$ (σ_{Rep}) (b.). Results are generated from three replicates each of samples.

when using SLLE with 0.094 M Na_2CO_3 on soil samples. The extreme range in variability is probably due to the fact that only three data points were used in the LE calculation. White et al (2012) reported replicate precision of <10% when using ambient-temperature, 0.1 M NaOH over the course of several days. As another example, Krausse et al (1983) reported cv_{Rep} values ranging from 0.27% to 14.2% when testing three single extraction techniques on diatom

samples.

2.3.6 Analysis of Depth Profiles

The depth patterns generated by LE indicate that RSi values peak at the bottom of the profiles for Soils 1 and 3 (Fig. 2.7). This is in contrast to the classic “top heavy” distribution as seen in other studies (Fig. 2.10). This is most likely due to methodological differences. As an example of this, many studies have used floatation techniques to extract silt-sized BSi (e.g. Alexandre et al 1997; Blecker et al 2006), where values are typically highest near the surface and decrease with depth. This is to be expected, given that BSi is deposited through litterfall at the surface. However, by focusing on silt-sized BSi, floatation cannot account for clay-sized forms of RSi, which may be biogenic or nonbiogenic in origin. Although the amount of clay-sized BSi

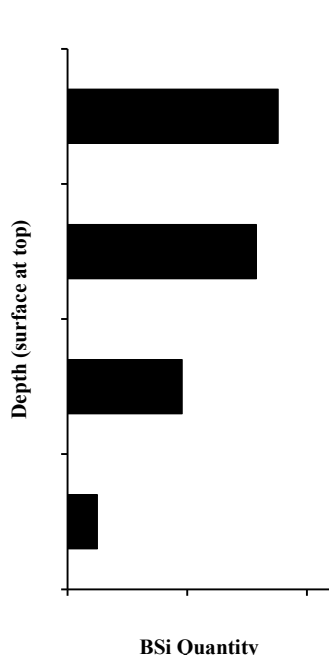


Figure 2.9. Typical pattern of BSi content with depth, as generated from density separation.

in soils remains to be quantified, its amount can approach 50% of the total BSi in certain plants (Jones & Beavers 1964a; Sommer et al 2006). This implies that a large amount of clay-sized BSi can exist in soils through litterfall. Floatation of BSi focuses solely on RSi of biological origin and therefore it implicitly does not consider other, abiotic factors and processes which may produce RSi.

Other studies which employed SLLE found RSi peaks at depth in some soils, while others peaked near the surface (Saccone et al 2007; White et al 2012). This

implies that depth distributions of RSi in soils is variable, and is probably the result of interplay between several processes which vary in dominance through space and time.

2.3.6.1 Soil 1

Soil 1 contained considerably more RSi at all depths when compared to the other soils, averaging 87.61 mg g^{-1} . Volcanic glass content in a nearby soil approached 10% (Jacobs & Mason 2007), which probably explains why Soil 1 contains the most measured RSi. RSi totals can also be influenced by phytolith production, which results in a net upward movement of silica, thereby minimizing losses from leaching (Lucas et al 1993). This is especially the case for the grassland-dominated Soil 1, since grasses are prolific phytolith producers.

RSi content in Soil 1 peaks in the A1b horizon (Brady Soil). Interestingly, sand- and silt-sized volcanic glass drops to a minimum at this depth (Fig. 2.2). There are at least three possible explanations for this peak in RSi. First, the Brady Soil may contain relict phytoliths, given that regional records indicate that it formed predominantly under grassland vegetation (Johnson & Willey 2000). Phytoliths have been found in the Brady Soil at other sites (Woodburn et al 2011). However, if plant biocycling were able to produce this peak, by analogy one would expect to find a similar peak in the modern soil. On the other hand, any relict phytoliths in the Brady Soil may have undergone dissolution and breakdown, making them unrecognizable.

Second, this peak may be the result of a buildup of fine grained particles during loess aggradation. Indeed, clay particle peaks have been noted within the Brady Soil throughout the region (Jacobs & Mason 2007). These clay peaks are not the result of pedogenic processes within the soils, but rather from a slackening of loess deposition during the more humid late Pleistocene to early Holocene transition. It has been noted elsewhere that the proportion of finer particles deposited increases as dust production rates decrease (Jacobs & Mason 2007). An increase of RSi delivered from clay minerals is unlikely, given the relatively small amount of RSi found in the clay minerals processed here and elsewhere (Table 2.4; Koning et al 2002). The possibility exists that clay-sized RSi particles could occupy a greater proportion of voids, thereby facilitating a greater amount of RSi per unit of volume. This in turn would lead to a greater amount of RSi measured in the A1b horizon. As will be shown in Chapter 3, an inverse relationship exists between RSi content and soil texture: Clay content increases with distance from the source area due to fining while RSi totals decrease. This may be due to a greater proportion of inherited RSi existing in the silt fraction or mineral sorting with distance (Bettis III et al 2003). Thus, an increase in RSi totals due to more grains per unit volume is unlikely.

Third, the peak of RSi in the A1b horizon may be the result of pedogenic silica deposition. Weathering and downward movement of primary and secondary crystalline minerals is unlikely at this site, given the drier climate (Jacobs & Mason 2007). However, mobilization of RSi as amorphous silica has been documented in soils of similar vegetation, parent material, and climate as Soil 1 (Brown & Mahler 1987). If pedogenic RSi is present, it most likely originated from weathered volcanic glass and phytoliths.

Pedogenic deposition of RSi in the A1b could have occurred by lessivage or dissolution and subsequent reprecipitation. Lessivage is unlikely at this site, given that no silans were documented. Deposition of dissolved RSi onto grains and ped faces could have occurred by way of precipitation of relatively pure amorphous silica due to saturated conditions as soil water was removed (Schaetzl & Anderson 2005). On the other hand, dissolved silica could have become adsorbed to Al and Fe oxide, clay mineral, and even organic matter surfaces (McKeague & Cline 1963b). Silica adsorption to metal oxide surfaces in particular can suppress solubility, which may explain why the estimated k-value for the A1b horizon was lower than overlying horizons (Table 2.6). This suggests that at least some of the RSi present here is adsorbed to metal oxides.

2.3.6.2 Soil 2

Average RSi content in Soil 2 was 59.48 mg g^{-1} . Soil 2 contains inherited RSi in the form of cristobalite. While its quantity is not known in Soil 2, cristobalite generally displays lower solubilities relative to volcanic glass, which may partially explain why it displays slightly lower values than Soil 1.

Unlike Soil 1, Soil 2 does not display any significant change in RSi totals with depth (Fig. 2.7). This could indicate that very little downward movement of RSi has occurred. However, the very slight increase of RSi at the surface could be the result of phytolith production. The lack of an RSi peak in the B horizon, unlike Soil 1, is bolstered by the fact that the argillic B horizon is relatively weakly developed (Table 2.3). This soil, which is proximal to the loess source area, contains discrete layers of fine sand interbedded within the solum, which could hamper movement of clay particles and RSi. Nevertheless, the presence of silans and clay coatings in the Bt1 horizon indicates that at least some pedogenic deposition has occurred. As with Soil 1, *k*-values decrease with depth (Table 2.6), suggesting that adsorption has occurred.

2.3.6.3 Soil 3

A wide range of values were found for Soil 3, which displayed an increase of RSi with depth, similar to Soil 1. Average RSi content for Soil 3 was 45.96 mg g^{-1} . Biotic effects on weathering may be significant in the environment of Soil 3, where forest vegetation could have increased silica weathering and mobility. On the other hand, forest species tend to use less overall silica per unit mass than grasslands (Epstein 1994). Hence, biocycling of silica under forests may not be sufficient enough to offset leaching.

It is difficult to disentangle biotic and pedogenic (abiotic) weathering, since climate is such a fundamental driver of vegetation composition. However, from a climatic standpoint, it is reasonable to state that pedogenic weathering is more advanced for Soil 3 and least for Soil 1. Taken together, the increased rate of pedogenic and biotic weathering at Soil 3 would act to transform primary and secondary forms of silica into RSi. Clay coatings are pronounced in the

Bt1 horizon, suggesting that dissolution of primary and secondary silica (or inherited RSi) has occurred. Estimated k-values (Table 2.6) decrease with depth, as with the other soils.

2.3.6.4 Further Comments on the Depth Profiles

Aside from inheritance, RSi content can also be influenced by phytolith production, which results in a net upward movement of silica, thereby minimizing losses from leaching (Lucas et al 1993). This is especially the case for the grassland-dominated Soils 1 and 2, because grasses are prolific phytolith producers. For example, the yearly phytolith deposition rate of a forest in France was measured at approximately 22 kg ha^{-1} (Bartoli 1983), which is similar to short grass prairie ecosystems ($22\text{-}26 \text{ kg ha}^{-1}$; Blecker et al 2006). The deciduous tree species at Soil 3 probably produce fewer phytoliths per unit weight when compared to tallgrass prairie species.

Preservation of soil phytoliths is largely dependent on climate (Blecker et al 2006) and the presence of inherited RSi (Henriet et al 2008). The drier climate and large pool of volcanic glass at Soil 1 may explain why it contains more phytoliths per unit weight than Soil 2. For Soil 3, phytolith preservation is lessened by a more humid climate and the fact that deciduous tree phytoliths tend to exhibit higher solubilities (Bartoli & Wilding 1980).

RSi form and composition most likely varies with depth in these soils. As will be shown in Chapter 3, sand- and silt-sized BSi in Soils 1 and 3 decreases steadily with depth, while nonbiogenic forms progressively increase. The same pattern was found for Mollisols nearby to Soil 2. This indicates that silica use by plants results in the transformation of inherited forms to BSi.

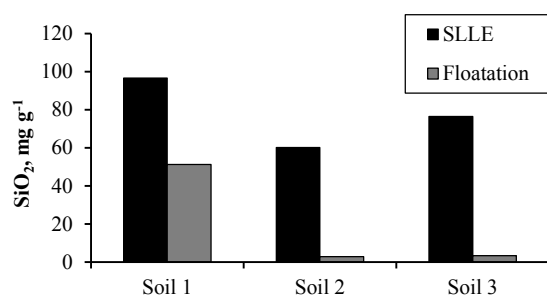


Figure 2.10. Comparison of RSi measured at the bottom of each profile (approx. 40-50 cm) using SL (LE_{trad}) and floatation. Floatation data for Soils 1 and 3 are from Chapter 2, while data for Soil 2 is a composite of four nearby Mollisols (Chapters 2 & 3).

However, sand- and silt-sized RSi totals for all three soils at the bottom of the profiles were only a fraction of the total RSi measured using SLLE (Fig. 2.11). RSi peaks at depth must therefore originate from clay-sized particles. It cannot be stated with any certainty whether the clay-sized RSi originates from biogenic or nonbiogenic

sources, or both. However, the presence of RSi peaks generally coincident with clay-sized particle peaks suggests that fine-grained RSi is dominated by pedogenic processes rather than biotic.

The depth profiles presented here demonstrate that clay-sized RSi can make up a sizeable proportion of the total RSi pool. Given their relatively large surface area to volume ratios, it is speculated that clay-sized RSi is much more susceptible to short term cycling within soils. Further, the existence of RSi peaks at depth suggests that this fraction of total RSi must be considered in any attempt to quantify total RSi in soils.

2.4. Conclusions

The efficacy of SLLE, as described here, for the measurement of RSi within soils is confirmed. This Chapter has shown that SLLE, using 0.5 M NaOH and six data points, can yield results which have similar accuracy and precision as the more labor-intensive power model.

SL of various sediment types indicates that primary and secondary minerals contribute only negligible amounts of RSi and that forms of silica with solubilities greater than or equal to laboratory-grade diatomite are fully depleted by 150 minutes.

Breakpoint analysis revealed that the timing of nonlinear depletion can vary from sample to sample, and that this is most likely a reflection of composite RSi solubility. A standard breakpoint time of 150 minutes offers the most convenient option, and it yields very similar results to the most robust power model (which doesn't rely on breakpoints). The use of six data points at 30 minute intervals from 150 to 300 minutes is recommended to ensure accuracy and precision.

When performing SLLE on soil samples, this method was able to extract all forms of RSi with solubilities similar or greater than laboratory-grade diatomite, including lower solubility pedogenic forms. Other RSi extraction methods, such as floatation and SLLE with weaker alkali solvents, are unable to fully extract all of these forms.

Analysis of RSi content with depth for the study soils revealed interesting patterns. RSi content for all three soils was probably influenced by phytolith production, while biotic weathering was most intense at the forest-dominated Soil 3. Evidence for pedogenic movement of RSi is evident for all soils, in the form of a relationship between RSi content and clay particle content, as well as clay coatings and silans.

An inherent drawback of the SLLE method is that it cannot discriminate between RSi forms. SLLE may be most efficacious if it is used in tandem with other methods. For example, floatation can shed light on the forms and quantities of sand- and silt- sized RSi particles present. If the RSi totals measured using floatation are subtracted from RSi totals generated by SLLE, then one would have a reasonable estimation of clay-sized RSi. Further, acid extraction

techniques, such as water, acetic, citric, and oxalic, can target certain RSi pedogenically-weathered fractions. As a final example, SLLE can be used in conjunction with NaOH-extractable Al measurements to make inferences regarding fractions of RSi.

CHAPTER 3. REACTIVE SILICA IN LOESS-DERIVED SOILS OF CENTRAL NORTH AMERICA

3.1. Introduction

The purpose of this chapter is to identify and quantify various reactive silica (RSi) pools in soils formed in loess across the midcontinent of North America. In this chapter, I show that inherited forms of RSi can constitute a significant proportion of the total pool. Further, in all of the soil profiles I analyzed, most RSi exists in the $<10\ \mu\text{m}$ fraction. Taken together, both of these findings suggest that silt-sized biogenic RSi particles (phytoliths) make up only a small proportion of the total RSi pool.

RSi, as used here, is defined as all forms of silica exhibiting solubilities greater than primary and secondary silicate minerals. Of the various forms, amorphous silica is the most common, and it includes plant-produced microscopic opaline bodies termed phytoliths, volcanic glass, and pedogenic coatings or precipitates (Drees et al 1989). Other forms include silica adsorbed to Al and Fe oxyhydroxides, short range order clays, and poorly ordered forms such as cristobalite. RSi can be inherited from soil parent materials, for example from loess sedimentation or volcanic ash deposits. *In situ* weathering processes can also create or modify RSi. Pedogenic and biotic weathering can induce dissolution of minerals and RSi and subsequent deposition as precipitates or adsorbed forms (Saccone et al 2006). Similarly, plant use of silica can lead to the creation of phytolith pools within soils (Blecker et al 2006).

Many techniques exist to quantify RSi in soils. As discussed in Chapter 2, most of these are designed to target specific fractions, such as biogenic silica (BSi; phytoliths). The most

popular and traditional quantification method is floatation, which mechanically extracts all silt-sized RSi particles, typically larger than 2 to 20 μm (Reyerson 2004; Alexandre et al 1997; Cornelis et al 2010b). While this method does not account for clay-sized RSi, and thus underestimates total RSi, it is useful for classification of forms through the use of microscopy. For example, Borelli et al (2010) used the floatation technique coupled with microscope classification to categorize RSi particles as either BSi or volcanic glass. In addition, this method can be used to estimate the relative contribution of silt-sized RSi to the total RSi pool.

Chemical extraction methods (Saccone et al 2006) are able to measure all size fractions of RSi, but cannot discriminate between forms. The two most popular chemical extraction techniques are single extraction and sequential leaching; both are discussed in Chapter 2. A modified version of DeMaster's sequential leaching technique (termed SLLE) was presented in Chapter 2, and it is also used here to quantify total RSi.

Other chemical extraction techniques have been designed to target specific fractions of RSi, and are discussed in detail in Sommer et al (2006). Of these methods, the oxalate extraction technique was originally designed to measure amorphous and poorly crystalline Fe compounds within soils (Schwertmann 1964). It was observed that this technique also liberated silica, and it has since been used in several studies (Kelly et al 1998; Saccone et al 2007; Cornelis et al 2011). The oxalate extraction technique is thought to release silica from dissolved, exchangeable, and adsorbed forms, as well as short range order clays (Wada 1989; Kodama & Ross 1991; Saccone et al 2006). This method probably also releases silica from sharp edges of mineral grains and shards if agitation during the dissolution procedure is used.

The use of SLLE, floatation, and oxalate extraction techniques in tandem may prove beneficial for several reasons. First, SLLE can quantify total RSi, while the other methods can

measure individual fractions. Floatation can categorize silt-sized biogenic and nonbiogenic forms, while oxalate can yield information regarding pedogenically weathered RSi. Further insights into the drivers of soil development can be gained by comparing the various fractions to each other. For example, what proportion of total RSi is composed of silt-sized particles and pedogenically altered forms? Further, subtracting the floatation-extractable values from total RSi would yield an estimate of clay-sized RSi fractions. To my knowledge, this has never been attempted in the literature.

The use of multiple RSi analyses in tandem has increased in recent years. Saccone et al (2007) and Saccone et al (2006) used sequential leaching to determine total RSi in various temperate soils. In addition, the authors employed single extraction techniques using various solvents to isolate several pedogenically altered RSi fractions. Cornelis et al (2011) employed similar methods but also extracted RSi using the floatation method in order to qualitatively identify the origin of forms present.

This study expands upon previous work by applying multiple methods for measuring RSi to soils formed in loess from across the midcontinent of North America. Loess-derived soils were used because they allow an initial assessment of the relative importance of factors potentially influencing the total content and specific forms of RSi, such as climate, vegetation, and inheritance from sediment source areas. Loess deposits across the midcontinent share broadly similar mineralogy and grain size, but they span a wide range of climate and vegetation (Bettis III et al 2003). Furthermore, there is evidence that some loess-derived soils may have significant inherited RSi content (Mason, 1992; Mason & Kuzila 2000; Jacobs and Mason 2007), but this issue is relatively understudied. The presence of inherited RSi in many soil orders is well known (particularly in Andisols; Borelli et al 2010), but its abundance and variability has not

been quantified for major parent materials such as loess. Of particular interest to researchers attempting to quantify total BSi in soils is the fact that RSi inheritance can modify pool sizes (Henriet et al 2008). Loess-derived soils are also well-suited for studying the processes which modify the vertical distribution of RSi within soils. Although most loess deposits display some vertical zonation related to changing sources or environmental conditions, they lack the large textural discontinuities present in some other parent materials, making it easier to identify effects of pedogenic processes on RSi distributions.

The goals of this paper are to 1) measure total RSi content in a range of soils formed in loess from central North America, with differing sediment source areas, vegetation, and climate; 2) identify and quantify several RSi fractions within those soils; and 3) characterize vertical distributions of RSi and identify possible explanations for them. This chapter expands upon previous work (Saccone et al 2006; Saccone et al 2007; Cornelis et al 2011) by estimating the size of previously unexplored RSi pools, including clay-sized and inherited fractions.

3.2. Study Region and Methods

3.2.1 Study Soils

Seven soils formed in loess were used here, including newly sampled profiles from southeastern Minnesota and soils sampled for previous research projects. The location of each soil is shown in Figure 3.1, and their characteristics are listed in Table 3.1. All soils were formed in stable upland settings with <2% slopes. Erosion is nonexistent to minimal at all sites. The soils were sampled using either hydraulic probe cores (Nebraska soils, KA, TQ) or soil pits

(Minnesota soils). Soils were described by genetic horizon (Appendix 5) using standard soil survey methods (Soil Survey Staff 1993). Samples were collected from each soil at 10-20 cm intervals to a depth of approximately 200 cm, generally corresponding to horizons. Some soils were sampled by genetic horizon (AL2, KO1, TQ) so sample spacing is somewhat irregular, while others were sampled at regular 10 cm intervals (8G00, 5G00, 3G00, KA).

3.2.1.1 Nebraska Soils

Located in the eastern half of Nebraska, 8G00, 5G00, and 3G00 are Mollisols formed in Late Pleistocene and Holocene-aged loess (Mason 2001; Mason et al 2003). The dust that was

deposited to form the parent material of these soils originated from the nonglaciogenic erosion of the Oligocene-aged White River Group and other rocks and sediments to the west and northwest (Aleinikoff et al 1998; Mason 2001).

Holocene-aged Bignell Loess is approximately 50 cm thick at the proximal 8G00 and 5G00 sites, and less than 30 cm at the distal 3G00 site (Jacobs & Mason 2007). Bignell Loess was deposited episodically throughout the Holocene (Mason & Kuzila 2000; Mason et al 2003),

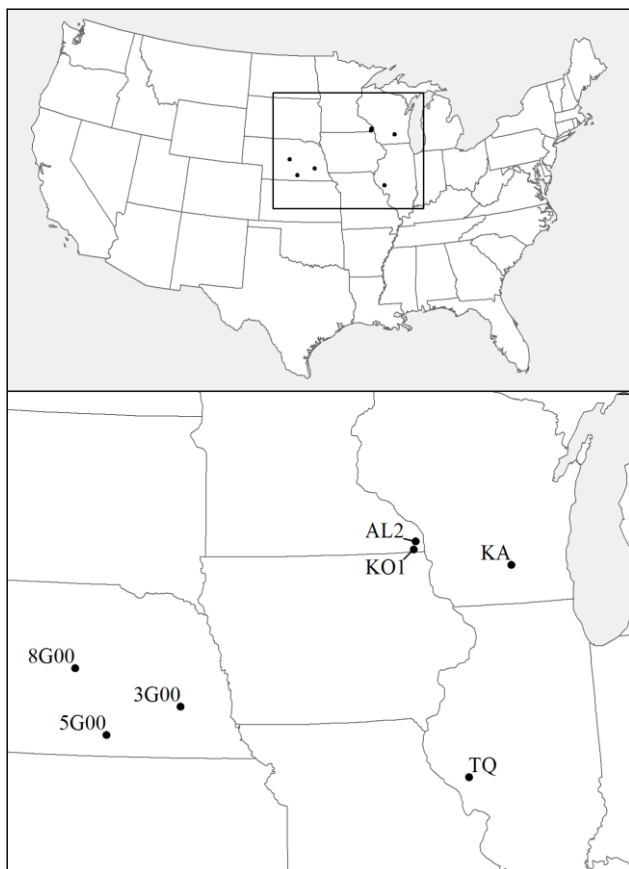


Figure 3.1. Maps of study soil locations.

indicating that the upper horizons of modern soils at 8G00, 5G00, and 3G00 contain relatively recently deposited loess. A paleosol termed the Brady Soil underlies the Bignell Loess, and it demarks a time period of relatively little loess accumulation during the late Pleistocene-Holocene transition (14 to 11 cal yr BP; Johnson & Willey 2000; Mason et al 2003; Miao et al 2007; Mason et al 2008; Muhs et al 2008). The Brady Soil was formed within the uppermost layer of the late-Pleistocene Peoria Loess, which extends below the 200 cm sampling depths used here. At the 8G00 and 5G00 sites, the Brady Soil is clearly visible as a distinct buried A horizon of granular microstructure as well as higher organic C and clay content, which has acquired some characteristics of B horizons after burial. At the distal 3G00 site, lower rates of Holocene loess accumulation resulted in shallower burial of the Brady Soil and its morphology has been more thoroughly transformed into that of a B horizon, with significant loss of organic matter (Jacobs & Mason 2007). Relatively few illuvial coatings were identified in thin

Table 3.1. Study soil characteristics. MAP and MAT are mean annual precipitation and temperature, respectively.

Soil	Series ¹	Taxonomy ¹	Dominant Vegetation ²	MAP ³	MAT ³
8G00	Hall	Fine-silty, mixed, superactive, mesic pachic argiustoll	Mixed grass prairie	585.0	8.2
5G00	Holdrege	Fine-silty, mixed, superactive, mesic typic argiustoll	Mixed grass prairie	645.4	10.0
3G00	Hastings	Fine, smectic, mesic udic argiustoll	Mixed grass prairie	710.7	11.3
AL2	Seaton	Fine-silty, mixed, superactive, mesic typic hapludalf	Deciduous broadleaf forest	888.7	6.7
KO1	Port Byron	Fine-silty, mixed, superactive, mesic typic hapludoll	Tallgrass prairie	888.7	6.7
KA	Elburn	Fine-silty, mixed, superactive, mesic aquic argiudoll	Tallgrass prairie	836.9	7.8
TQ	Fayette	Fine-silty, mixed, superactive, mesic typic hapludalf	Deciduous broadleaf forest	906.5	11.2

¹Soil series and taxonomy from Soil Survey Staff 1999. ²Vegetation data from Zawacki & Hausfater (1969); Marschner (1974); Gröger (1973). ³Normalized 1971-2001; data from NOAA Staff 2002.

sections from just below the buried Brady Soil A horizons in 8G00 and 5G00 (Jacobs & Mason 2007). Pedogenic clay coatings were found within the modern B horizon (interpreted as the former Brady Soil A horizon) of 3G00, so some illuviation has occurred there after Brady Soil burial.

Due to fining of dust particles with distance from the sediment source area (Pye 1995), average clay content increases eastward in the parent material of the Nebraska soils, and there are parallel trends in soil horizon textures. Within the soils, clay content peaks in the Brady Soil for 8G00 and 5G00, and within the modern “Bt” for 3G00 (Jacobs & Mason 2007). These clay peaks are thought to originate from a fining of particles as dust production slackened during the late Pleistocene-Holocene transition, rather than through clay translocation or weathering (Jacobs & Mason 2007). Clay particles are mostly smectitic (Jacobs & Mason 2007); however the presence of RSi has not been explored.

The Nebraska soils are likely to contain significant amounts of inherited RSi. Silt-rich sediments of the White River Group – a major source of late Pleistocene loess – have been documented to contain an average of 53% rhyolitic and andesitic volcanic glass (Swinehart et al 1985). Volcanic glass has similarly been documented in the loess soils of central and eastern Nebraska, though in lower abundance (Mason & Kuzila 2000; Mason et al 2003). A recent study found silt-sized glass content approaching 10% in the 8G00 soil (Jacobs & Mason 2007). Glass solubilities are relatively high when compared to primary and secondary silicate minerals (Iler 1979; Drees et al 1989), creating a relatively large inherited source of RSi.

Extensive use of silica by grassland species can result in relatively high rates of phytolith deposition through litterfall. However, phytolith preservation in soils is also a function of climatic conditions and soil properties. Working with a transect of soils across the central Great

Plains, Blecker et al (2006) found an inverse relationship between soil phytolith content and mean annual precipitation. Although wetter climatic conditions resulted in more biomass per unit area and thus higher rates of phytolith production, soil phytolith turnover rates were higher in the more humid zones due to more intense weathering and biocycling. Hence, it is likely that phytolith content within the Nebraska soils should decrease eastward, as more humid climatic conditions prevail. Phytolith preservation can also be modified by the presence of inherited forms of RSi, which can mitigate phytolith dissolution (Henriet et al 2008). Working in tropical volcanic soils formed under a bamboo forest, Meunier et al (1999) documented soil horizons composed almost entirely of phytoliths. Similarly, Parr & Sullivan (2005) found an average phytolith content of 265.73 mg g^{-1} for six soils formed under bamboo forest in a tropical volcanic setting (calculated from data in that paper). Hence, the preferential weathering of volcanic glass within the Nebraska soils could act to stabilize soil phytoliths, thereby yielding larger pools than otherwise would be expected.

Clay-sized RSi within soils has never been directly explored. Based upon clay-sized phytolith content in some plant species, Jones & Beavers (1964a) estimated that soil clay-sized BSi content could approach 50% of total BSi, but this has never been verified. Within the Nebraska soils, the proportion of clay-sized relative to total RSi could be much higher, given the eolian origin. On the other hand, weathering processes could act to strip clay-sized RSi relatively quickly due to their high surface area to volume ratios, leaving a greater proportion of larger grains.

Pedogenic RSi, in the form of adsorbed forms and short range order clays, is most likely low in the Nebraska soils due to a lack of significant weathering in the modern soils. However, pedogenic RSi content may be higher within the Brady Soil (as compared to the modern soil),

due to its relatively more advanced state of weathering. Similarly, pedogenic RSi may increase eastward due to more intense weathering.

Regional paleoreconstructions suggest that open vegetation with both trees and grasses was present for much of the late Pleistocene and even into the earliest Holocene (Fredlund 1989; Johnson 1989; Rousseau & Kukla 1994; Johnson & Willey 2000). However warmer and drier conditions of the Holocene favored grassland which has persisted to modern times (Grüger 1973; Mason et al., 2008).

3.2.1.2 Minnesota Soils

The soil AL2 is a Typic Hapludalf that was formed under deciduous broadleaf forest at the time of the 19th century public land survey, while KO1 is a Mesic Typic Hapludoll that was under tall grass prairie (Fig. 3.1; Table 3.1). Located within close proximity to each other, these two soils are situated on the loess mantled, bedrock controlled uplands of southeastern Minnesota. These two soils share many similar factors of soil formation: mean annual precipitation and temperature are similar; both are found on stable upland settings formed in thick loess; they share the same dust source area and are roughly equidistant from it; and the time of pedogenesis is the same. In fact, the only marked difference is vegetation.

Loess deposition at these sites originated mostly from the region immediately to the west (Mason & Nater 1994; Mason et al 1994), which includes pre-Illinoian till of the Iowan Erosion Surface (Ruhe 1969), and late Pleistocene Wisconsinan till from the Des Moines Lobe (Mason 1992). A large component of Des Moines Lobe sediments originated from the northern Great Plains, which contains material reworked from the Cretaceous Pierre Shale (Gill & Cobban

1973; Jones & Blatt 1984; Lusardi et al 2011). Beds within the Pierre Shale on the northern Great Plains have been shown to contain large amounts of cristobalite in the silt fraction (up to 70%), and probably significant amounts of clay-size grains as well (Jones & Blatt 1984). Cristobalite is a poorly crystallized form of silica, which tends to exhibit solubilities between amorphous silica and quartz (Iler 1979; Drees et al 1989). Glacial erosion and transport, and subsequent eolian deflation and sorting may have produced smaller cristobalite grains as well as rough edges, thus making them possible RSi sources. Cristobalite has been identified in Soil 2 used in Chapter 2, but its abundance is not known (Mason 1992).

When comparing the two soils, phytolith content is expected to be higher for the Mollisol KO1 due to grassland vegetation. On the other hand, pedogenic RSi may be higher in the Alfisol AL2 due to slightly greater rates of weathering under forest. However this could work in the opposite fashion, whereby increased acidity may lead to greater RSi mobility and desilication.

Paleoreconstructions at sites adjacent to the study area to the north, south, and west indicate that boreal forest persisted into the early Holocene, followed by a shift to mesic deciduous forest (Chumbley et al 1990; Dorale et al 1992; Baker et al 1996; Denniston et al 1999). Drier conditions during the mid-Holocene caused a shift to grassland vegetation, followed by another shift to oak savanna approximately 3400 cal. yr BP (Baker et al 2002). Prior to Euro-American settlement, vegetation within this region for most of the late Holocene was mixed prairie and oak savanna with scattered areas of forest and grassland (Marschner 1974; Minnesota DNR Staff 2009). The distribution of vegetation communities in this ecotonal region was probably controlled by topography through its influence on the spread of wildfires (Grimm 1983, 1984; Baker et al 2002).

3.2.1.3 Wisconsin & Illinois Soils

TQ is a Typic Hapludalf from west-central Illinois (Fig. 3.1; Table 3.1). This soil was formed in Peoria Loess, which was deposited during and after the last glacial maximum, and prior to the Holocene (Hansel & Johnson 1996). The loess originated mostly from valley-train deposits from the Illinois River Valley (Frye et al 1968; Grimley et al 1996), and loess deposition coincided with the westward advancement of the Lake Michigan and Lake Erie lobes (Frye et al 1968). Lake Michigan lobe glacial till is composed primarily of Devonian and Mississippian shales and to a lesser extent Silurian dolomite (Willman & Frye 1970). Similarly, Peoria Loess which was deposited on the Illinois River bluffs is high in illite content, reflecting the sedimentary origin (Frye et al 1968). Thus, the inherited RSi component from local dust sources in this soil was expected to be small.

On the other hand, evidence for far-travelled, fine dust has been documented in this soil (Mason & Jacobs 1998). This fine dust is thought to originate from regions as far west as the Great Plains, and therefore it may contain significant amounts of RSi, similar to the Nebraska soils. Deposition of this fine dust may have occurred during the final phase of loess aggradation, or later in the Holocene.

When compared to the other soils, phytolith content was expected to be relatively low due to forest vegetation. Pedogenic RSi may similarly be low due to increased weathering, but the presence of relatively stable forest throughout much of the Holocene may have facilitated the buildup of these pedogenic forms.

As recorded in surveyor notes, pre-settlement vegetation at the TQ site consists of unbroken hardwood forest, which continues as a narrow strip along the eastern bluffs of the

Illinois River (Zawacki & Hausfater 1969; Kilburn et al 2009). The preservation of a thin A horizon over a light-colored E horizon at the TQ site indicates that the soil has not been plowed (Mason & Jacobs 1998). Aside from surveyor notes, vegetation reconstructions for the west-central Illinois region are scarce. Nevertheless, biome maps generated from pollen data (Williams 2002; Williams et al 2004) indicate the presence of cool mixed forest throughout the latest Pleistocene until approximately 8000 yr BP, after which it was replaced by temperate deciduous forest.

KA is located approximately 100 kilometers northeast of Madison, WI (Fig. 3.1; Table 3.1). This soil was formed in approximately 180 cm of loess underlain by till of the Green Bay Lobe. Most dust originated from the Upper Mississippi Valley (UMV) to the west and was transported to KA through repeated re-entrainment across the sand plains of central Wisconsin (Jacobs & Mason 2011). The timing of loess deposition is not known with any certainty, but it occurred after deglaciation in the Late Pleistocene.

Clay mineralogy of the parent material of KA and other loess on the Green Bay Lobe is dominated by smectite, with vermiculite, illite, kaolinite, and chlorite (Jacobs & Mason 2011). Prior work has provided no evidence on the presence or abundance of RSi in this loess.

Paleoreconstructions from nearby lakes in the region indicate *Picea* dominance during the late Pleistocene, followed by a shift to deciduous species in the early Holocene and finally oak savanna and grassland during the middle Holocene (Maher 1982; Winkler 1986; Winkler et al 1988). The modern vegetation at the site of KA was tall grass prairie at the time of 19th century public land surveys. The site is presently cultivated.

3.2.2 Analytical Methods

To compare profiles of RSi between soils, the content of each RSi form was estimated for standard depths of 2.5, 25, 45, 75, 95, and 195 cm. Additional sampling at finer sampling resolution was performed in some cases in order to gauge variation with depth.

3.2.2.1 Total RSi (alkali-extractable)

A modified version of the DeMaster method (DeMaster 1981) was utilized to measure total RSi, or RSi_{Tot} . This method, termed sequential leaching with linear extrapolation (SLLE), is described in full detail in Chapter 2. Briefly, a 10-15 mg homogenized sample was immersed in 500 mg 0.5 M NaOH at 85° C for five hours. Aliquots were drawn off at 30 minute intervals from 150 to 300 minutes and measured colorimetrically using a modified version of the molybdate blue method as outlined by Jones & Dreher (1996). To account for and subtract silica dissolved from silicate minerals, a linear regression calculation was performed on the resulting six data points and extrapolated back to time 0. The resulting y-intercept represents the corrected RSi estimate.

In order to gauge the variation of RSi_{Tot} , 10-18 samples were processed for each soil, at 10-20 cm intervals. As noted above, only the standard depths were used to calculate mean RSi_{Tot} content.

Precision of the method was determined by processing several replicate samples. Three replicates each were processed for 8G00 5-10 cm, KO1 0-8 cm, and TQ 0-13 cm. Replicates for 8G00, TQ, and another soil had previously been processed for Chapter 2, and these data were

also used here. The means and standard deviations of each sample replicate group were then calculated. Precision was then determined by calculating coefficient of variation percentages (standard deviation divided by mean multiplied by 100). Finally, the mean of all coefficients of variation was used as an overall estimate of precision for all samples.

3.2.2.2 RSi greater than 10 μm (floatation-extractable)

A modified version of Pearsall (1989) was used to extract silt- and sand-sized RSi particles. In this method, all RSi particles $>10\ \mu\text{m}$ were extracted and quantified ($\text{RSi}_{>10}$). Six samples each were processed for each soil, corresponding to the standard depths outlined above. Samples were first dried overnight at 50°C , and then homogenized using a mortar and pestle. To remove carbonates, approximately 2 g of sample was placed in a 125 ml glass beaker followed by 10 ml 10% HCl at ambient temperature. The supernatant was then diluted with deionized water (MilliQ), allowed to settle for 15 minutes, and then poured off. The dilution/decantation step was repeated 3 times. Organic matter was removed by adding 30 ml concentrated HNO_3 . The samples were then heated to near boiling and stirred occasionally. A pinch of KClO_3 was added to each beaker to accelerate the reaction. The supernatant was then diluted and decanted three times. Following this, 5-10 ml of 30% H_2O_2 was added to each beaker and heated to 50°C for 2-3 hours. The samples were then allowed to sit unheated overnight, after which the supernatant was diluted and decanted three times. The samples were then washed into 50 ml plastic centrifuge tubes. Any remaining water was centrifuged and poured off. Aggregates were dispersed by adding 50 ml of $0.5\ \text{g L}^{-1}$ $(\text{NaPO}_3)_6$ (sodium metaphosphate) and agitating overnight.

Particles smaller than 10 μm were next removed by gravity sedimentation. The samples were washed into 2000 ml graduated cylinders, which were filled to capacity using 0.5 g L⁻¹ (NaPO₃)₆. The liquid was mixed thoroughly to fully suspend the samples. The cylinders were allowed to sit undisturbed. Following the settling times as outlined by Tanner & Jackson (1947), particles smaller than 10 μm were removed from the upper 10 cm using a vacuum pump. The clay removal process was repeated 12-15 times for each sample, depending on the amount of <10 μm particles present. The remaining sediment was transferred back to the 50 ml plastic centrifuge tubes, and any remaining supernatant was centrifuged and decanted three times.

Following this, any remaining supernatant was removed using a Pasteur pipette. The samples were then immersed in ZnBr₂ set to a density of 2.5 g cm⁻³. A density of 2.3 g cm⁻³ is commonly used in phytolith analysis (Alexandre et al 1997; Reyerson 2004; Blecker et al 2006). However, 2.5 g cm⁻³ was used here to ensure adequate recovery of slightly higher density RSi forms such as volcanic glass. Following immersion, the samples were centrifuged at 3000 rpm for 4 minutes. The floating RSi particles were then removed using a Pasteur pipette and dispensed into 15 ml plastic centrifuge tubes. The volume of supernatant extracted was then replaced with fresh ZnBr₂. The extraction procedure was repeated six times for all samples to ensure nearly complete recovery of all RSi. The RSi extract was then diluted with water and mixed thoroughly. The tubes were then centrifuged and the supernatant was poured off. This was repeated at least four times to ensure complete removal of ZnBr₂.

The RSi extracts (along with approximately 2 ml water) were next transferred to pre-weighed 5 ml glass vials using Pasteur pipettes. The vials were filled to capacity and shaken. The extracts were allowed to settle for 15 minutes and the remaining supernatant was removed using

Pasteur pipettes. This step was done to remove any remaining clay particles. Following this, the samples were dried at 100° C overnight and then weighed.

The floatation method extracts all $RSi_{>10}$, regardless of origin. Microscope identification and classification of the extracts was then performed in order to categorize particles as biogenic (BSi) or nonbiogenic (NSi) in origin. Following the extraction procedure, small amounts of the extracts were mounted on microscope slides using Canada Balsam and allowed to cure. Analysis was performed on a Nikon petrographic microscope at 400x magnification, although polarized light was seldom used. The entire slide was scanned by transects, and all particles encountered were classified by morphology as either BSi or NSi. Morphological features such as size, shape, texture, and symmetry were considered for each grain to ensure objective classification. In many cases grains exhibited characteristics which suggested a biological origin, but could not be positively identified as BSi due to fragmentation or severe weathering. These grains were then added to the NSi category. The weights of BSi and NSi in each sample were calculated by multiplying proportion of each category by the $RSi_{>10}$ weight.

As with RSi_{Tot} , precision for $RSi_{>10}$ was determined through replicate analysis: Three replicates of KO1 0-8 cm were processed. Precision for BSi and NSi estimates was determined by summing variance from $RSi_{>10}$ as well as the microscope classification technique.

3.2.2.3 RSi Smaller than 10 μm (alkali-extractable minus floatation-extractable)

RSi Smaller than 10 μm ($RSi_{<10}$) was estimated by subtracting $RSi_{>10}$ from RSi_{Tot} . Precision was determined by summing errors generated from the RS_{Tot} and $RSi_{>10}$ measurement

techniques. Quantification of BSi and NSi particles $<10\ \mu\text{m}$ was not possible since the SLLE method (which measures RSi_{Tot}) cannot differentiate between these two fractions.

3.2.2.4 Pedogenic/shard RSi (oxalate-extractable)

The oxalate dissolution procedure used here is a modified version of the methods used by Loeppert & Innskeep (1996) and Saccone et al (2007), which in turn were modified from Schwertmann (1964) and McKeague & Day (1966). This method was developed to target short range order clays (Saccone et al 2007; Cornelis et al 2011). However, these forms are expected to be negligible within the study soils. The oxalate extraction is known to remove RSi forms normally not targeted by less aggressive solvents, such as dissolved, exchangeable, and adsorbed silica. Further, the agitation step described below probably induces dissolution of fine edges and shards or lower solubility material (this would occur with any solvent, so long as agitation is used). Hence, the RSi extracted by oxalate can be thought of as a combination of pedogenically altered and various other readily available forms of silica.

The oxalate solvent was prepared by mixing 17.56 g of reagent grade $[\text{COOH}]_2 \cdot 2\text{H}_2\text{O}$ (oxalic acid) and 28.4 g $[\text{COONH}_4] \cdot \text{H}_2\text{O}$ (ammonium oxalate) into approximately 800 ml deionized H_2O . The pH was then adjusted to 3.0 using HCl, diluted to 1 L, and stored in an opaque plastic bottle.

Approximately 0.5 g of air-dried, homogenized sample was added to a 50 ml plastic bottle, to which 50 ml oxalate solution was added. Occasionally 1 g samples were used; in these cases 100 ml oxalate solution was used to maintain a similar solid-solution ratio. Once the oxalate solution was added to the samples, the reaction bottles were immediately shielded from

light and agitated for 60 minutes using magnetic stir bars at 100 rpm. The sample supernatant was then poured into 50 ml plastic centrifuge tubes, spun at 5000 rpm for 10 minutes, and allowed to rest for an additional 5 minutes. Thus, the samples were exposed to oxalate dissolution for a total of 75 minutes. A portion of the clear supernatant was then transferred to 20 ml plastic vials and stored away from light sources.

Silica concentrations were then measured colorimetrically using a modified version of the molybdate blue technique as described by Jones & Dreher (1996). See Chapter 2 for a description of reagent mixing procedures. Accurate and precise liquid volumes were maintained through the use of a digital pipettor and bottletop dispensers. Using the pipettor, a 2 ml aliquot of the oxalate-silica solution was transferred to a 30 ml opaque plastic bottle. To remove any residual liquid in the pipette tip, 2 ml of deionized water (MilliQ) was aspirated and then dispensed into the plastic bottle. Occasionally smaller aliquots were used when silica concentrations were too high (usually 1 ml). In these cases, a blank of unused oxalate solution was added to bring the total volume of oxalate to 2 ml and thereby ensure that the total volume, molarity, and pH were identical for all samples. An aliquot of 2 ml 0.67 M H_2SO_4 was then added to the bottle to acidify the solution. The bottles were then mixed by swirling and allowed to sit for 30 minutes. Next, 5 ml of molybdate reagent was added, mixed thoroughly, and allowed to sit for five minutes. 5 ml of the tartaric acid and 9 ml of the reducing solution reagents were added and mixed thoroughly. Color was allowed to develop for exactly one hour for all samples.

Silica concentrations were measured using a Milton Roy Spectronic 21 spectrophotometer. Standard curves were prepared daily or when switching to a new batch of reagents. Silica standards were prepared from a stock silica solution of $1000 \mu\text{g ml}^{-1}$. The silica

standard concentrations were: 0.00 (reagent blank), 0.08, 0.16, 0.24, 0.32, and 0.40 $\mu\text{g ml}^{-1}$.

Three replicates of the KO1 0-8 cm sample were used to determine precision.

3.2.2.5 Particle Size, Organic C, and pH

Particle size, organic C, and pH data from many of the soils used here were measured in previous studies and/or by other workers (Table 3.2). The methods used were identical for all the soils, except as noted below.

Particle size was determined using the pipette method (Gee & Bauder 1986). Due to the fact that sand content was found to be minimal in most cases, it was combined with the silt fraction. Several replicates of a soil sample not used in this study were processed to determine precision.

Organic C was measured by loss on ignition. All soil profiles except AL2 and KO1 were processed at 360° C for 2 hours (Schulte & Hopkins 1996). AL2 and KO1 were combusted at 400° C for 16 hours, which is a slightly modified version of that used by Nelson & Sommers (1996) which in turn was adapted from Ben-Dor & Banin (1989). Organic matter content was then converted to organic C using the predictive equations of Konen et al (2002). Several

replicates of a soil sample not used

in this study were processed to

determine precision.

Soil pH was measured by

immersing soil samples in a 1:1

ratio of deionized water, and

Table 3.2. List of data gathered by other researchers.

Measurement	Soil Profile	Reference
Particle Size	8G00, 5G00, 3G00	Jacobs & Mason (2007)
	KA	Jacobs & Mason (2011)
	TQ	Mason & Jacobs (1998)
Organic C	8G00, 5G00, 3G00	Jacobs & Mason (2005)
	KA	J. Mason (unpublished)
pH	KA	J. Mason (unpublished)

measured using a benchtop pH meter after 2 hours Precision was not determined for pH.

3.3. Results

Summary data (whole-profile averages for each measurement) are reported in Table 3.3, while the full data set is listed in Appendix 6. The summary data should be approached with caution, as the averages do not factor in soil density, which could vary from profile to profile. Nevertheless, if density is assumed to be nearly similar across soil profiles, the data presented in Table 3.3 serve to rank the soil profiles by measurement in a qualitative fashion. Results for all

Table 3.3. Soil whole-profile averages $\pm$ ranges, compiled from 5, 25, 45, 75, 95, and 195 cm approximate depths. All measurements expressed as mg g^{-1} except pH.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extractable RSi
	<i>Total</i>	<i>Clay-Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>	
All Soils	64.31 $\pm$ 42.43	52.48 $\pm$ 37.24	11.82 $\pm$ 25.23	6.80 $\pm$ 17.26	5.03 $\pm$ 18.94	0.50 $\pm$ 0.36
8G00	87.22 $\pm$ 8.52	58.25 $\pm$ 25.45	28.97 $\pm$ 18.04	14.02 $\pm$ 14.01	14.95 $\pm$ 16.23	0.37 $\pm$ 0.30
5G00	77.02 $\pm$ 7.52	56.41 $\pm$ 29.36	20.61 $\pm$ 23.77	11.22 $\pm$ 14.27	9.39 $\pm$ 9.49	0.50 $\pm$ 0.29
3G00	75.20 $\pm$ 9.65	66.97 $\pm$ 15.49	8.23 $\pm$ 9.85	5.02 $\pm$ 7.21	3.20 $\pm$ 2.64	0.65 $\pm$ 0.26
AL2	50.93 $\pm$ 17.55	44.74 $\pm$ 18.18	6.19 $\pm$ 3.58	2.50 $\pm$ 3.23	3.69 $\pm$ 2.92	0.39 $\pm$ 0.18
KO1	59.62 $\pm$ 19.09	52.62 $\pm$ 17.02	7.00 $\pm$ 5.62	4.30 $\pm$ 5.83	2.70 $\pm$ 3.86	0.67 $\pm$ 0.15
KA	52.70 $\pm$ 32.50	46.78 $\pm$ 25.13	5.91 $\pm$ 8.29	5.36 $\pm$ 8.26	0.55 $\pm$ 0.51	0.42 $\pm$ 0.14
TQ	47.46 $\pm$ 33.65	41.61 $\pm$ 32.83	5.85 $\pm$ 6.48	5.16 $\pm$ 6.60	0.69 $\pm$ 0.49	0.46 $\pm$ 0.13

measurements are shown graphically in Figure 3.2. These data are expressed as mg g^{-1} dry soil weight (except pH); percentages can be ascertained by dividing values by 10. While most particle size data is expressed as percentages, it is reported here as mg g^{-1} for consistency with the other data. Since RSi_{Tot} is composed of various fractions, it becomes advantageous to determine the relative contribution of each fraction to the total in each sample. This serves as a

way to visualize how the proportions of each fraction changes within and across soils. These data are displayed in Figure 3.3.

3.3.1 RSi_{Tot} (alkali-extractable)

In general, RSi_{Tot} values decrease from west to east for the Nebraska soils (Fig. 3.1). Many of these values are the highest recorded for all soils. On average, the Minnesota soils contained approximately 30% less overall RSi_{Tot} than the Nebraska soils, and AL2 contained slightly less RSi_{Tot} than KO1. Average RSi_{Tot} for KA was intermediate to AL2 and KO1, while TQ yielded the lowest value for all soils. Compared to the Nebraska soils, KA contained 33% less RSi_{Tot} , while TQ was 40% lower.

RSi_{Tot} content peaks between 25 and 65 cm for the Nebraska soils (Fig. 3.2). Peaks of RSi_{Tot} for 8G00 and 5G00 occur near or at the top of the Brady Soil, and remain relatively high well into the B horizon of that paleosol. RSi_{Tot} content in 3G00 is highest in the modern B horizon, which has been documented as a former A horizon of the Brady Soil (Jacobs & Mason 2007). Both of the Minnesota soils displayed two distinct RSi_{Tot} peaks. The lower peak occurred at approximately 175 cm for both soils, while the upper peaks were found at 79.5 and 27.5 cm for AL2 and KO1, respectively. KA was the only soil to display an RSi_{Tot} peak at the surface. RSi_{Tot} content in the TQ soil peaked at 39 cm, but remained elevated throughout the B horizon.

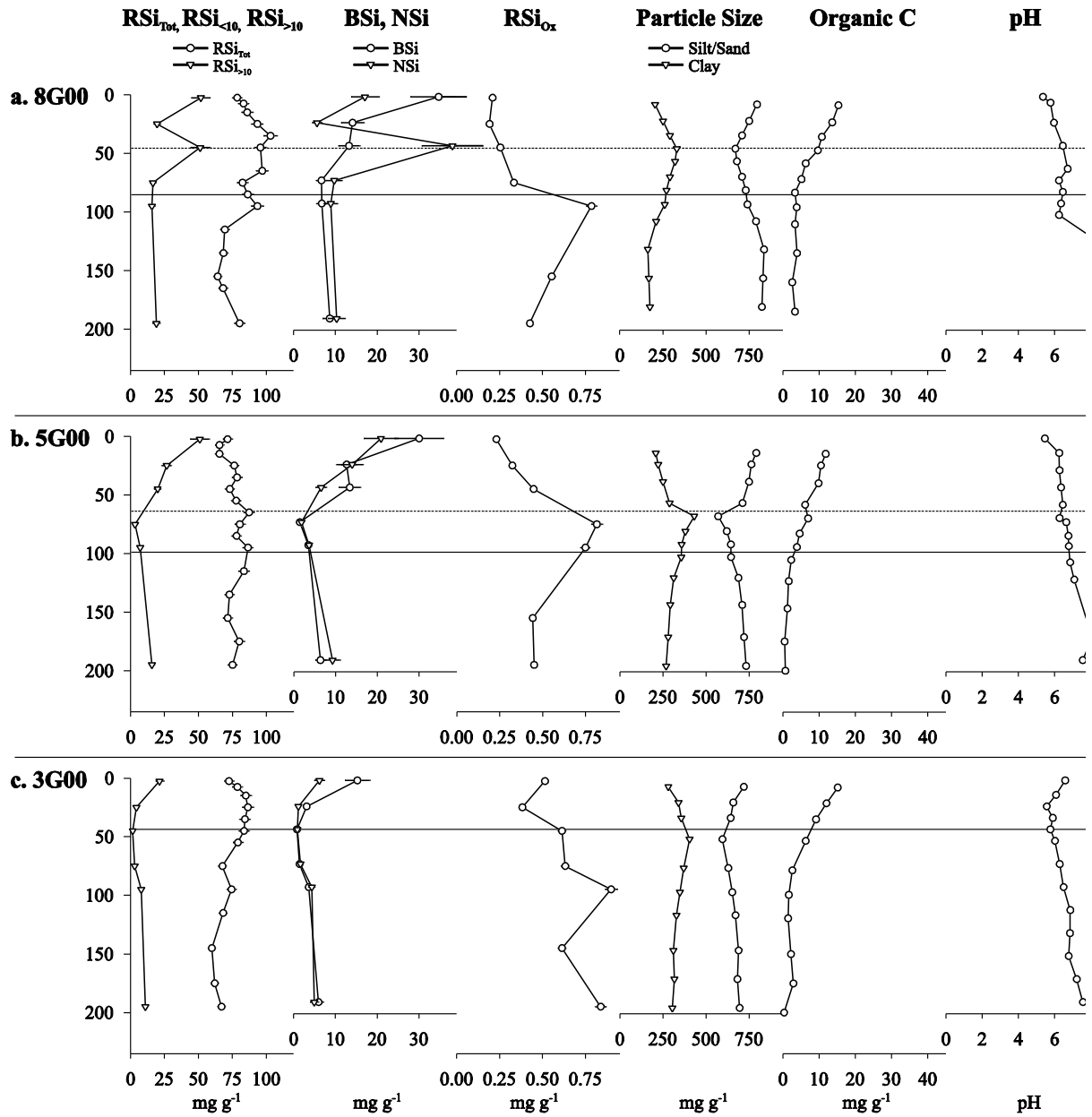


Figure 3.2. RSi, particle size, organic C, and pH data for soil profiles. RSi_{<10} can be determined as the difference between RSi_{Tot} and RSi_{>10}. Error bars represent 2σ as determined from replicates. Error bars which are not visible are smaller than symbols. Horizontal stippled and solid lines represent the top of Brady Soil Ab and Bt horizons, respectively (line for 3G00 represents modern Bt).

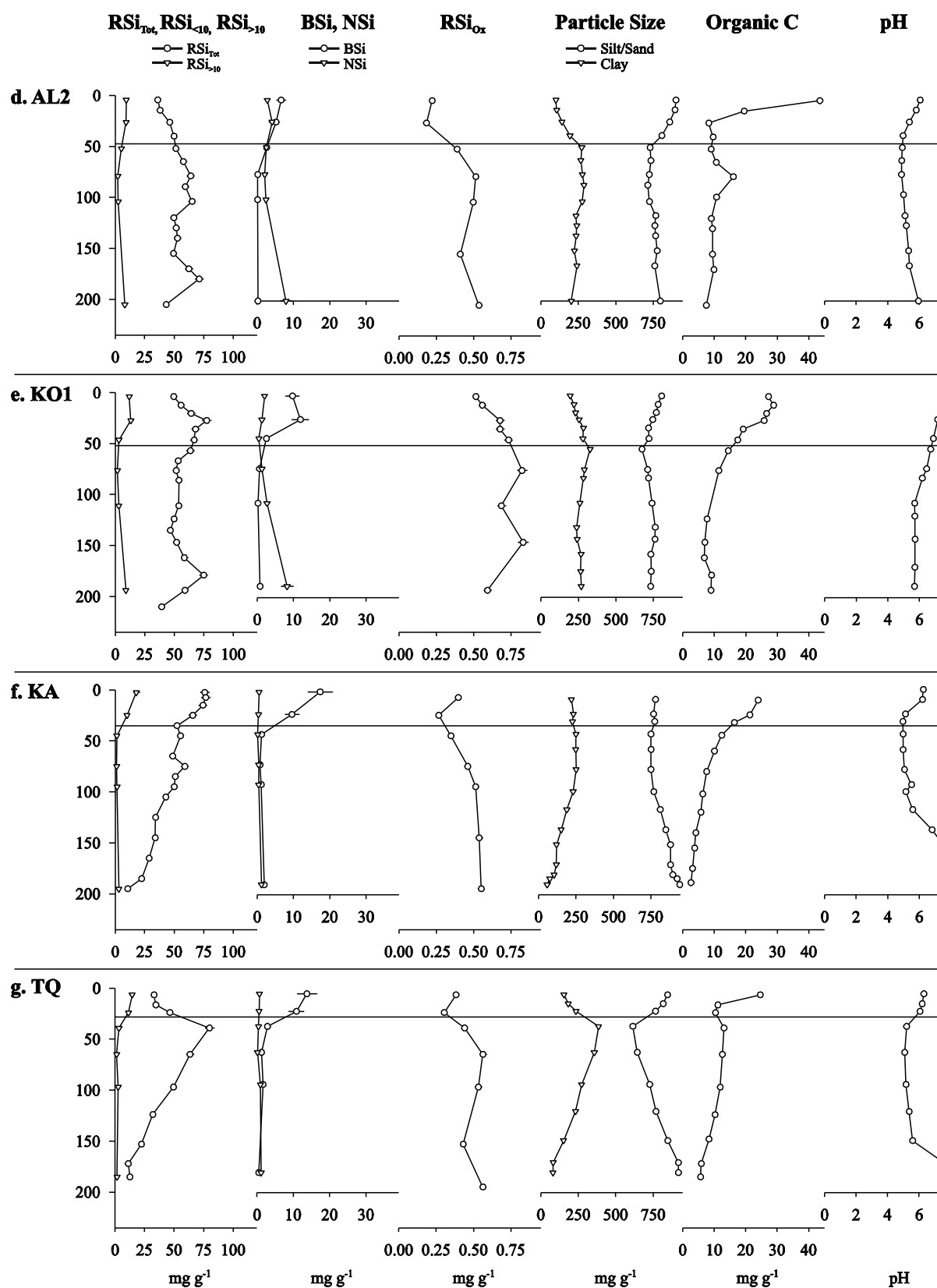


Figure 3.2. Continued. Horizontal lines represent top of Bt horizons.

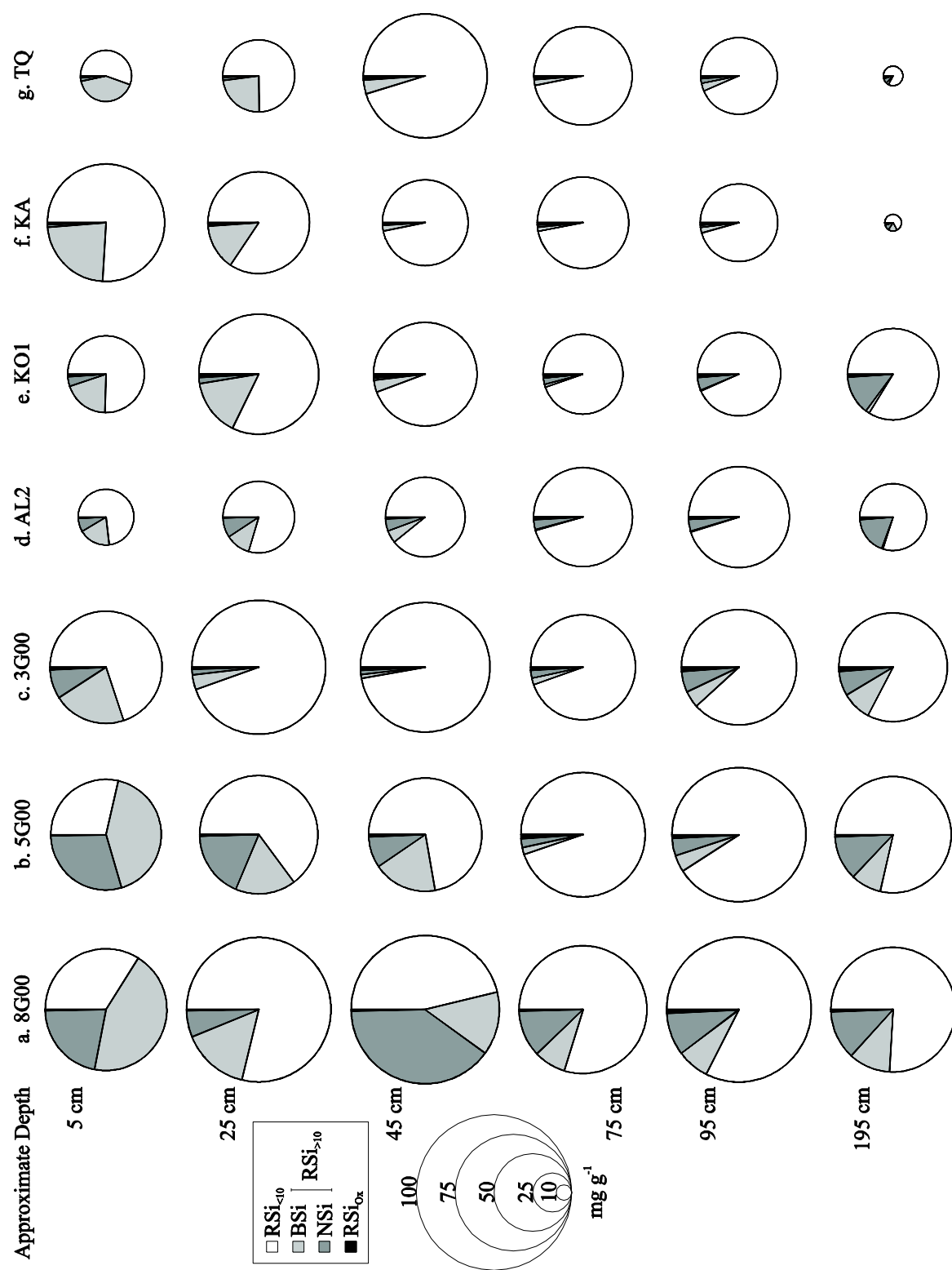


Figure 3.3. Proportions of RSi_{L10} , BSi and NSi (as subfractions of RSi_{L10}), and RSi_{ox} relative to RSi_{Tot} . Size of each pie chart denotes RSi_{Tot} amount.

3.3.2 $\text{RSi}_{<10}$ (alkali-extractable minus floatation-extractable)

Although quite variable, $\text{RSi}_{<10}$ content generally increased eastward in the Nebraska soils (Table 3.3). $\text{RSi}_{<10}$ content was 19% lower in the Minnesota soils, and AL2 contained less than KO1. KA contained similar $\text{RSi}_{<10}$ content as AL2, while TQ yielded the lowest amount (31% less $\text{RSi}_{<10}$ when compared to the Nebraska soils).

$\text{RSi}_{<10}$ content peaks at 95 cm for both 8G00 and 5G00, which occur within the Brady Soil B horizons (Fig. 3.2). The $\text{RSi}_{<10}$ peak for 3G00 is much shallower, at 25 cm (lower Ap horizon). As with the Nebraska soils, $\text{RSi}_{<10}$ content in the Minnesota soils increased with depth into B horizons. Maximum content was approximately 63 mg g^{-1} for both soils, but they occurred at different depths: 104 cm for AL2, and 27.5 cm for KO1. $\text{RSi}_{<10}$ content in KA peaked at the surface, at 57.78 mg g^{-1} and decreased with depth. $\text{RSi}_{<10}$ content peaked at 39 cm in TQ.

Relative proportions (Fig. 3.3) indicate that most RSi resides in the $<10 \mu\text{m}$ fraction for all soils. The relative proportion of $\text{RSi}_{<10}$ (Fig. 3.3) increased with depth in all soils, peaking in illuvial horizons. These peak percentages varied from 83.20% (8G00, 90-100 cm) to 97.97% (3G00, 40-50 cm). At the surface, $\text{RSi}_{<10}$ percentages ranged from 28.66% (5G00) to 76.34% (KA).

3.3.3 $\text{RSi}_{>10}$ (floatation-extractable)

Unlike $\text{RSi}_{<10}$ but similar to RSi_{Tot} , silt-sized RSi particles ($\text{RSi}_{>10}$) decreased eastward. In the Nebraska soils, average whole-profile $\text{RSi}_{>10}$ content was highest in 8G00, followed by 5G00 and 3G00 (Table 3.3). In the Minnesota soils, $\text{RSi}_{>10}$ content was higher in the Mollisol

KO1, but both soils were considerably lower than the Nebraska soils. $RSi_{>10}$ average content for KA and TQ were similar, but slightly lower than the Minnesota soils.

Within the Nebraska soils, average $RSi_{>10}$ content was highest at the surface and decreased with depth, with one exception (Fig. 3.2): In the 8G00 soil, $RSi_{>10}$ reached a secondary maximum at 45 cm. Microscopic analysis of $RSi_{>10}$ particles at this depth revealed an abundance of sand-sized glass particles. This lower peak coincides with the top of the Brady Soil. Content was highest at the surface for AL2, while KO1 peaked at 27.5 cm. Slightly less $RSi_{>10}$ content at the surface of KO1 is probably a result of incomplete organic matter removal during the digestion process, which led to some $RSi_{>10}$ still bound to aggregates. Thus, the value reported for this depth should be considered a minimum. $RSi_{>10}$ content for both KA and TQ decreased with depth.

In all soils, minimum $RSi_{>10}$ content coincided with clay content and $RSi_{<10}$ peaks in illuvial horizons (Fig. 3.2). At the bottom of the soil profiles, $RSi_{>10}$ content again increased, possibly from a greater concentration of unweathered inherited forms. These depth patterns are also reflected in Figure 3.3, where the relative proportion of $RSi_{>10}$ tended to decrease with depth into illuvial horizons and increase slightly near the bottom of the profiles.

Average BSi and NSi content in the Nebraska soils decreased eastward, similar to $RSi_{>10}$ (Table 3.3). Within the Minnesota soils, AL2 contained less BSi than KO1. Conversely, slightly more NSi was found in AL2 than KO1. KA contained slightly more BSi than TQ. NSi content in KA and TQ was considerably lower than the other soils.

In most cases, BSi content was highest at the surface (Fig. 3.2). The only exception was KO1, which peaked at 27.5 cm. Minima were found in illuvial horizons. BSi content in the Nebraska soils increased slightly near the bottoms of the profiles. NSi content followed a similar

pattern as $RSi_{>10}$, where content decreased with depth into illuvial horizons followed by slight increases into C horizons. As a reminder, NSi includes inherited forms (glass, cristobalite), as well as forms of unknown origin. These latter forms can include fragmented or weathered BSi which cannot be identified by morphology.

The proportion of whole-profile $RSi_{>10}$ content was highest for 8G00 and 5G00, at 33% and 27%, respectively. The remaining soils all contained 11-12%. Not surprisingly, proportions of BSi fell to low or negligible levels with depth in all soils (Fig. 3.3). Hence, silt- and sand-sized BSi does not contribute significantly to RSi pools below approximately 50 cm. The relative contribution of NSi to total RSi was also greatest near the surface, but it can also be seen that this fraction's proportions again increase below illuvial horizons. Thus, NSi content is both a reflection of weathering processes (unknown forms near the surface which probably originate from weathered BSi) and weathering state (unweathered inherited forms of silica found at deeper depths).

3.3.4 RSi_{Ox} (oxalate-extractable RSi)

Average whole-profile oxalate RSi_{Ox} content for the Nebraska soils increased eastward, opposite of the RSi_{Tot} trend (Table 3.3). KO1 contained slightly more RSi_{Ox} than 3G00, and AL2 was approximately half of KO1. KA and TQ yielded similar values, which were intermediate to the others.

Depth trends revealed that RSi_{Ox} increased with depth in most soils, generally peaking in illuvial horizons (Fig. 3.2). RSi_{Ox} in 8G00 and 5G00 peaked within the Brady Soil, and in the B horizons for the remaining soils except KA. In KA, RSi_{Ox} content increased to a maximum at the

bottom of the profile. Slightly elevated RSi_{Ox} values were found at the surface in all soils except 5G00 and KO1.

When analyzing Figure 3.3, it can be seen that the percentages of RSi_{Ox} relative to totals are very low for all soils, ranging from 0.21% (8G00 20-30 cm) to 5.16% (KA 190-200 cm).

3.4. Discussion

3.4.1 RSi_{Tot}

As noted in Chapter 2, RSi_{Tot} values generated by the SLLE method used here are much higher than other methods used in the literature. Chemical extraction methods always measure higher amounts of RSi than floatation methods, because the latter do not extract clay-sized RSi particles. This disparity becomes evident when comparing the RSi_{Tot} and $\text{RSi}_{>10}$ data presented here (Fig. 3.2; Table 3.3).

The solvent used here, 0.5 M NaOH, exhibits a higher pH when compared to the more commonly used 0.1 M Na_2CO_3 (13.7 versus 11.2). Hence, the use of 0.5 M NaOH facilitates the more complete extraction of lower solubility forms of RSi. It is possible but unlikely that the use of such an aggressive solvent may induce dissolution of clay minerals, such as kaolinite, illite, or montmorillonite, but this point discussed further in section 3.4.2.

As shown in Table 3.3, the Nebraska soils contain more RSi_{Tot} than the other soils. These large amounts of RSi_{Tot} most likely stem from inherited volcanic glass sourced from the volcanoclastic White River and Arikaree Groups (Aleinikoff et al 1998). Silt- and sand-sized

volcanic glass has been identified in this study (Table 3.3) as well as others (Mason & Kuzila 2000; Jacobs & Mason 2007).

The eastward decrease in RSi_{Tot} content in the Nebraska soils can be explained in two ways (Table 3.3). First, annual precipitation increases eastward also, suggesting that increased rates of weathering may result in RSi losses. Second, C horizon RSi_{Tot} is less in 3G00 than the other two profiles, suggesting that the differences may be more related to the concentration of inherited RSi in the loess, rather than weathering, which should have been minimal in C horizons. In that case, the eastward trend of decreasing RSi may be sedimentary, related to distance from dust sources. The Nebraska Sand Hills are the immediate dust source (Mason 2001; Mason et al 2003), and thus 8G00, 5G00, and 3G00 are proximal, intermediate, and distal to the dust source, respectively. An increasing fining of dust with distance is evident in the particle size data (Table 3.3), where 3G00 contains more clay than the other two soils. If a greater proportion of glass was in the coarse and medium silt fractions, or in the silt fraction in general as opposed to the clay fraction, sorting with distance would result in less RSi_{Tot} at the distal 3G00 site. Indeed, the average content of $NSi_{>10}$ most of which is composed of glass, decreases eastward (Table 3.3). Another study (Jacobs & Mason 2007) found similar results, where volcanic glass content of 8G00 was significantly higher than 5G00.

In all the Nebraska soils, RSi_{Tot} increases away from the surface (Fig. 3.2). This is unlikely to be a sedimentary effect, as suggested for average RSi_{Tot} , although it has been proposed that the final phase of loess accumulation in some areas was characterized by increased fine silt and clay content (e.g. Mason and Jacobs 1998). Clay content actually increases downward to a subsurface peak in all three soils (Fig. 3.2), so if the vertical profile of RSi_{Tot} was

mainly a function of the particle size we would expect a subsurface peak coinciding with the clay.

An alternative explanation would be downward translocation of RSi during pedogenesis. Movement of $\text{RSi}_{>10}$ can be ruled out, because this size fraction decreases with depth. Movement of $\text{RSi}_{<10}$ is more likely, given that this fraction should be subject to the same pedogenic processes which induce clay mineral mobility. Pedogenic coatings have not been documented in the horizons corresponding to the Brady Soil in 8G00 and 5G00. Although some occur below that depth they are sparse, indicating that clay mineral illuviation is not a major process in development of these soils (Jacobs & Mason 2007). Clay coatings do occur in the B horizon of 3G00 (interpreted as the former Brady Soil A horizon), possibly because the more humid climate at that site favored some illuviation during the Holocene after Brady Soil burial. However, the lack of clay coatings does not preclude the possibility that at least some RSi has been illuviated. For example, amorphous silica coatings have been documented below 20 cm in Haploxerolls of western Idaho (Brown & Mahler 1987). The soils analyzed in that study formed under broadly similar climatic and lithologic conditions as 8G00 and 5G00, indicating that RSi movement is certainly possible in the Nebraska soils.

If RSi coatings are present in the Nebraska soils, they could originate from breakdown of inherited forms (glass) or BSi. It is difficult to quantify the relative contribution of these two forms to illuviation, but it will be noted that most $\text{RSi}_{>10}$ in the A horizons of these soils exists as BSi. Further, the amount of clay-sized BSi in certain Poaceae species can approach 50% of total BSi (Jones & Beavers 1964a; Sommer et al 2006). This implies that a large amount of clay-sized BSi can exist in soils through litterfall. Plant biocycling of silica has been found to be a dominant driver of silica mobility in many soils (Lucas et al 1993; Derry et al 2005; Cornelis et al 2011).

Within 8G00 and 5G00, RSi_{Tot} levels remain generally elevated through the Brady Soil (Fig. 3.2). As discussed in Chapter 2, several possibilities could explain this observation. First, the Brady Soil may contain relict phytoliths, given that regional records indicate that it formed predominantly under grassland vegetation (Johnson & Willey 2000). Phytoliths have been found in the Brady Soil at other sites (Woodburn et al 2011). However, BSi content decreases with depth from the modern surface and reaches minimal levels in the Brady Soil, indicating that this fraction does not contribute substantially to RSi_{Tot} . On the other hand, the breakdown of BSi into other forms through time cannot be ruled out.

Second, this peak might be sedimentary, in the sense that more RSi was deposited with the loess in which the Brady Soil then developed. Clay content peaks have been noted within the Brady Soil throughout the region, however, and are interpreted as primarily the result of a decrease in particle size of the loess deposited just before and during Brady Soil development (Jacobs & Mason 2007). Increased RSi_{Tot} deposition as the loess became finer would conflict with the spatial trend observed for the three Nebraska soils, in which profile average RSi_{Tot} content decreases eastward along with particle size.

Third, the peak of RSi in the A1b horizons of 8G00 and 5G00 may be the result of pedogenic RSi formation during the time of Brady Soil development. If pedogenic RSi is present, it most likely originated from weathered volcanic glass and phytoliths, although contributions from the breakdown of primary and secondary minerals is also a possibility. As further evidence of this, it will be noted in Figure 3.2 that BSi content reaches minimum values within the Brady Soil. Assuming that this paleosol once contained similar BSi content as the modern soils, then a significant amount must have been lost upon burial. This suggests that these

paleosols were or are still subject to weathering processes after burial. After weathering, the original BSi may have remained within the Brady Soil as pedogenically altered RSi.

A fourth possibility exists, in which RSi is translocated from overlying horizons. Movement of RSi from above would be impeded by the clay-rich Brady Soil, resulting in deposition. RSi deposited in this fashion may originate from the modern surface and/or from former surfaces which were in much closer proximity to the Brady Soil.

Dissolved silica could have become adsorbed to Al and Fe oxide, clay mineral, and even organic matter surfaces (McKeague & Cline 1963b). Silica adsorption to metal oxide surfaces in particular can suppress solubility, and lower k -values (dissolution constants) were documented for the upper Brady Soil in 8G00 (Soil 1; Chapter 2). However, Figure 3.2 indicates that RSi_{Ox} content within Brady Soil horizons, while slightly elevated, compose only a very small fraction of RSi_{Tot} . Therefore, adsorbed forms may be able to lower k -values slightly, but the majority of RSi exists in the amorphous fraction.

The presence of RSi peaks away from the surface is somewhat contradictory to what is known about RSi cycling under grassland vegetation (Blecker et al 2006). On average, grasses contain more silica per unit weight than trees (1-3% versus <1%; Raven 2003) and seasonal regrowth of above ground biomass by grasses translates into accelerated uptake of silica and subsequent return to the topsoil. This biocycling effect acts to release large amounts of phytoliths at the surface where they are exposed to weathering processes, which in turn should lead to a decrease of RSi with depth. RSi peaks with depth suggest that plant biocycling is not the only process at work in these soils. Figure 3.2 reveals that RSi content generally peaks with peak clay content. The presence of an argillic horizon can impede downward water movement. As the

water is evaporated or absorbed into peds, dissolved silica can precipitate or adsorb onto grain surfaces. These peaks are further exaggerated by an excess of RSi from inheritance.

Average RSi_{Tot} for the Minnesota soils (AL2 and KO1) was significantly lower than the Nebraska soils. Three possibilities may explain this. Both AL2 and KO1 contain a significant inherited fraction, in the form of cristobalite (similar to Soil 2 from Chapter 2). Cristobalite generally displays lower solubilities relative to the volcanic glass, which may partially explain the higher RSi_{Tot} values found in the Nebraska soils. Second, while cristobalite has been positively identified in soils of this region (Mason 1992), its quantity is not known. Thus, an alternative (or supplemental) explanation for the lower average RSi_{Tot} found in the Minnesota soils may simply be due to lower quantities of inherited RSi relative to the Nebraska soils. Indeed, C horizon RSi_{Tot} content is significantly lower in the Minnesota soils when compared to the Nebraska group. Assuming a homogeneous distribution of inherited RSi in the unaltered loess before pedogenesis, this indicates that the amount of RSi originally present (before pedogenesis) in the Minnesota soils was less, whether it be from lower solubility or content or both. Some RSi has undoubtedly been lost from the soil profiles due to weathering. However, if the Minnesota soils originally contained similar amounts of RSi_{Tot} as the Nebraska soils (approximately 80 mg g^{-1}), this would require the removal of approximately 30% of RSi by weathering. This seems unlikely, given the relatively young age of these soils (12-14 kyr).

The KO1 soil profile contains approximately 9 mg g^{-1} more average RSi_{Tot} than AL2. Unlike the Nebraska soils, these soils are roughly equidistant from the dust source area, and thus particle sorting with distance cannot explain the difference. Further, these soils share similar climate and topographic positions. The only major difference between the two soils is vegetation: AL2 is an Alfisol dominated by hardwood forest, while KO1 is a Mollisol formed under tallgrass

prairie (although it is currently cultivated). Increased use of silica by grasses may explain this trend.

Similar to the Nebraska soils, both AL2 and KO1 display elevated levels of RSi_{Tot} at depth. The peak of RSi_{Tot} for KO1 occurs at a much shallower depth than AL2, which may be due to plant biocycling of RSi. A lower peak of RSi_{Tot} also occurs at approximately 175 cm for both of these soils. No shallowly buried paleosols comparable to the Brady Soil have been recorded in this region, and there is no evidence for pedogenesis at this depth based on soil morphology, particle size, and organic C data. These lower peaks were observed in other soils of the region, varying in depth from 140 to over 200 cm (data not shown). This could result from slight variations in detrital RSi as the loess was aggrading. Another possibility would be the presence of redoximorphic features, which are present at these depths. Repeated wetting and drying episodes have been shown to release RSi as redoximorphic potentials change (Rückert 1992; Sommer et al 2006). Brinkman (1970, 1979) suggested that the oxidation of Fe compounds produces excess H^+ , resulting in clay mineral dissolution and thus the release of dissolved silica.

KA displayed average RSi_{Tot} content similar to the Minnesota soils, while TQ yielded the lowest values out of all soils studied. As noted earlier, TQ may contain inherited RSi in the form of far-travelled dust from the Great Plains (Mason & Jacobs 1998), and the same may be true for KA. However, C horizon RSi_{Tot} content for both of these soils was very low, at 20.63 and 11.87 mg g^{-1} for KA and TQ, respectively. This suggests that very little RSi was inherited from the loess parent material. Although the possibility exists that the loess in which upper soil horizons formed had greater initial amounts of RSi, there is no independent evidence of a major change in loess sources that would bring more inherited RSi (in the form of volcanic glass, cristobalite, etc.) to these sites.

KA was the only soil to display a classic “top heavy” depth distribution, where RSi_{Tot} peaks at the surface. In this case, continual upward movement of RSi by plant uptake (biocycling) may be the dominant process which affects RSi mobility and its distribution within the profile. Within the KA profile, RSi_{Tot} levels gradually decrease throughout the profile, while $RSi_{>10}$ reaches negligible levels at the top of the B horizon. This suggests that $RSi_{>10}$ is less mobile within the profile, while the remainder of RSi_{Tot} , $RSi_{<10}$, is able to more fully translocate downward. $RSi_{<10}$ could result from pedogenic weathering of silicates and/or breakdown of BSi. A gradual decrease with depth suggests that RSi is, in general, controlled by plant processes. In all of the other Mollisols, illuvial horizon RSi peaks may be the result of inherited RSi, whereby the downward movement of excess amounts may outpace biocycling.

RSi_{Tot} in TQ displays a large peak at 39 cm followed by a gradual decline with depth. This peak occurs in the upper B horizon, and coincides with a clay content maximum. As with all of the other soils except KA, the RSi_{Tot} peak may be the result of water movement impeded by an argillic horizon. The steady decrease with depth below the upper B suggests that movement is not entirely impeded. The dramatic increase of RSi_{Tot} into the upper B horizon strongly suggests leaching from A and E horizons.

3.4.2 $RSi_{<10}$

The data presented here demonstrate that most RSi exists in the fine silt- and clay-sized fraction. When estimating $RSi_{<10}$ for the standard depths (Fig. 3.3), its relative proportion ranges from 28.66% (5G00, 2.5 cm) up to 97.97% (3G00, 45 cm). This emphasizes the point that $RSi_{<10}$ must be considered in any RSi quantification study. As alluded to in section 4.1, it may be

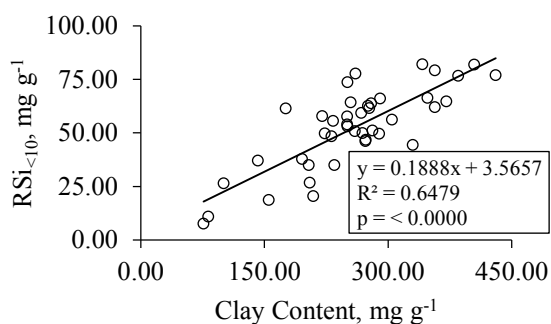


Figure 3.4. Scatterplot of clay particle and RSi_{<10} content.

argued that RSi_{<10} originates from clay mineral dissolution. Indeed, a positive relationship exists between clay content and RSi_{<10} (Fig. 3.4). This relationship can be interpreted as indicating that about 19%

of the clay measured in particle size

analysis is dissolved during the SLLE process and included in RSi_{<10}. On the other hand, it was noted in Chapter 2 that the RSi_{Tot} content of a sample of illite (a common clay mineral known to be present in many of these soils) was only 8.38 mg g⁻¹ (0.838%). A recent study (Koning et al 2002) examined other clay minerals, and the RSi content of those are presented in Table 3.4. It should be noted that Koning et al (2002) utilized an automated system for the extraction of aliquots, and power models were used in lieu of linear extrapolation. Nevertheless, their RSi_{Tot} results are broadly comparable to the SLLE method because they used 0.5 M NaOH at 85° C with continuous mixing.

As can be seen in Table 3.4, the RSi quantities extracted from common clay minerals are very low (mostly less than 1%). If the 11.50 mg g⁻¹ estimate for montmorillonite is used as an upper estimate for all well-ordered clay minerals, we would assume that 1.15% of the clay mineral content would be measured as RSi during the SLLE process. Thus, it appears that the positive relationship between RSi_{<10} and clay content cannot be explained by clay mineral dissolution, and instead must reflect dissolution of more soluble silica from clay-sized particles that are not clay minerals (e.g. fine particles of amorphous silica).

It still may be argued that fine clays in soils may be more susceptible to dissolution than pure clay mineral samples. The ratio of fine clay to total clay is known to increase in illuvial

Table 3.5. Comparison of the amounts of RSi expected from increasing quantities of clay minerals, to amounts predicted by equation from Figure 3.4.

Clay Content	Expected ¹	Predictive Eq. ²
<i>mg g⁻¹</i>		
100.00	1.15	22.45
200.00	2.30	41.33
300.00	3.45	60.21
400.00	4.60	79.09
500.00	5.75	97.97

¹Assumes RSi content of 1.15% for clay minerals.

²Equation is $y = 0.1888x + 3.5657$

horizons relative to eluvial horizons (Glenn et al 1960; Fanning & Jackson 1966). However, a study which documented the mineralogy of loess-derived clays of the Upper Midwest found a positive relationship between fine clay content and amorphous silica content (Glenn et al 1960). The greater surface areas typically encountered with

fine clays act as adsorption sites for RSi, favoring higher RSi content in illuvial horizons with high fine clay content.

As noted in Chapter 2, k-values (dissolution constants) were slightly lower in the illuvial horizons of the soils studied, indicating slightly lower RSi solubilities in those layers. The presence of short range order clays, such as allophane or imogolite, could explain these lower k-values and higher RSi_{Tot} concentrations. Indeed, a small amount of allophane may be present in the Nebraska soils, since its inherited glass originated from volcanoclastic sediments. However, this does not explain the higher RSi_{Tot} concentrations found in all of the other soils, where short range order clays probably do not exist.

A more likely explanation for the lower k-values, as mentioned earlier, is the presence of RSi adsorbed to Fe and Al surfaces, which are known to suppress silica solubility (Jones & Handreck 1963). Even though RSi_{Ox} concentrations are quite low in all of the soils (Fig. 3.2),

levels tend to peak in B horizons. These higher levels in turn would require more time to fully dissolve, thus explaining the lower k-values seen in Chapter 2. The low

Table 3.4. RSi content of some common clay minerals.

Mineral	RSi, mg g ⁻¹	Reference
Illite	8.38	This study
Illite	4.90	Koning et al (2002)
Kaolinite	7.90	Koning et al (2002)
Montmorillonite	11.50	Koning et al (2002)

RSi_{Ox} values observed in B horizons suggests that most RSi does not exist in an adsorbed state. Figure 3.2 further shows that RSi_{>10} levels are quite low in B horizons. By process of elimination, most RSi in B horizons must therefore exist as clay-sized amorphous silica. As discussed earlier, RSi_{<10} is subject to translocation, similar to clay mineral particles.

3.4.3 RSi_{>10}

RSi_{>10} amounts were always less than RSi_{Tot}, given that the former does not extract and measure particles smaller than 10 μm . The relative amount of RSi_{Tot} composed of RSi_{>10} ranged considerably, from 2.03% (3G00 40-50 cm) to 71.34% (5G00 0-5 cm) and the average content was 18.10%. Hence, RSi_{>10} is a secondary component of the total RSi pool in these soils. This again emphasizes the point that a disproportionate amount of RSi exists in the clay-sized fraction.

Except for a discrete layer of glass in 8G00, RSi_{>10} decreased in abundance with depth in all soils. This is despite the fact that the Nebraska and Minnesota soils contain significant amounts of inherited forms, which suggests that RSi_{>10} concentrations are predominantly controlled by biotic processes, i.e. phytolith production. Loss of clay content in eluvial horizons will act to amplify RSi_{>10} totals, since these measurements are expressed as mg SiO₂ per mg dry soil weight. Nevertheless, it can be seen in Figure 3.2 that RSi_{>10} concentrations near the surface are always higher than those found in C horizons. This indicates that RSi_{>10} has been preferentially built up near the surface.

RSi_{>10} concentrations reach minimum levels in illuvial horizons. These trends were seen in Argentinian soils as well (Borelli et al 2010). These cannot be explained by dilution by a

buildup of clay content, which is not large enough to account for the decreases in $RSi_{>10}$.

Below this layer, $RSi_{>10}$ again increases slightly in the Nebraska and Minnesota soils in the form of unweathered NSi. Taken together, this suggests that NSi content has been lost from A and B horizons. Rates of phytolith deposition are great enough to replenish NSi losses in A horizons, but not below this. As shown in Figure 3.2, most $RSi_{>10}$ near the surface is composed mostly of BSi. BSi composition near the surface is somewhat lower for the Nebraska soils, which could indicate a lack of weathering of inherited forms, or greater quantities of unclassifiable forms (fragmented phytoliths). Proportions of NSi are negligible near the surface in the other soils. Inherited cristobalite could have been lost in the upper horizons in the Minnesota soils, while KA and TQ probably had very little to begin with.

BSi content reached negligible levels in B horizons in the Minnesota soils, KA, and TQ. BSi in the Nebraska soils remained slightly elevated with depth, and in some cases composed 50% of $RSi_{>10}$ below 100 cm. Phytolith translocation is unlikely in these soils, given their young ages and dry climate. This deep BSi content could be phytoliths buried *in situ* during loess aggradation. Indeed, buried phytoliths have been found in soil profiles of the region (Woodburn 2011) as well as others (Reyerson 2004). The lack of deep BSi in the other soils could be due to a lack of vegetation during loess aggradation and/or mass accumulation rates which outpaced phytolith deposition. Losses due to weathering are unlikely, given that inherited forms are present in the Minnesota soils.

The relatively large amounts of NSi found in many of these soils is a reminder that it is important to account for nonbiogenic forms. Many studies have worked under the assumption that all $RSi_{>10}$ extracted was of biogenic origin (Verma & Rust 1969; Bartoli 1983; Reyerson 2004; Blecker et al 2006), although many have not (Wilding & Drees 1971; Borelli et al 2008;

Borelli et al 2010). Excess NSi can introduce error into any attempt to quantify BSi, and detailed information about the study soil should be ascertained in order to determine if inheritance is likely. For example, the Nebraska soils contain significant amounts of glass, even though they are not volcanic in origin. In cases such as this, the proportion of NSi and BSi particles in $RSi_{>10}$ extracts should be routinely estimated.

3.4.4 RSi_{Ox}

As a percentage of RSi_{Tot} , RSi_{Ox} for the study soils ranged from 0.21% (8G00 25 cm) to 5.16% (KA 195 cm). The mean value was 0.50%. For these soils at least, the relative contribution of RSi_{Ox} to RSi_{Tot} is minimal.

Within the Nebraska soils, average RSi_{Ox} content increased eastward. RSi_{Ox} content in 3G00 may be greater due to the more humid climate, although changes in particles size with distance from the loess source area seem more likely. Finer particles would produce a greater proportion of fine edges, which could be partially dissolved during the RSi_{Ox} process. For the Minnesota soils, KO1 contained substantially more RSi_{Ox} than AL2. Saccone et al (2007) found a similar result, where Mollisols were found to contain more RSi_{Ox} than other soil orders, which was attributed to a less weathering and a greater amount of BSi content. However, this may also be an artifact of particle size, as KO1 contains a greater proportion of clay content (Table 3.3). The fact that RSi_{Ox} content within the Nebraska soils increases as BSi content decreases eastward suggests that phytoliths (or weathering in general) may not be as important as particle size. The Mollisol KA and Alfisol TQ yielded similar, intermediate values. The lack of any clear difference between these soils suggests that the role of vegetation is not an important factor here.

Taken together, the origin of RSi_{Ox} in these soils is equivocal, but it seems more likely that this form originates more from fine edges and shards than from pedogenically altered RSi.

In absolute terms, RSi_{Ox} for all samples ranged from 0.18 to 0.90 mg g^{-1} . As a comparison, Saccone et al (2007) recorded RSi_{Ox} values from 0.016 to 1.402 mg g^{-1} for a variety of soil orders collected from North America and Europe. That study also analyzed soils from the Great Plains, which yielded similar results to the Nebraska soils (0.135 to 0.991 mg g^{-1} for Saccone's study, versus 0.19 to 0.90 mg g^{-1} for the Nebraska soils). Another study documented RSi_{Ox} values from 0.07 to 0.60 mg g^{-1} for Cambisols in central France (Cornelis et al 2011). RSi_{Ox} content tended to peak in illuvial horizons (Fig. 3.2). In some cases increases in RSi_{Ox} coincided with peaks in clay content (5G00, AL2, TQ), but not in others. In general, RSi_{Ox} increased as clay content increased; the relationship is weak, but statistically significant (Fig. 3.5). This relationship has been documented in other studies (Kelly et al 1998; Saccone et al 2007; Cornelis et al 2011), and it has been attributed to illuviation processes. The considerable amount of scatter shown in Figure 3.5 most likely originates from the fact that the oxalate extraction procedure measures other RSi fractions besides adsorbed silica, including shards and rough edges. Utilization of other extraction methods may clarify this. For example, the use of a weaker solvent, such as water or CaCl_2 (Henriet et al 2008) presumably would target shards and

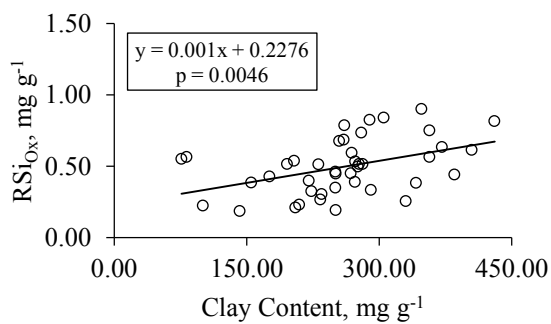


Figure 3.5. Scatterplot of clay particle and RSi_{Ox} content.

rough edges, thereby allowing for their contribution to be subtracted from the RSi_{Ox} values. This was not explored further in this study.

When considering the relationship between RSi_{Ox} and pH, many previous

studies have shown that silica adsorption decreases under increasing acidity (McKeague & Cline 1963b; Beckwith & Reeve 1963, 1964; Brown & Mahler 1988). A weak but statistically significant relationship was found here (Fig. 3.6). As stated above, the large amount of scatter probably stems from the fact that oxalate does not specifically target adsorbed forms.

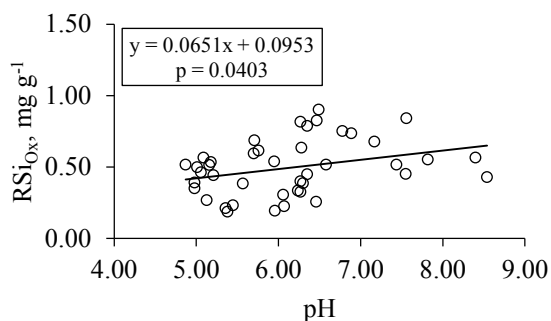


Figure 3.6. Scatterplot of pH and RSiO_x content.

3.4.5 Implications and Future Questions

This work expands the current knowledge of RSi in soils. It is clear that RSi_{Tot} in soils is much larger than previously expected, even in soils which do not contain sizeable inherited pools. Most RSi exists in the clay-sized fraction, which has been largely unexplored. The weathering pathways which lead to this size fraction are poorly documented. Possible sources include the physical breakdown RSi_{>10} and minerals, as well as dissolution/precipitation reactions which lead to the formation of clay-sized grains and coatings. The greater surface area to volume ratios of RSi_{<10} probably lead to greater rates of cycling in soils (when compared to RSi_{>10}), but again this has not been documented.

Further, the proportion of RSi_{<10} which is biogenic in origin is currently unknown. In the soils studied here, RSi_{Tot} was on average at least an order of magnitude larger than BSi, indicating that unaltered silt-sized particles of recognizable biotic origin are a small component.

In surface layers, where BSi content is most concentrated, RSi_{Tot} was still considerably larger. Global annual deposition of BSi in soils is estimated at 60 – 200 Tmol yr⁻¹ (Conley 2002), but the proportion of this which exists as silt-sized grains is unknown. Although Jones & Beavers (1964a) provided rough estimates based upon clay-sized phytoliths found in plants, no study has attempted to categorize $RSi_{<10}$ as biogenic or nonbiogenic in origin. The use of elemental ratios such as Si/Ge and Si/Al as well as stable isotopes could provide valuable insight into these research questions.

When considering the coupled Si-C cycles (Song et al 2012), further work is required to better understand how RSi originating from inheritance, in situ weathering, and biotic processes affect C cycling within soils. A relationship does exist between organic C and RSi content (Torn et al 1997; Cusack et al 2012). However, when considering grasslands and forests, does the former increase C retention, simply because of higher rates of phytolith production? Or are the greater volumes of organic C typically found in Mollisols simply a result of a slightly drier climate?

3.5. Conclusions

In those soils devoid of inherited RSi, an Alfisol also displayed RSi_{Tot} peak in the B horizon, while the Mollisol peaked at the surface. These data suggest that biocycling by grasses is sufficient to maintain high levels of RSi near the surface, while lower rates of cycling under forest result in net downward movement of RSi. In the soils with a significant inherited RSi component, RSi_{Tot} peaks coincided with illuvial horizons regardless of vegetation, suggesting that the downward movement of excessive quantities of RSi can outpace plant

biocycling. Deposition within illuvial horizons may be from amorphous silica precipitation onto ped faces and grains, although in situ breakdown of BSi could have occurred in the Nebraska paleosols.

A disproportionate amount of RSi_{Tot} is found in the fine $RSi_{<10}$ fraction, averaging 81.91% of the total. Thus, traditional methods of quantifying RSi in soils, such as floatation techniques, drastically underestimate RSi_{Tot} . Chemical extraction methods, such as the SLLE technique used here, are able to extract and measure all size fractions of RSi. While the SLLE method uses 0.5 M NaOH, which is more aggressive than the extracting solution used in some other studies, experiments on pure clay minerals suggest only minor dissolution on 0.5 M NaOH.

The $RSi_{>10}$ fraction accounted for 18.10% of RSi_{Tot} . Within the $RSi_{>10}$ fraction, BSi was slightly more prevalent than NSi, indicating that biotic processes are important factors for this size fraction. Most $RSi_{>10}$ was composed of BSi at soil surfaces, and decreased with depth. NSi was also common above soil B horizons, and much of this may be composed of weathered or fragmented BSi. Below B horizons, $RSi_{>10}$ increased slightly, and much of this was composed of unweathered NSi. However, BSi was common in deep horizons in the Nebraska soils, probably due to in situ burial during loess aggradation.

RSi_{Ox} data indicate that the origin of this fraction is somewhat equivocal, but most probably originates from fine edges and shards. This fraction was minimal in all soils, averaging 0.96%. This indicates that most RSi in these soils exists as amorphous silica, or in the case of the Minnesota soils, some may exist as unweathered cristobalite.

CHAPTER 4. FORMS AND QUANTITIES OF REACTIVE SILICA ACROSS A PRAIRIE-FOREST ECOTONE IN SOUTHEASTERN MINNESOTA, USA

4.1. Introduction

As shown in Chapter 3, reactive silica (RSi) pools can vary considerably within and across soils. In this chapter I focus solely on the effects of vegetation on soil RSi. I demonstrate that grassland soils contain significantly more total, clay-sized, and oxalate-extractable RSi in eluvial horizons, and possibly more silt-sized RSi as well. This study is the first to unequivocally show vegetation-induced changes to soil RSi.

I define RSi as all forms of silica exhibiting solubilities greater than primary and secondary silicate minerals. Amorphous silica (ASi) includes plant-produced microscopic opaline bodies termed phytoliths, volcanic glass, and pedogenic coatings or precipitates. Other forms include silica adsorbed to clay, organic matter, and oxyhydroxide surfaces, short range order clays, poorly ordered forms such as cristobalite, and silica in solution (dissolved silica or DSi). RSi can originate from inheritance, for example from loess sedimentation or volcanic ash deposition. *In situ* weathering processes can also create or modify RSi. For example, plant use of silica produces phytoliths which are released into the soil following litterfall and decay. Chemical leaching of silicate minerals or other forms of RSi can result in RSi coatings in the subsoil, indurated layers, and clay mineral neoformation over longer time periods (Chadwick et al 1987; Folkoff & Meentemeyer 1987; Chartres 1990; Barré et al 2009). Aside from DSi, RSi can range in size from sub-micron clay-sized particulates up to sand-sized grains and larger.

Most previous work which has attempted to quantify RSi in soils has focused on biogenic silica (Bartoli 1983; Alexandre et al 1997; Reyerson 2004; Blecker et al 2006; Alexandre et al 2011). Biogenic silica (BSi) collectively refers to all forms of RSi originating from biotic processes. These include phytoliths, diatoms, and spicules, among others. Most studies of soil BSi typically use the floatation technique to extract silt-sized particles larger than 2-20 μm . As I demonstrate in Chapter 3, this technique underestimates the true BSi pool size since it cannot extract clay- and fine-silt sized particles.

Studies which compare soil BSi across vegetation communities generally find larger pools under grasslands due to greater phytolith production in those species (Blecker et al 2006; Alexandre et al 2012). Thus, it has been generally assumed until recently that BSi content is primarily a function of the type of vegetation present. However, the amount of BSi found in a particular soil can be influenced by other factors such as inheritance and degree of soil weathering (Meunier et al 1999; Henriot et al 2008), soil productivity and landscape position (Jones & Beavers 1964a), and erosional and depositional processes (Alexandre et al 2011). Working across a bioclimosequence in the Great Plains of North America, Blecker et al (2006) concluded that soil BSi content was a cumulative result of vegetation and climate. However, changes to soil properties and parent material RSi content across space were not explicitly addressed, and the degree to which they influenced the results is unknown. As another example, Alexandre et al (2011) compared BSi content under African savannas to tropical rainforest vegetation where it was recognized that soil BSi content could be influenced by a number of edaphic factors as well as differing climate and vegetation. The difficulty in holding all other factors equal highlights a nagging problem for all sequence studies when attempting to analyze change across large regions.

Biosequence studies conducted at smaller scales are more able to minimize undesired differences. When Upper Midwestern soil orders formed under similar upland settings were compared, Mollisols generally contained greater amounts of BSi (Jones & Beavers 1964b; Verma & Rust 1969). Working within a tree plantation in eastern France, Bartoli (1983) was able to show that BSi content under deciduous trees was approximately 3 times lower than coniferous stands. Cornelis et al (2010b) found similar results when comparing three coniferous and two deciduous tree species on a 35 yr old plantation. However, considerable overlap existed in the data, possibly due to the young age of the plantation.

It is only recently that researchers have begun to adapt and refine techniques pioneered in other disciplines in order to investigate RSi in totality. Cornelis et al (2011) and Saccone et al (2007) used alkali and acid dissolution techniques to investigate the quantities and forms of RSi present in various midlatitude soils. In Chapter 3, I used these techniques as well as the traditional floatation method to classify RSi by form as well as by particle size. No study has attempted to quantify total RSi (and its fractions) across a biosequence.

Few works exist which have attempted to constrain the sensitivity of RSi to vegetation change. Blinnikov et al (2011) showed that differences in floatation-extractable BSi as well as alkali-extractable RSi can occur within the span of years to decades. Perturbation of RSi as a result of disturbance is similarly fast-paced. Saccone et al (2008) and Conley et al (2008) demonstrated RSi (mainly in the form of DSi) redistribution but no losses within soils as a result of forest cutting in the 1960s. Clymans et al (2011b) found net increases in RSi export to watersheds following agricultural use over centuries, which was attributed to amorphous silica (mainly as BSi) dissolution. Kelly et al (1998) showed clear differences between native Hawaiian highland forest and 100-yr pasture grassland. These studies indicate that RSi in general

and DSi in particular are extremely sensitive to changes in vegetation. However, little is known regarding the sensitivity of RSi pools to natural vegetation change.

In this chapter I analyze RSi profiles across a forest-grassland ecotone in southeastern Minnesota, USA. Across this relatively small region, factors which could affect RSi content such as climate, parent material, topography, and soil age are held constant. These soils probably shared a similar pedogenic trajectory until the late Holocene, after which divergence occurred under forest and grassland vegetation. Hence, this chapter aims to 1) document changes in RSi content as result of vegetation alone; and 2) provide a rough estimate on the sensitivity of RSi to vegetation change.

4.2. Methods

4.2.1 Study Area

The study area is situated south of the Root River, in Houston County, Minnesota in the so-called Driftless Area of Minnesota (Fig. 4.1). Although not technically within the Driftless area due to early- to mid-Pleistocene glaciation, southeastern Minnesota exhibits topography similar to southwestern Wisconsin (Mason 1995). The study area is situated in a dissected ridge and valley system, with local relief of approximately 30 m in the west and 170 m in the east, adjacent to the Mississippi River (Mason et al 1994). Bedrock is composed of Paleozoic marine sedimentary rocks, with several layers of sandstone, shale, dolomite, and limestone (Mossler 2008; Ojakangas 2009). Uplands are gently sloping to flat, and are separated by steeply sloping valleys. Most upland sites within the study area are currently cultivated, although rare exceptions

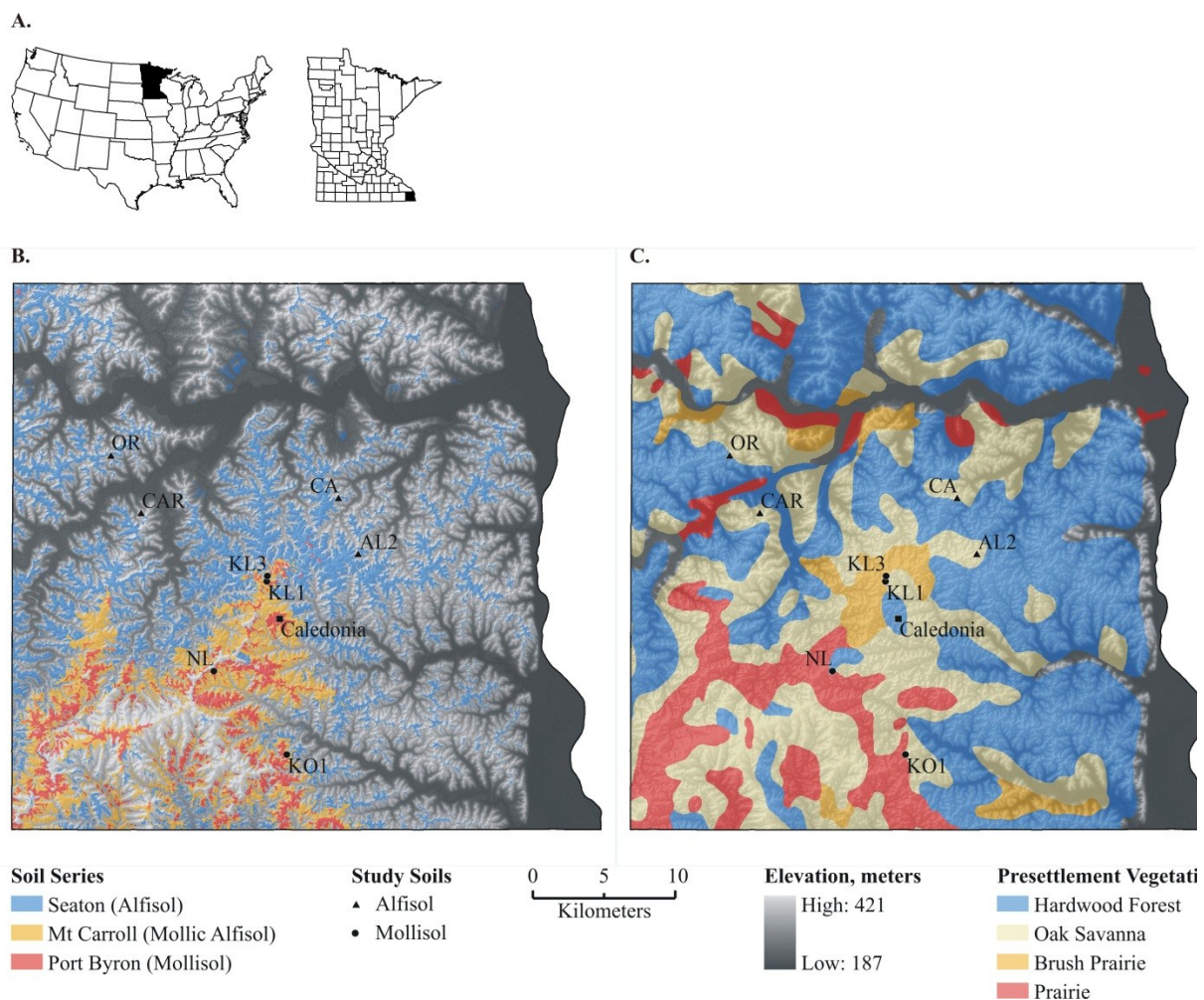


Figure 4.1. Maps of the study area. A. Location of Houston County. B. Distribution of Seaton, Mt Carroll, and Port Byron soil series (data from Soil Survey Staff 1999). C. Distribution of presettlement vegetation (data from MN DNR Staff 2009). Location of study soils are shown in maps B and C.

exist where wooded lots have never been plowed. Forest exists on slopes which are too steep for cultivation.

Pleistocene-aged loess units overlie bedrock on upland sites. The uppermost and most extensive is the late-Pleistocene aged Peoria Loess (Mason 1992). This loess unit varies in thickness from 0.5 m to approximately 4.0 m at upland sites, although the sites studied here were in loess thicker than 2.0 m. Other older loess and paleosol units are found throughout the area, but they were not sampled for this study. For a description of these, see Mason (1995).

Loess deposition at these sites originated mostly from the region immediately to the west (Mason et al 1994), which includes pre-Illinoian till of the Iowan Erosion Surface (Ruhe 1969), and late Pleistocene Wisconsinan till from the Des Moines Lobe (Mason 1992). A large component of Des Moines Lobe sediments originated from the northern Great Plains, which contains material reworked from the Cretaceous Pierre Shale (Gill & Cobban 1973; Jones & Blatt 1984; Lusardi et al 2011). Beds within the Pierre Shale have been shown to contain large amounts of cristobalite in the silt fraction (up to 70%), and probably significant amounts of clay-size grains as well (Jones & Blatt 1984). Cristobalite is a poorly crystallized form of silica, which tends to exhibit solubilities between amorphous silica and quartz (Iler 1979; Drees et al 1989). Cristobalite has been identified in Soil 2 used in Chapter 2, but its abundance is not known (Mason 1992). As shown in Chapter 3, southeastern Minnesota soils in which cristobalite has been identified contain significantly larger RSi pools when compared to other Upper Midwestern soils which do not contain an inherited component. Hence, despite its lower solubility, inherited cristobalite does contribute to soil RSi stocks. Variation of cristobalite quantities across the study sites is assumed to be minimal given similar upland settings and the fact that these sites are roughly equidistant from the sediment source area.

The climate of Houston County is classified as humid continental (McKnight et al 2005). At the city of Caledonia in central Houston County, mean annual precipitation is 888.7 mm, with most falling in the summer months. Mean annual temperature is 6.7° C, with cold winters and warm humid summers (NOAA Staff 2002). Ages listed in this paper are presented as calibrated years before present (cal yr B.P.) unless otherwise noted.

The vegetation history of this area since the Late Pleistocene has involved phases similar to those observed in many other parts of the upper Midwest, although it is now clear that the

timing of those phases has varied across the region. An Arctic plant macrofossil assemblage found in Houston County near the study sites suggests tundra-like conditions with few if any trees near the time of the last glacial maximum (~21,000 cal yr B.P.) (Baker et al 1999). Subsequent vegetation history within the region is recorded either by plant macrofossils and other data from alluvial sediments or by stable carbon isotopes in speleothems near the study sites (Baker et al 2002; Chumbley et al 1990; Baker et al 1996; Dorale et al 1992; Denniston et al 1999). *Picea*-dominated boreal forest was well established in the region by 13,000 cal yr B.P., followed by its replacement by relatively dense deciduous forest at approximately 10,000 cal yr B.P. (Chumbley et al 1990; Baker et al 1996; Baker et al 2002). Those studies, as well as speleothem data (Dorale et al 1992; Denniston et al 1999) indicate that forest was replaced by tallgrass prairie from approximately 5500 to 3400 cal yr B.P. This is in contrast to the much earlier establishment of prairie at Kirchner Marsh in east-central Minnesota (8000 yr B.P.; Wright et al 1963; Watts et al 1966). However, the late expansion of prairie in southeastern Minnesota coincides with regional drying and savanna growth in southern Wisconsin and Illinois (Maher et al 1982; Winkler et al 1986; Swain et al 1986; Winkler et al 1988; Nelson et al 2006).

There is evidence for expansion of oak savanna or forest at the expense of prairie after 3400 cal yr B.P. (Chumbley et al 1990; Baker et al 1996; Baker et al 2002), Arboreal pollen levels remained fairly constant through the late Holocene based on data to the north (Baker et al 2002) and south (Chumbley et al 1990; Baker et al 1996); therefore, the configuration of boundaries between prairie, savanna, and forest observed in the study area in the 19th century may have been established by about 3400 cal yr BP. It is unlikely that these boundaries were completely static, however.

Studies from the Big Woods, a forest area bordering prairie in south central Minnesota, offer insight into vegetation dynamics within the last 1000 yr. Grimm (1983) found recent establishment of deciduous forest at the expense of oak savanna and prairie during the last 300 yr, which he attributed to the relatively cooler and wetter climate of the Little Ice Age (LIA). Umbanhowar (2004) later revised the timing of forest establishment, concluding that forest gradually replaced prairie beginning at approximately 850 yr B.P. This revised chronology places forest establishment at the beginning of the LIA. Grimm (1983) found many examples of forest residing on Mollisols which he attributed to encroachment during the LIA. Forest over Mollisols was similarly found in Houston County in some locations, indicating that ecotonal shifts can outpace soil formation. For example, a high ridge underlain by the Platteville or Galena dolomites (north and west of the city of Caledonia) is dominated by forest, oak savanna, and brush prairie, in the presettlement vegetation shown in Figure 4.1b., yet Mollisols are interspersed throughout in localized pockets (Fig. 4.1a.).

Somewhat counterintuitively, previous research in Minnesota has shown that tree establishment rates are higher during periods of drought rather than greater precipitation (Umbanhowar 2004; Ziegler et al 2008; Shuman et al 2009). It was hypothesized that drier periods result in lower biomass production and therefore less competition from prairie species as well as fewer fires (Ziegler et al 2008). Expansion of forest during the LIA was also found in northwestern Wisconsin (Hotchkiss et al 2007). Regional establishment of forest in former prairie and oak savanna sites during the LIA is a good indicator that forest was also expanding in Houston County at that time.

Vegetation distributions throughout Houston County, as recorded by land surveyors just prior to Euro-American settlement in the 19th century, were a patchy mosaic (Marschner 1974;

Minnesota DNR Staff 2009). In general, prairie was located primarily to the south and west, occupying broad uplands and some stream bottomlands and south-facing slopes (Fig. 4.1). Forest was found in a broad arc, generally to the north and east, and occupying areas of greater local relief. Oak savanna (labeled as oak barrens in previous works) and “brush prairie” form buffer zones between prairie and forest. Interpretations of vegetation distributions based on land surveyor notes must be approached with caution, however. These reconstructions are most accurate where vegetation boundaries cross section lines, or at section corners (using witness trees). Reliability can be compromised with distance from these points, especially within the interior of sections.

In the Big Woods to the northwest, the distribution of prairie, savanna, and forest are thought to have been controlled by topography and fire at the local scale (Grimm 1983, 1984; Umbanhowar 2004). Within Houston County, the presence of relatively undissected, broad uplands could have facilitated the movement of frequent wildfires from the south and west. Wildfire frequency would have been diminished to the north and east, where deep valleys can act as firebreaks.

The complexity of the pre-settlement vegetation (Fig. 4.1b.) as well as the paleoreconstructions listed above suggest that the distribution of vegetation was dynamic and subject to short term fluctuations. Given the available evidence, it seems likely that earliest establishment of the modern forest-prairie ecotone was 3400 cal. yr B.P. However, encroachment of forest during the LIA in the Big Woods to the northwest suggests that the modern ecotone may have come to occupy its current location much later than this. Especially at a local scale, it is likely that the ecotone has undergone minor shifts throughout the late Holocene that are not recorded by regional paleoecological data.

Given the dynamic nature of the modern ecotone, the presettlement vegetation pattern shown in Figure 4.1b. may not be a reliable indicator of soils that have had either forest or prairie vegetation cover for long enough to significantly influence RSi content. The distribution of soils classified in the Alfisol and Mollisol orders is likely to be more useful in this regard, since the criteria for differentiating these orders include morphological features closely associated with either forest or grassland vegetation, which are the result of pedogenic processes acting over hundreds to thousands of years (Parsons et al 1962; Hole & Nielsen 1968). Alfisols tend to have thin A horizons (ochric epipedons) overlying leached E horizons. Mollisols display thicker A horizons (mollic epipedons). Alfisols all display clay-enriched argillic B horizons, but these can occur in Mollisols as well. The Houston County soil survey classifies all well-drained Mollisols formed in loess as Hapludolls, lacking an argillic horizon formed by clay illuviation (Lueth 1984). This is misleading, however, since previous research has shown that many loess-derived Mollisols in the county have relatively clay-rich B horizons with illuvial clay coatings (Mason 1992; Mason & Nater 1994). There is only minor textural contrast between relatively clay-rich A and B horizons in many of these Mollisols, so the soil survey may be technically correct, in that there is not enough downward clay increase to define a diagnostic argillic horizon. The significance of these observations for this study is that a loess-derived Mollisol in this area could be transformed into an Alfisol, or vice versa, by a change in vertical textural contrast from upper horizons into the B. This might result from a change in the depth or intensity of bioturbation, for example. Change from one soil order to the other would not require formation of much more clay, or loss of existing clay, through the slow process of mineral weathering.

A map of upland Mollisols, Alfisols, and transitional Mollic Alfisols (Fig. 4.1b.) show a general correspondence with the pre-settlement vegetation, although many local exceptions exist.

Many of the areas of Alfisols that were under forest at the time of the public land survey are likely to have had prairie cover before the readvance of forest beginning around 3400 cal. yr B.P. and possibly continuing into the last millennium. If so, then soil morphology has already adjusted to much of this late Holocene vegetation change. Areas of mismatch between soil order and vegetation may record locations of the most recent fluctuations of the ecotone.

With that background, soil orders were used to select profiles for use in this study, rather than vegetation recorded in the public land survey. As a consequence, the results most directly indicate whether there are significant differences in total RSi content and RSi profiles of Alfisols and Mollisols, formed in identical parent material and under the same climate. Based on well-known relationships between these soil orders and vegetation in the Midwestern U.S. (Hole and Nielsen, 1968) and the approximate correspondence of soil order and presettlement vegetation in the study area, it is reasonable to interpret the results more broadly in terms of the effects of vegetation on RSi. In contrast to the snapshot of 19th century vegetation available from the public land survey notes, the morphology used to differentiate soil orders should indicate predominant vegetation cover over at least hundreds of years, increasing the likelihood that any effects of vegetation on RSi will be detected. To test for such effects, several RSi measurement and identification techniques were utilized to measure and identify soil RSi pools.

4.2.2 Soils Used for the Study

A suite of eight soils were used for this study, four Mollisols and four Alfisols (Fig. 4.1). Candidate soils were selected if they were formed on stable upland settings, in loess >2 m thick. Evidence of erosion, such as profile truncation, was not found at any of the soils. Mollisols of the

Port Byron series and Alfisols of the Seaton series (Lueth 1984) were used for consistency within soil orders. Of the soils used here, I sampled seven in 2008 and 2009 and the remaining soil was sampled by J. Mason in 1994 as part of another study (OR; Mason & Jacobs 1998). Prior to field work, several candidate sampling sites were selected by analyzing soil, topographic, and pre-settlement vegetation maps. However, the ultimate selection of a soil for use in this study largely depended upon soil morphology as determined during field and lab work. For example, several candidate Mollisols were later determined to in fact be Mollic Alfisols after closer inspection. Descriptions for each of the soils used here are provided in Appendix 7.

The four Alfisols are found north of the city of Caledonia. AL2 was procured from a wooded lot and has never been plowed, according to the landowner. However, the site was selectively logged in the 1960s. The soil CAR was taken from a state forest. This soil lacks a well-expressed E horizon, suggesting that it might have been plowed at some time since mid-19th century agricultural settlement, but the mature forest cover indicates that any period of cultivation must not have lasted very long. The soil CA is currently used as a pasture, and OR is used as a hay field. Both of these soils have Ap horizons (plow layers) and lack E horizons, so they were cultivated in the past.

Two of the Mollisols are found south of Caledonia and two are found to the north. All are currently cultivated for row crops. The two southern Mollisols, KO1 and NL, are found on the broad flat uplands west and southwest of Caledonia. The two northern Mollisols, KL1 and KL3, are located on a narrower ridgetop. KL1 and KL3 are found at the extreme northern limit for Mollisols in this region.

At some of the soil sites, the type of pre-settlement vegetation is contradictory to the soil order found (Fig. 4.1). For example, KL1, KL3, AL2, and CA are located in areas mapped as brush prairie or oak barrens in the vegetation reconstruction from land survey notes compiled by the Minnesota DNR. This may reflect either recent vegetation change prior to the land survey or error in the vegetation reconstruction from the survey notes.

4.2.3 Analytical Methods

The methods used here are the same as Chapter 3, and they are briefly described here. Sequential leaching with linear extrapolation (SLLE) was used to measure total RSi (RSi_{Tot}). RSi particles larger than 10 μm ($RSi_{>10}$) were measured by floatation and classified as either biogenic (BSi) or nonbiogenic/unknown (NSi) through the use of microscopy. RSi particles and coatings smaller than 10 μm ($RSi_{<10}$) were estimated by subtracting $RSi_{>10}$ from RSi_{Tot} . Pedogenically altered RSi in the form of adsorbed silica as well as shards and rough edges were extracted through the use of the oxalate method (RSi_{Ox}). The oxalate method also extracts short range order clays, but these are assumed to not be present in these soils. Particle size was measured by the pipet method of Gee & Bauder (1986). Observations in the lab indicated that the sand fraction was minimal for most samples, and it was therefore combined with the silt fraction. Hence, for simplicity, only clay content is presented here. Organic carbon was measured using a modified version of Ben-Dor & Banin (1989) and organic matter was converted to organic carbon using the predictive equations of Konen et al (2002). Sample pH was measured using 1:1 mixture of soil and deionized water. Precision for all measurements except pH was estimated by processing replicate samples, and is expressed by ± 1 standard deviations.

Measurements for each soil were performed at standard depths of 2.5, 25, 45, 75, and 95 cm. In some cases soil sample depths did not correspond directly with the standard depths, but these were usually within 5-10 cm. In order to summarize data in each soil order, mean values were calculated by standard depth. This allows for the detection of differences between soil orders by depth and independent of genetic horizons. An alternative approach is to group standard depths by pedogenic layer or soil horizon; that is, by eluvial and illuvial layers. In each soil order, the 2.5 cm and 25 cm depths were grouped and averaged for eluvial layers, while illuvial layers consisted of 45, 75, and 95 cm depths. Variation in each grouping (by standard depth and pedogenic layer) is expressed by 95% confidence intervals. As can be seen from the soil descriptions in Appendix 7, the boundaries separating eluvial from illuvial layers vary in depth from soil to soil. Nevertheless, the use of a cutoff threshold between 25 and 45 cm serves as a convenient and objective way to differentiate eluvial from illuvial. Some measurements were taken at a finer sampling resolution than the standard depths, but these extra measurements were not used when calculating mean values for a given soil order. In sum, the variables used to compare Alfisols and Mollisols are the mean distributions of soil properties as measured at specific standard depths and by pedogenic layer (e.g. mean RSi_{Tot} at 25 cm in Mollisols; mean eluvial layer clay content in Alfisols).

To test for significant differences, Alfisol and Mollisol variables, except pH, were then compared to each other using Student's t-test. Comparisons of pH across soil orders are of limited value because the recent liming history of the cultivated soils is unknown. All variable data were log transformed in order to meet assumptions of normality and homogenous variance (e.g. Umbanhowar 2004). All calculations were performed in Sigma Plot version 11.0. Group

means were considered significantly different if the resulting p-value was <0.05 . However, p-values <0.10 and <0.20 are reported as well.

After log transformation, some variables did not pass tests for normality and/or equal variance at the $\alpha = 0.05$ level (Shapiro-Wilk and Levene Median tests). In these cases, the nonparametric Mann-Whitney Rank Sum test was used in lieu of the t-test. However, a comparison of the results generated by the t-test and the Mann-Whitney test revealed negligible differences in p-values. Hence, the t-test was used for all variables.

The validity of the significance tests could be called into question since study soils were not selected completely randomly or systematically due to practical reasons. However, there is no reason to assume bias in the soils, as they were all pre-selected from soil survey map data. Sampling of specific sites was based on accessibility and in-field determination of suitability (lack of erosion, land cover, etc.). The ultimate use of a soil for this study was then objectively determined in the lab based solely on soil morphological properties, not RSi. There was no attempt to select or discard soils in order to meet a specific outcome.

Within the soils themselves, measurements made at each standard depth and/or pedogenic layer are not truly independent of one another, because weathering, translocation, and turbation processes can act to mobilize RSi from one layer to another.

4.3. Results

Mean measurement values for Alfisols and Mollisols by standard depth are shown in Figure 4.2. Table 4.1 also lists average values as well as t-test results. A complete listing of all measurements for each soil is shown in Appendix 8.

4.3.1 RSi_{Tot}

Differences amongst the soil orders were greatest at the surface and decreased with depth (Fig. 4.2). Mollisols contained significantly ($\alpha = 0.05$) more RSi_{Tot} in the 2.5 and 25 cm depths, as well as the eluvial layer as a whole (Table 4.1). No statistical difference was detected at any depth below 25 cm.

Patterns of RSi_{Tot} with depth (Fig. 4.2) show that content increases with depth for both soil orders. On average, peak RSi_{Tot} content peaked at the 25 cm layer for Mollisols, and 75 cm for Alfisols.

4.3.2 $RSi_{<10}$

As a reminder, $RSi_{<10}$ was estimated by subtracting $RSi_{>10}$ from RSi_{Tot} . Similar to the findings of Chapter 3, the soils used here were dominated by $RSi_{<10}$, comprising an average of 90.97% of RSi_{Tot} .

A statistical difference between the soil orders was found only at the 2.5 cm depth (Table 4.1). However, eluvial horizons were different at the $\alpha = 0.10$ level. No statistical differences in means were found below 45 cm.

Depth patterns (Fig. 4.2) reveal that $RSi_{<10}$ tended to peak with depth in both soil orders. As with RSi_{Tot} , the depth of greatest $RSi_{<10}$ content was slightly shallower for Mollisols (25 cm versus 75 cm for Alfisols).

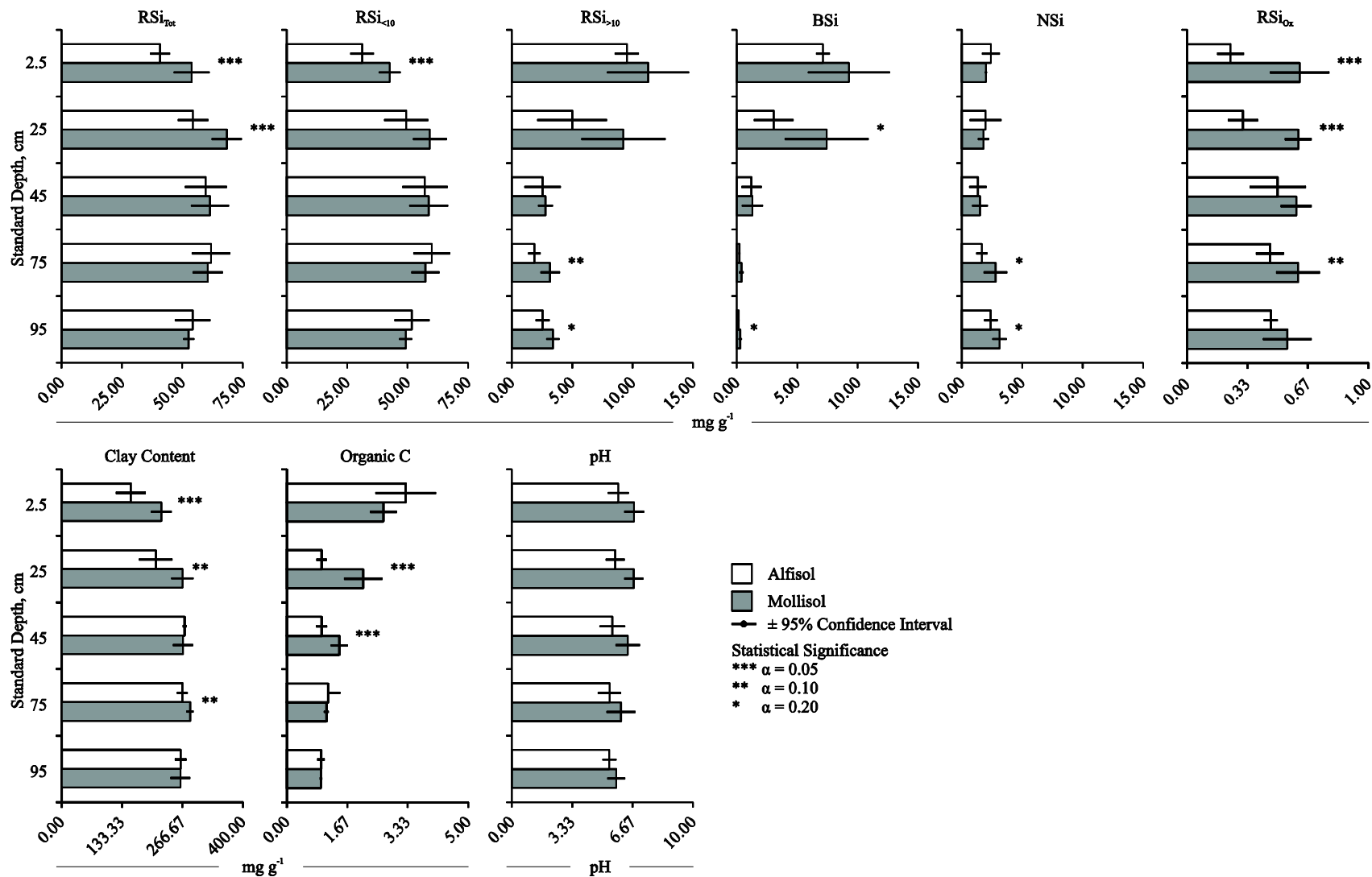


Figure 4.2. Average measurements for Alfisols and Mollisols, by standard depths. Note the changes in scale for RSi measurements. T-test analyses were not performed on pH data.

Table 4.1. Soil order averages and t-test results by standard depth and pedogenic layer (eluvial and illuvial). Alfisols are shown in the first row of each depth, followed by Mollisols on the second row. All measurements except pH are expressed as mg SiO₂ g⁻¹ dry soil weight. Uncertainty is ± 1 standard deviation. T-test results are listed below Mollisol averages and presented as t-score; p-value; degrees of freedom.

Depth, cm		RSi _{Tot}	RSi _{<10}	RSi _{>10}	BSi	NSi	RSi _{Ox}	Clay Content	OC
2.5	Alf	40.76 $\pm$ 4.90	31.23 $\pm$ 5.82	9.53 $\pm$ 1.19	7.12 $\pm$ 0.67	2.40 $\pm$ 0.88	0.24 $\pm$ 0.09	152.84 $\pm$ 38.99	3.28 $\pm$ 1.00
	Mol	53.88 $\pm$ 8.89	42.61 $\pm$ 5.39	11.27 $\pm$ 4.12	9.28 $\pm$ 4.10	1.99 $\pm$ 0.53	0.62 $\pm$ 0.20	220.29 $\pm$ 26.52	2.66 $\pm$ 0.43
	T	2.79; 0.03; 6	2.84; 0.03; 6	0.65; 0.54; 6	0.859; 0.43; 6	-0.57; 0.59; 6	4.08; 0.01; 6	2.55; 0.04; 6	-1.05; 0.34; 6
25	Alf	54.44 $\pm$ 7.56	49.44 $\pm$ 10.87	5.00 $\pm$ 3.48	3.04 $\pm$ 1.98	1.96 $\pm$ 1.57	0.31 $\pm$ 0.10	207.74 $\pm$ 44.08	0.96 $\pm$ 0.16
	Mol	68.43 $\pm$ 7.53	59.20 $\pm$ 8.43	9.23 $\pm$ 4.21	7.44 $\pm$ 4.19	1.79 $\pm$ 0.53	0.61 $\pm$ 0.09	266.93 $\pm$ 29.21	2.11 $\pm$ 0.63
	T	2.60; 0.04; 6	1.41; 0.21; 6	1.44; 0.20; 6	1.65; 0.15; 6	0.35; 0.74; 6	3.78; 0.01; 6	2.02; 0.10; 6	4.09; 0.01; 6
45	Alf	59.71 $\pm$ 10.46	57.16 $\pm$ 11.35	2.55 $\pm$ 1.80	1.22 $\pm$ 0.98	1.33 $\pm$ 0.84	0.50 $\pm$ 0.19	271.63 $\pm$ 4.27	0.96 $\pm$ 0.17
	Mol	61.48 $\pm$ 9.34	58.69 $\pm$ 9.65	2.79 $\pm$ 0.71	1.29 $\pm$ 1.04	1.50 $\pm$ 0.78	0.60 $\pm$ 0.10	268.38 $\pm$ 26.74	1.44 $\pm$ 0.27
	T	0.27; 0.80; 6	0.24; 0.82; 6	0.66; 0.54; 6	-0.05; 0.96; 6	0.25; 0.81; 6	1.09; 0.32; 6	-0.31; 0.77; 6	3.10; 0.02; 6
75	Alf	61.88 $\pm$ 9.62	60.02 $\pm$ 9.22	1.86 $\pm$ 0.59	0.21 $\pm$ 0.08	1.65 $\pm$ 0.54	0.46 $\pm$ 0.09	266.23 $\pm$ 13.41	1.14 $\pm$ 0.39
	Mol	60.50 $\pm$ 7.44	57.32 $\pm$ 6.94	3.17 $\pm$ 0.95	0.38 $\pm$ 0.20	2.79 $\pm$ 1.15	0.61 $\pm$ 0.14	283.73 $\pm$ 8.86	1.09 $\pm$ 0.07
	T	-0.20; 0.85; 6	-0.45; 0.67; 6	2.22; 0.07; 6	1.41; 0.21; 6	1.66; 0.15; 6	1.95; 0.10; 6	2.13; 0.08; 6	0.01; 1.00; 6
95	Alf	54.32 $\pm$ 10.47	51.77 $\pm$ 8.72	2.55 $\pm$ 0.69	0.15 $\pm$ 0.04	2.40 $\pm$ 0.65	0.46 $\pm$ 0.04	262.62 $\pm$ 14.18	0.94 $\pm$ 0.11
	Mol	52.62 $\pm$ 2.75	49.21 $\pm$ 3.15	3.40 $\pm$ 0.64	0.28 $\pm$ 0.16	3.13 $\pm$ 0.70	0.55 $\pm$ 0.16	262.38 $\pm$ 26.07	0.99 $\pm$ 0.11
	T	-0.26; 0.80; 6	-0.46; 0.67; 6	1.82; 0.12; 6	1.84; 0.12; 6	1.60; 0.17; 6	0.83; 0.44; 6	-0.060; 0.95; 6	0.61; 0.57; 6
Eluvial	Alf	47.60 $\pm$ 9.39	40.33 $\pm$ 12.64	7.26 $\pm$ 3.41	5.08 $\pm$ 2.58	2.18 $\pm$ 1.20	0.27 $\pm$ 0.09	180.29 $\pm$ 48.43	2.12 $\pm$ 1.40
	Mol	61.16 $\pm$ 10.89	50.90 $\pm$ 11.03	10.25 $\pm$ 4.01	8.36 $\pm$ 3.96	1.89 $\pm$ 0.37	0.62 $\pm$ 0.37	234.34 $\pm$ 30.95	2.38 $\pm$ 0.58
	T	2.69; 0.02; 14	1.91; 0.08; 14	1.41; 0.18; 14	1.60; 0.13; 14	0.10; 0.92; 14	5.67; 0.00; 14	2.81; 0.01; 14	1.11; 0.29; 14
Illuvial	Alf	58.64 $\pm$ 9.36	56.32 $\pm$ 9.58	2.32 $\pm$ 1.11	0.53 $\pm$ 0.73	1.79 $\pm$ 0.78	0.47 $\pm$ 0.11	266.83 $\pm$ 11.13	1.01 $\pm$ 0.25
	Mol	58.20 $\pm$ 7.62	55.08 $\pm$ 7.77	3.12 $\pm$ 0.75	0.65 $\pm$ 0.73	2.47 $\pm$ 1.09	0.59 $\pm$ 0.13	263.43 $\pm$ 19.23	1.17 $\pm$ 0.26
	T	-0.06; 0.95; 22	-0.28; 0.78; 22	2.49; 0.02; 22	0.89; 0.39; 22	1.36; 0.19; 22	2.31; 0.03; 22	0.56; 0.58; 22	1.69; 0.11; 22

3.3 RSi_{>10}, BSi, NSi

RSi_{>10} is a summation of all forms of RSi greater than 10 μm . Microscopy allowed for the classification of RSi_{>10} particles as either biogenic (BSi) or nonbiogenic/unknown (NSi) in origin. As a whole, the quantities of these forms were minor when compared to RSi_{<10}, always less than 10% of the total (Fig. 4.2; Table 4.1).

No statistical differences were detected at any standard depth, but Mollisols contained significantly more RSi_{>10} within the illuvial horizons (Table 4.1). RSi_{>10} content was highest at the surface for both soil orders, reaching minima at 45 to 75 cm, and increasing slightly at 95 cm (Fig. 2).

When considering BSi content, Mollisols contained considerably more in eluvial horizons, but the greater range in variability found across these soil profiles precluded any statistical significance. Indeed, eluvial horizons BSi content of the northern Mollisols, KL1 and KL3, was similar to the Alfisols (Appendix 8). By contrast, the southern Mollisols, KO1 and NL, was considerably higher. As with RSi_{>10}, BSi content was highest at the surface and decreased with depth; however there was no secondary increase at 95 cm (Fig. 4.2).

NSi content in both Alfisols and Mollisols were quite similar at all layers. Given this lack of dissimilarity, the t-tests revealed no significant differences between the soil orders. However, illuvial horizons were distinct at the $\alpha = 0.10$ level. Analysis of depth patterns (Fig. 4.2) revealed that both soil orders followed a similar pattern as that seen in RSi_{>10}. NSi was higher at the surface, reached minimal amounts at 45 cm, and increased thereafter. Peak NSi content in the Alfisols occurred at the surface, which may be due to the propensity for tree phytoliths to

fragment quite easily (they were thus classified as NSi because they could not be identified as BSi based on morphology). Mollisols on the other hand, reached peak NSi content at 95 cm.

Despite the lack of statistical differences between the soil orders, it is noteworthy that Mollisols contained slightly more $RSi_{>10}$, BSi, and NSi at more standard depths and pedogenic layers.

4.3.4 RSi_{Ox}

RSi_{Ox} was the smallest RSi fraction measured, at less than 1% of the total. Notwithstanding, the greatest differences between Alfisols and Mollisols were found in this RSi fraction. The soil orders were significantly different at 2.5 and 25 cm depths as well as both eluvial and illuvial layers (Table 4.1).

RSi_{Ox} content peaked at 45 cm in Alfisols and decreased below this depth (Fig. 4.2). Mollisols remained relatively constant with depth.

4.3.5 Clay Content

Alfisols contained less clay content than Mollisols. The soil orders were statistically different at 2.5 cm as well as for eluvial horizons (Table 4.1). Alfisols peaked in clay content at 45 cm and remained constant below this depth. Mollisols were somewhat similar, but they peaked at 75 cm (Fig. 2). Textural contrasts between eluvial and illuvial horizons were greater in the Alfisols.

4.3.6 Organic C

Mollisols contained significantly more OC at the 25 and 45 cm depths due to thicker A horizons (Table 4.1). However, eluvial horizons were not statistically different.

Not surprisingly, depth patterns (Fig. 4.2) show that OC content is highest at the surface and decreases with depth. However, Alfisols reach minimal OC levels by 25 cm, while Mollisols decrease steadily.

4. Discussion

4.1 Comparison of Soil Orders

The Alfisols used in this study tended to have thinner A horizons, and lower eluvial horizon clay content, creating greater textural contrast with underlying illuvial horizons than in the Mollisols. Mollisol A horizons were thicker, resulting in higher OC content at 25 cm and a more gradual downward increase in OC than in the Alfisols. These morphological differences are typical for these two orders. Below 30-40 cm, soils in both orders are quite similar in most properties. This is not surprising given that these soils formed in virtually identical parent material and climate, and most have probably been under both forest and prairie at various times in their development. The most common explanations for contrasting pedogenesis under forest and prairie are greater belowground organic matter addition and more active deep bioturbation under prairie (Hole and Nielsen, 1968). Both of these vegetation effects should be greatest in the upper solum.

The RSi data also show differences between the soil orders, but generally only in the eluvial horizons (Fig. 4.2; Table 4.1). Differences in vegetation cover apparently do not produce large differences in whole-profile RSi_{Tot} content, at least over the time that the ecotone has been near its present position, since whole profile RSi_{Tot} is similar for soils in the two orders. Mollisols do contain significantly more RSi_{Tot} in the upper 30 cm, however; below this level the two soil orders were essentially identical. The presence of greater amounts of RSi_{Tot} in Mollisol eluvial horizons may be the result of increased cycling of silica by grasses than by trees and other forest vegetation (Bartoli 1983; Blecker et al 2006). Renewal of above ground grass biomass on an annual basis would result in rapid uptake of silica from RSi that dissolves, along with constant replenishment of RSi through deposition of phytoliths. In contrast, lower rates of uptake and deposition by vegetation under forest could lead to depletion of RSi from upper horizons of the Alfisols, through dissolution and downward translocation. It should be noted, however, that there is little evidence of greater RSi accumulation in illuvial horizons of the Alfisols, so what is lost from their eluvial horizons may be lost from the profile as a whole rather than simply transferred to lower parts of the solum.

An unknown amount of RSi has probably been lost from these soils due to land use changes following Euro-American settlement. All of the Mollisols were used for maize cultivation at the time of sampling. Of the Alfisols, AL2 was never plowed, but was selectively logged in the 1960s. CAR has been under forest cover for at least several decades, while CA and OR are currently used for pasture and hay production. Previous work has shown that vegetation disturbance can result in DSi redistribution and loss within several yr (Conley et al 2008; Saccone et al 2008). Struyf et al (2010) demonstrate that conversion of native vegetation to cropping results in an initial increase of RSi export from soils to watersheds, most likely from

the most labile forms of RSi, such as DSi. Over longer time periods (decades to centuries), RSi exports to watersheds are lowered below pre-disturbance levels as labile forms are depleted, and any exports after this are thought to originate from amorphous silica dissolution.

Within the Alfisols, whole-profile RSi content as well as its vertical distribution was generally similar despite differences in land use. This suggests that disturbance has had a minimal or similar impact on the soils. However, a greater proportion of the total RSi stock is held as DSi within Alfisols (Markewitz & Richter 1998). Hence it is possible that Alfisols could have lost a significant proportion of their total RSi stocks due to mobilization of DSi. While DSi fractions were not studied here, any losses are most likely minimal relative to total RSi given the similarity of total RSi stocks. The same is probably true for Mollisols, given that their profiles of RSi are quite similar to the Alfisols, except for somewhat greater contents in eluvial horizons.

A disproportionate amount of RSi_{Tot} content is composed of $RSi_{<10}$, confirming the findings of Chapter 3. Given that $RSi_{<10}$ occurs in the clay- and fine-silt fractions, it is subject to the same pedogenic processes which induce clay mineral translocation. Indeed, the difference in the vertical distribution of clay content between Alfisols and Mollisols is a key indicator which distinguishes these soil orders, and this difference is a result of contrasting biotic processes associated with grassland and forest. It can therefore be inferred that the vertical distribution of $RSi_{<10}$ is a result of biotic processes as well.

As a reminder, $RSi_{<10}$ is estimated from RSi_{Tot} , which in turn is measured through the use of chemical dissolution. The possibility therefore exists that at least some of the silica measured originates from clay mineral dissolution. This point was discussed at length in Chapter 3, where it was concluded that clay minerals probably contribute negligible amounts. Clay minerals obtained from rock outcrops contribute at most 1.15% RSi_{Tot} (see Table 3.4, Chapter 3).

However, a positive relationship between clay content and RSi_{Tot} was described in that chapter (see Fig. 3.4 in Chapter 3). The same relationship was observed here (Fig. 4.3). As discussed in Chapter 3, this relationship is probably the result of clay mineral properties acting to increase RSi deposition. The higher bulk density and lower permeability of clay-rich horizons can inhibit water movement through the soil, while the higher surface area to volume ratios encountered there facilitates RSi deposition. In fact, amorphous silica has been associated with clay mineral concentrates from soils; as clay particle size decreases, the proportion of amorphous silica increases (Glenn et al 1960). While no attempt was made to further analyze the nature of the relationship between clays and RSi in the soils studied here, the findings of Glenn et al (1960) raise two points. First, the RSi component associated with soil clays is not from the clay minerals

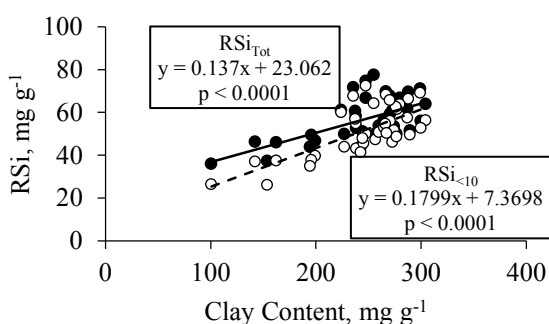


Figure 4.3. Scatterplot of clay particle versus RSi_{Tot} content (black circles, solid regression line) and $RSi_{<10}$ content (white circles, dashed regression line). Regression coefficients are shown in the figure.

themselves, but rather it is a depositional feature. Second, the authors noted that the RSi associated with the clays displayed very high silica to metal (Fe and Al) ratios, indicating that the silica existed mostly in the amorphous state, rather than adsorbed.

$RSi_{>10}$ content was not significantly different at any depth, although illuvial

horizons as a whole were statistically different. Lack of significant differences can be attributed to the large variation encountered in the Mollisols (Fig. 4.2). This variation is even more pronounced in BSi content. Eluvial horizon $RSi_{>10}$ and BSi content for KL1 and KL3 (northern Mollisols) was considerably lower than KO1 and NL (southern Mollisols). One plausible explanation is that these soils are found at the extreme northern edge of the large area of

Mollisols on uplands of central Houston County (Fig. 4.1). While they do display typical Mollisol morphology, they may not have been under grassland for as long as the southern Mollisols. Alternatively, the soils at the northern sites may have been affected by a moderate amount of erosion under cultivation, removing RSi-rich material from the upper part of the A horizon.

NSi content was generally similar for the two soil orders. However, Alfisols contained slightly more NSi in eluvial horizons. As mentioned in the results section, phytoliths produced by woody species tend to exhibit more fragile and asymmetric morphologies as well as higher solubilities. These phytoliths would be expected to break down and fragment quite easily in soils, thus making their identification as BSi difficult. By default, these unknown forms were placed in the NSi category.

NSi content is also slightly higher at the 75 and 95 cm depths in the Mollisols. At these depths, most NSi present is most likely inherited, unweathered cristobalite. This may indicate that less overall weathering has occurred at depth in the Mollisols. However, given the Holocene vegetation history, these small differences in NSi content would have to have developed within the past 3400 yr or less. Assuming equal NSi content between the two soil orders at the beginning of their divergence 3400 yr ago or later, then the re-establishment of forest over the Alfisols would renew the weathering and breakdown of NSi particles at depth. This seems plausible, given that changes at depth should be manifested in the most reactive components first; in this case, the highly soluble NSi.

RSi_{Ox} content was distinctly different between the soil orders. Mollisol RSi_{Ox} content remained relatively constant with depth, while Alfisols contained significantly less in eluvial horizons. This could reflect a more pronounced contrast in Al and Fe oxide content between

eluvial and illuvial horizons in the Alfisols. A relationship between clay content and RSi_{Ox} was observed in the Alfisols but not the Mollisols (Fig. 4.4). This affinity of RSi_{Ox} for clay content suggests greater rates of RSi adsorption onto clay and oxyhydroxide surfaces. RSi_{Ox} includes RSi adsorbed on those oxides, so it is lower in the Alfisol E horizons with low oxide content, and higher in the Bt horizons where Fe and Al oxides are associated with clay minerals. On the other hand, Saccone et al (2007) observed greater quantities of RSi_{Ox} in Mollisols, which they attributed to lower overall rates of weathering and a greater proportion of angular RSi shards originating from soil phytolith breakdown.

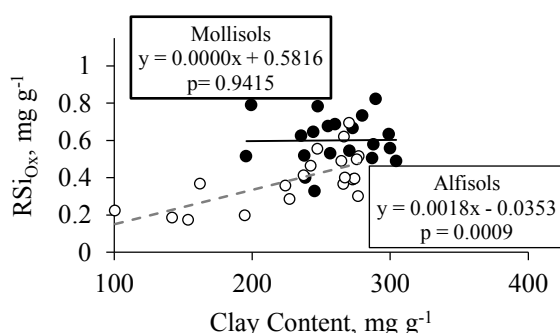


Figure 4.4. Scatterplot of clay particle versus RSi_{Ox} content for Mollisols (black circles, solid regression line) and Alfisols (white circles, dashed regression line). Regression coefficients are shown in the figure.

4.4.2 Implications

The results clearly demonstrate differences in soil morphological properties and RSi pools across a forest-prairie ecotone. Although not technically a biosequence, the use of soil orders is a reasonable proxy for long-term

vegetation. By holding all other factors constant, this study confirms that vegetation communities do in fact alter RSi content and vertical distribution.

By analyzing soil orders which diverged from one another within the last 3400 yr, this study also yields a rough estimate of the sensitivity of RSi content to vegetation change. While it is known that DSi can be altered over the course of a few yr to decades (Conley et al 2008; Saccone et al 2008), this study is the first to provide a maximum amount of time required for the

measureable alteration of particulate forms of RSi. Conversion to agriculture has been shown to cause noticeable changes to particulate RSi over the course of a few centuries (Clymans et al 2011b), and the same is most likely true under natural vegetation change. This implies that changes to vegetation over the course of the Holocene have caused shifts in the way that silica is cycled in soils, particularly in ecotonal regions.

Differences between the soil orders may be somewhat muted here due to the dynamic nature of the forest-prairie ecotone. Fluctuations over the course of the late Holocene could have left multiple imprints of forest and prairie on a single soil, thereby muting the effects of long-term dominant vegetation. Comparison of soil orders over a larger region would probably yield greater differences in RSi content. The differences observed between the Mollisols suggest this; the northern Mollisols, which are located in closer proximity to the modern ecotone, appear to be more transitional in nature.

4.5. Conclusions

These results demonstrate that soils formed under forest and prairie exhibit distinct RSi signatures. This study has compared morphological properties and RSi pools in soil orders which have diverged within the last 3400 yr. Differences were most pronounced in eluvial horizons, where weathering has been more intense. Lack of differences in illuvial horizons may be the result of similar vegetative history during the early and mid Holocene. RSi_{Tot} and $RSi_{<10}$ content peaked in illuvial horizons for all soils. Depth distributions of clay content, RSi_{Tot} , $RSi_{<10}$, and RSi_{Ox} revealed that Alfisols tended to show a greater contrast between eluvial and illuvial horizons, possibly due to less intense biocycling of silica and/or greater weathering intensity.

RSi_{>10} and BSi were greatest near soil surfaces. Although Mollisols contained, on average, more RSi_{>10} and BSi content in eluvial horizons, a greater range in variability precluded any statistical differences when compared to Alfisols. NSi content was greatest at the bottom of profiles for Mollisols, and at surfaces for Alfisols, possibly due to weathered and fragmented BSi.

5. REFERENCES

- Aksakal, E. L., Angin, I., & Oztas, T. (2012). Effects of diatomite on soil physical properties. *Catena*, 88, 1-5.
- Aleinikoff, J. N., Muhs, D. R., & Fanning, C. M. (1998). Isotopic evidence for the sources of late Wisconsin (Peoria) Loess, Colorado and Nebraska: Implications for paleoclimate. In A. J. Busacca (Ed.), *Dust aerosols, loess soils & global change: An interdisciplinary conference and field tour on dust in ancient environments and contemporary environs* (pp. 124-127). Pullman, WA: Washington State University College of Agriculture and Home Economics.
- Alexandre, A., Meunier, J. D., Colin, F., & Koud, J. M. (1997). Plant impact on the biogeochemical cycle of silicon and related weathering processes. *Geochimica et Cosmochimica Acta*, 61(3), 677-682.
- Alexandre, A., Bouvet, M., & Abbadie, L. (2011). The role of savannas in the terrestrial Si cycle: A case-study from Lamto, Ivory Coast. *Global and Planetary Change*, 78(3-4), 162-169.
- Alexandre, A., Crespín, J., Sylvestre, F., Sonzogni, C., & Hilbert, D. W. (2012). The oxygen isotopic composition of phytolith assemblages from tropical rainforest soil tops (Queensland, Australia): Validation of a new paleoenvironmental tool. *Climate of the Past*, 8(1), 307-324.
- Bailey-Watts, A. E. (1976). Planktonic diatoms and some diatom-silica relations in a shallow eutrophic Scottish loch. *Freshwater Biology*, 6, 69-80.

- Baker, R. G., Bettis III, E. A., Denniston, L. A., González, L. A., Strickland, L. E., & Krieg, J. R. (2002). Holocene paleoenvironments in southeastern Minnesota - chasing the prairie-forest ecotone. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 177, 103-122.
- Baker, R. G., Bettis III, E. A., Schwert, D. P., Horton, D. G., Chumbley, C. A., Gonzalez, L. A., et al. (1996). Holocene paleoenvironments of northeast Iowa. *Ecological Monographs*, 66(2), 203-234.
- Baker, R. G., Mason, J. A., & Maher, L. J. (1999). Petaloid organs preserved in an arctic plant macrofossil assemblage from full-glacial sediments in southeastern Minnesota. *Quaternary Research*, 52(3), 388-392.
- Bartoli, F. (1983). The biogeochemical cycle of silicon in two temperate forest ecosystems. In R. Hallberg (Ed.), *Environmental biogeochemistry. proc. 5th international symposium, Stockholm, 1981* (pp. 469-476) *Ecological Bulletins* (Stockholm), 35.
- Bartoli, F., & Wilding, L. P. (1980). Dissolution of biogenic opal as a function of its physical and chemical properties. *Soil Science Society of America Journal*, 44(4), 873-878.
- Beckwith, R. S., & Reeve, R. (1963). Studies on soluble silica in soils. I. The sorption of silicic acid by soils and minerals. *Australian Journal of Soil Research*, 1, 157-168.
- Beckwith, R. S., & Reeve, R. (1964). Studies on soluble silica in soils. II. The release of monosilicic acid from soils. *Australian Journal of Soil Research*, 2, 33-45.

- Ben-Dor, E., & Banin, A. (1989). Determination of organic matter content in arid-zone soils using a simple "loss-on-ignition" method. *Communications in Soil Science and Plant Analysis*, 20, 1675-1695.
- Berner, R. A. (1990). Atmospheric carbon dioxide levels over Phanerozoic time. *Science*, 249(4975), 1382-1386.
- Bettis, III., E.A., Muhs, D. R., Roberts, H. M., & Wintle, A. G. (2003). Last glacial loess in the conterminous USA. *Quaternary Science Reviews*, 22(18–19), 1907-1946.
- Bickmore, B. R., Nagy, K. L., Gray, A. K., & Brinkerhoff, A. R. (2006). The effect of $\text{Al}(\text{OH})_4^-$ on the dissolution rate of quartz. *Geochimica et Cosmochimica Acta*, 70(2), 290-305.
- Blecker, S. W., McCulley, R. L., Chadwick, O. A., & Kelly, E. F. (2006). Biologic cycling of silica across a grassland bioclimate sequence. *Global Biogeochemical Cycles*, 20(GB3023), 1.
- Blinnikov, M. S., Bagent, C. M., & Reyerson, P. E. (in press). Phytolith assemblages and opal concentrations from modern soils differentiate grasslands of controlled composition on experimental plots at cedar creek, Minnesota. *Quaternary International*, 1-13.
- Borelli, N., Alvarez, M. F., Osterrieth, M. L., & Marcovecchio, J. E. (2010). Silica content in soil solution and its relation with phytolith weathering and silica biogeochemical cycle in Typical Argiudolls of the Pampean plain, Argentina - a preliminary study. *Journal of Soils and Sediments*, 10, 983-994.

- Borelli, N., Osterrieth, M., & Marovecchio, J. (2008). Interrelations of vegetal cover, silicophytolith content and pedogenesis of Typical Argiudolls of the Pampean plain, argentina. *Catena*, 75(146), 153.
- Brimhall, G. H., Lewis, C. J., Ford, C., Bratt, J., Taylor, G., & Warin, O. (1991). Quantitative geochemical approach to pedogenesis - importance of parent material reduction, volumetric expansion, and eolian influx in lateritization. *Geoderma*, 51(1-4), 51-91.
- Brinkman, R. (1970). Ferrollysis, a hydromorphic soil forming process. *Geoderma*, 3(3), 199-206.
- Brinkman, R. (1979). *Ferrollysis, a soil-forming process in hydromorphic conditions*. Wageningen: PUDOC.
- Brown, T. H., & Mahler, R. L. (1987). Sorption of silica in a northern Idaho Palouse silt loam. *Soil Science*, 144(3), 181-189.
- Burke, I. C., Lauenroth, W. K., Vinton, M. A., Hook, P. B., Kelly, R. H., Epstein, H. E., et al. (1998). Plant-soil interactions in temperate grasslands. *Biogeochemistry*, 42(1/2), 121-143.
- Busacca, A. J., Nelstead, K. T., McDonald, E. V., & Purser, M. D. (1992). Correlation of distal tephra layers in loess in the channeled scabland and Palouse of Washington state. *Quaternary Research*, 37(3), 281-303.
- Chadwick, O. A., Hendricks, D. M., & Nettleton, W. D. (1987). Silica in duric soils: I. A depositional model. *Soil Science Society of America Journal*, 51, 975-982.

- Chartres, C. J. (1990). Poorly ordered silica and aluminosilicates as temporary cementing agents in hard-setting soils. *Soil Science Society of America Journal*, 54, 1060-1067.
- Chester, R., & Elderfield, H. (1968). The infrared determination of opal in siliceous deep-sea sediments. *Geochimica et Cosmochimica Acta*, 32(10), 1128-1140.
- Chumbley, C. A., Baker, R. G., & Bettis III, E. A. (1990). Midwestern Holocene paleoenvironments revealed by floodplain deposits in northeastern Iowa. *Science*, 249(4966), 272-274.
- Clymans, W., Govers, G., Van Wesemael, B., Meire, P., & Struyf, E. (2011a). Amorphous silica analysis in terrestrial runoff samples. *Geoderma*, 167-168, 228-235.
- Clymans, W., Struyf, E., Govers, G., Vandevenne, F., & Conley, D. J. (2011b). Anthropogenic impact on amorphous silica pools in temperate soils. *Biogeosciences*, 8(8), 2281-2293.
- Conley, D. J. (1998). An interlaboratory comparison for the measurement of biogenic silica in sediments. *Marine Chemistry*, 63(1-2), 39-48.
- Conley, D. J. (2002). Terrestrial ecosystems and the global biogeochemical silica cycle. *Global Biogeochemical Cycles*, 16(4), 68-1 - 68-8.
- Conley, D. J., Likens, G. E., Buso, D. C., Saccone, L., Bailey, S. W., & Johnson, C. E. (2008). Deforestation causes increased dissolved silicate losses in the Hubbard Brook Experimental Forest. *Global Change Biology*, 14(11), 2548-2554.

- Cornelis, J. -T., Delvaux, B., Cardinal, D., André, L., Ranger, J., & Opfergelt, S. (2010a). Tracing mechanisms controlling the release of dissolved silicon in forest soil solutions using Si isotopes and Ge/Si ratios. *Geochimica et Cosmochimica Acta*, 74(14), 3913-3924.
- Cornelis, J. -T., Ranger, J., Iserentant, A., & Delvaux, B. (2010b). Tree species impact the terrestrial cycle of silicon through various uptakes. *Biogeochemistry*, 97(2), 231-245.
- Cornelis, J. -T., Titeux, H., Ranger, J., & Delvaux, B. (2011). Identification and distribution of the readily soluble silicon pool in a temperate forest soil below three distinct tree species. *Plant and Soil*, 342(1), 369-378.
- Cusack, D. F., Chadwick, O. A., Hockaday, W. C., & Vitousek, P. M. (2012). Mineralogical controls on soil black carbon preservation. *Global Biogeochemical Cycles*, 26(2), GB2019.
- Dahlgren, R. A., & Ugolini, F. C. (1989). Effects of tephra addition on soil processes in spodosols in the Cascade range, Washington, U.S.A. *Geoderma*, 45(3-4), 331-355.
- Demaster, D. J. (1981). The supply and accumulation of silica in the marine environment. *Geochimica et Cosmochimica Acta*, 45(10), 1715-1732.
- DeMaster, D. J. (1991). Measuring biogenic silica in marine sediments and suspended matter. In D. C. Hurd, & D. W. Spenser (Eds.), *Marine particles: Analysis and characterization* (pp. 363-368). Washington, D.C.: American Geophysical Union.
- DeMaster, D. J. (1979). *The marine budgets of silica and ³²Si*. Unpublished Ph.D., Yale University, New Haven, CT.

- Denniston, R. F., González, L. A., Baker, R. G., Asmerom, Y., Reagan, M. K., Edwards, R. L., et al. (1999). Speleothem evidence for Holocene fluctuations of the prairie-forest ecotone, north-central USA. *The Holocene*, 9(6), 671-676.
- Derry, L. A., Kurtz, A. C., Ziegler, K., & Chadwick, O. A. (2005). Biological control of terrestrial silica cycling and export fluxes to watersheds. *Nature*, 433(7027), 728-731.
- Dorale, J. A., González, L. A., Reagan, M. K., Pickett, D. A., Murrell, M. T., & Baker, R. G. (1992). A high-resolution record of Holocene climate change in speleothem calcite from cold water cave, northeast Iowa. *Science*, 258(5088), 1626-1630.
- Drees, L. R., Wilding, L. P., Smeck, N. E., & Senkayi, A. L. (1989). Silica in soils; quartz and disordered silica polymorphs. In J. B. Dixon, & S. B. Weed (Eds.), *Minerals in soil environments* (pp. 913-974). United States (USA): Soil Science Society of America, Madison, WI.
- Drever, J. I. (1994). The effect of land plants on weathering rates of silicate minerals. *Geochimica et Cosmochimica Acta*, 58(10), 2325-2332.
- Eggemann, D. W., Manheim, F. T., & Betzer, P. R. (1980). Dissolution and analysis of amorphous silica in marine sediments. *Journal of Sedimentary Research*, 50(1), 215-225.
- Eisma, D., & van der Gaast, S. J. (1971). Determination of opal in marine sediments by X-ray diffraction. *Netherlands Journal of Sea Research*, 5(3), 382-389.
- Epstein, E. (2001). Silicon in plants: Facts vs. concepts. In L. E. Datnoff, G. H. Snyder & G. H. Korndörfer (Eds.), *Silicon in agriculture* (pp. 1-15). Amsterdam: Elsevier.

- Epstein, E. (1994). The anomaly of silicon in plant biology. *Proceedings of the National Academy of Sciences of the United States of America*, 91(1), 11-17.
- Epstein, E. (1999). Silicon. *Annual Review of Plant Physiology and Plant Molecular Biology*, 50(1), 641-664.
- Fanning, D. S., & Jackson, M. L. (1966). Clay mineral weathering in southern Wisconsin soils developed in loess and shale-derived till. *Clays and Clay Minerals*, 13, 175-191.
- Farmer, V. C., Delbos, E., & Miller, J. D. (2005). The role of phytolith formation and dissolution in controlling concentrations of silica in soil solutions and streams. *Geoderma*, 127(1-2), 71-79.
- Flach, K. W., Nettleton, W. D., Gile, L. H., & Cady, J. G. (1969). Pedocementation: Induration by silica, carbonates, and sesquioxides in the quaternary. *Soil Science*, 107(6), 442-453.
- Flower, R. J. (1993). Diatom preservation: Experiments and observations on dissolution and breakage in modern and fossil material. *Hydrologia*, 269/270, 473-484.
- Folkoff, M. E., & Meentemeyer, V. (1987). Climatic control of the geography of clay minerals genesis. *Annals of the Association of American Geographers*, 77(4), 635-650.
- Follett, E. A. C., McHardy, W. J., Mitchell, B. D., & Smith, B. F. L. (1965). Chemical dissolution techniques in the study of soil clays: Part I. *Clay Minerals*, 6, 23-43.
- Foster, M. D. (1953). Geochemical studies of clay minerals III. The determination of free silica and free alumina in montmorillonites. *Geochimica et Cosmochimica Acta*, 3(2-3), 143-154.

- Fredlund, G. G., Johnson, W. C., & Dort Jr., W. (1985). A preliminary analysis of opal phytoliths from the Eustis ash pit, Frontier County, Nebraska. *Institute for Tertiary-Quaternary Studies - TER-QUA Symposium Series, 1*, 147-162.
- Fröhlich, F. (1989). Deep-sea biogenic silica: New structural and analytical data from infrared analysis - geological implications. *Terra Nova, 1*, 267-273.
- Frye, J. C., Glass, H. D., & Willman, H. B. (1968). *Mineral zonation of Woodfordian loesses of Illinois*. Urbana, Ill.: State of Illinois Dept. of Registration and Education.
- Gee, G. W., & Bauder, J. W. (1986). Particle-size analysis. In A. L. Page (Ed.), *Methods of soil analysis, part 1. Physical and mineralogical methods* (pp. 383-411). Madison, Wisconsin: Soil Science Society of America.
- Gehlen, M., & van Raaphorst, W. (1993). Early diagenesis of silica in sandy North Sea sediments: Quantification of the solid phase. *Marine Chemistry, 42*(2), 71-83.
- Gill, J. R., & Cobban, W. A. (1973). *Stratigraphy and geologic history of the Montana group and equivalent rocks, Montana, Wyoming, and North and South Dakota*. Washington, D.C.: U.S. Government Printing Office.
- Glenn, R. C., Jackson, M. L., Hole, F. D., & Lee, G. B. (1960). Chemical weathering of layer silicate clays in loess-derived Tama silt loam of southeastern Wisconsin. In *Clays and Clay Minerals, 8th Conference* (pp.63-83). New York, NY: Pergamon Press.
- Goldberg, E. D. (1958). Determination of opal in marine sediments. *Journal of Marine Research, 17*, 178-182.

- Greenwood, J. E., Truesdale, V. W., & Rendell, A. R. (2001). Biogenic silica dissolution in seawater - in vitro chemical kinetics. *Progress in Oceanography*, 48(1), 1-23.
- Grimley, D. A. (1996). *Stratigraphy, magnetic susceptibility, and mineralogy of loess-paleosol sequences in southwestern Illinois and eastern Missouri*. Unpublished Ph.D., University of Illinois at Urbana-Champaign.
- Grimm, E. C. (1983). Chronology and dynamics of vegetation change in prairie-woodland region of southern Minnesota, U.S.A. *New Phytologist*, 93(2), 311-350.
- Grimm, E. C. (1984). Fire and other factors controlling the Big Woods vegetation of Minnesota in the mid-nineteenth century. *Ecological Monographs*, 54(3), 291-311.
- Grüger, J. (1973). Studies on the late Quaternary vegetation history of northeastern Kansas. *Geological Society of America Bulletin*, 84, 239-250.
- Hansel, A. K. (1996). *Wedron and Mason groups: Lithostratigraphic reclassification of deposits of the Wisconsin episode, Lake Michigan lobe area*. Champaign, IL: Illinois State Geological Survey.
- Hashimoto, I., & Jackson, M. L. (1958). Rapid dissolution of allophane and kaolinite-halloysite after dehydration. *Clays and Clay Minerals*, 7, 114-124.
- Henriet, C., De Jaeger, N., Dorel, M., Opfergelt, S., & Delvaux, B. (2008). The reserve of weatherable primary silicates impacts the accumulation of biogenic silicon in volcanic ash soils. *Biogeochemistry*, 90(2), 209-223.

- Hole, F. D., & Nielsen, G. A. (1968). Soil genesis under prairie. In P. Schramm (Ed.), *Proceedings of a symposium on prairie and prairie restoration* (pp. 28-33). Galesburg, IL: Knox College.
- Hotchkiss, S. C., Calcote, R., & Lynch, E. A. (2007). Response of vegetation and fire to Little Ice Age climate change: Regional continuity and landscape heterogeneity. *Landscape Ecology*, 22, 25-41.
- Hurd, D. C. (1973). Interactions of biogenic opal, sediment and seawater in the central equatorial Pacific. *Geochimica et Cosmochimica Acta*, 37(10), 2257-2266, IN1, 2267-2282.
- Hurd, D. C., & Birdwhistell, S. (1983). On producing a more general model for biogenic silica dissolution. *American Journal of Science*, 283(1), 1-28.
- Iler, R. K. (1979). *The chemistry of silica: Solubility, polymerization, colloid and surface properties, and biochemistry*. New York, NY: Wiley-Interscience.
- Iler, R. K. (1973). Effect of adsorbed alumina on the solubility of amorphous silica in water. *Journal of Colloid and Interface Science*, 43(2), 399-408.
- Jackson, M. L., Whittig, L. D., & Pennington, R. P. (1949). Segregation procedure for the mineralogical analysis of soils. *Proceedings - Soil Science Society of America*, 14, 77-81.
- Jacobs, P. M., & Mason, J. A. (2007). Late Quaternary climate change, loess sedimentation, and soil profile development in the central Great Plains: A pedosedimentary model. *Bulletin of the Geological Society of America*, 119(3-4), 462-475.

- Jacobs, P. M., Mason, J. A., & Hanson, P. R. (2011). Mississippi valley regional source of loess on the southern Green Bay lobe land surface, Wisconsin. *Quaternary Research*, 75, 574-583.
- Jacobs, P. M., & Mason, J. A. (2005). Impact of Holocene dust aggradation on A horizon characteristics and carbon storage in loess-derived Mollisols of the Great Plains, USA. *Geoderma*, 125(1-2), 95-106.
- Johnson, W. C., & Willey, K. L. (2000). Isotopic and rock magnetic expression of environmental change at the Pleistocene-Holocene transition in the central Great Plains. *Quaternary International*, 67, 89-106.
- Jones, L. H. P., & Handreck, K. A. (1963). Effects of iron and aluminum oxides on silica in solution in soils. *Nature*, 198, 852-853.
- Jones, R. L. (1969). Determination of opal in soil by alkali dissolution analysis. *Proceedings - Soil Science Society of America*, 33, 976-978.
- Jones, R. L., & Beavers, A. H. (1964a). Aspects of catenary and depth distribution of opal phytoliths in Illinois soils. *Soil Science Society of America Proceedings*, 28, 413-416.
- Jones, R. L., & Beavers, A. H. (1964b). Variation of opal phytolith content among some great soil groups in Illinois. *Soil Science Society of America Proceedings*, 28, 711-712.
- Jones, R. L., & Dreher, G. B. (1996). Silicon. In D.L. Sparks et al. (Eds.), *Methods of soil analysis, part 3. Chemical methods* (pp. 627-638). Madison, WI: Soil Science Society of America.

- Jones, R. L., & Blatt, H. (1984). Mineral dispersal patterns in the Pierre shale. *Journal of Sedimentary Research*, 54(1), 17-28.
- Kamatani, A., & Oku, O. (2000). Measuring biogenic silica in marine sediments. *Marine Chemistry*, 68(3), 219-229.
- Kamatani, A., & Riley, J. P. (1979). Rate of dissolution of diatom silica walls in seawater. *Marine Biology*, 55(1), 29-35.
- Karathanasis, A. D. (1989). Solution chemistry of fragipans - thermodynamic approach to understanding fragipan formation. In N. E. Smeck, & E. J. Ciolkosz (Eds.), *Fragipans: Their occurrence, classification, and genesis* (pp. 113-139). Madison, WI: Soil Science Society of America.
- Kelly, E. F., Chadwick, O. A., & Hilinski, T. E. (1998). The effect of plants on mineral weathering. *Biogeochemistry*, 42(1/2), 21-53.
- Kendrick, K. J., & Graham, R. C. (2004). Pedogenic silica accumulation in chronosequence soils, southern California. *Soil Science Society of America Journal*, 68(1295), 1303.
- Kidder, D. L., & Gierlowski-Kordesch, E. H. (2005). Impact of grassland radiation on the nonmarine silica cycle and Miocene diatomite. *Palaaios*, 20(2), 198-206.
- Kilburn, P., Tutterow, B., & Brugam, R. B. (2009). The tree species composition and history of barrens identified by government land surveyors in southwestern Illinois. *The Journal of the Torrey Botanical Society*, 136(2), 272-283.

- Kodama, H., & Ross, G. J. (1991). Tiron dissolution method used to remove and characterize inorganic components in soils. *Soil Science Society of America Journal*, 55, 1180-1187.
- Konen, M. E., Mason, J. A., Jacobs, P. M., Burras, C. L., & Talaga, B. J. (2002). Equations for predicting soil organic carbon using loss-on-ignition for north central U.S. soils. *Soil Science Society of America Journal*, 66(6), 1878-1881.
- Koning, E., Epping, E., & Van Raaphorst, W. (2002). Determining biogenic silica in marine samples by tracking silicate and aluminium concentrations in alkaline leaching solutions. *Aquatic Geochemistry*, 8(1), 37-67.
- Koning, E., Gehlen, M., Flank, A. -M., Calas, G., & Epping, E. (2007). Rapid post-mortem incorporation of aluminum in diatom frustules: Evidence from chemical and structural analyses. *Marine Chemistry*, 106(1-2), 208-222.
- Koning, E., Van Bennekom, J., Helder, W., Van Iperen, J., Brummer, G. -J., & Van Raaphorst, W. (1997). Settling, dissolution and burial of biogenic silica in the sediments off Somalia (northwestern Indian Ocean). *Deep-Sea Research Part II: Topical Studies in Oceanography*, 44(6-7), 1341-1360.
- Korndörfer, G. H., & Lepsch, I. Effect of silicon on plant growth and crop yield. In L. E. Datnoff, G. H. Snyder & G. H. Korndörfer (Eds.), *Silicon in agriculture* (pp. 133-147). Amsterdam: Elsevier.
- Krausse, G. L., Schelske, C. L., & Davis, C. O. (1983). Comparison of three wet-alkaline methods of digestion of biogenic silica in water. *Freshwater Biology*, 13, 73-81.

- Kurtz, A. C., Derry, L. A., & Chadwick, O. A. (2002). Germanium-silicon fractionation in the weathering environment. *Geochimica et Cosmochimica Acta*, 66(9), 1525-1537.
- Kutner, M. H., Nachtsheim, C. J., & Neter, J. (2004). *Applied linear regression models* (4th ed.). New York: The McGraw-Hill Companies, Inc.
- Landén, A., Holby, O., & Hall, P. O. J. (1996). Determination of biogenic silica in marine sediments - selection of pretreatment method and effect of sample size. *Vatten*, 52, 85-92.
- Langley-Turnbaugh, S. J., & Bockheim, J. G. (1998). Mass balance of soil evolution on late Quaternary marine terraces in coastal Oregon. *Geoderma*, 84(4), 265-288.
- Leinen, M. (1977). A normative calculation technique for determining opal in deep-sea sediments. *Geochimica et Cosmochimica Acta*, 41(5), 671-676.
- Lenton, T. M., & Britton, C. (2006). Enhanced carbonate and silicate weathering accelerates recovery from fossil fuel CO₂ perturbations. *Global Biogeochemical Cycles*, 20(GB3009).
- Loassachan, N., & Tada, K. (2008). Effect of solid to solution ratio on biogenic silica determination in coastal sediments. *Journal of Oceanography*, 64(5), 657-662.
- Loeppert, H. L., & Inskeep, W. P. (1996). Iron. In D. L. Sparks, et al. (Eds.), *Methods of soil analysis. part 3. Chemical methods* (pp. 640-663). Madison, WI: Soil Science Society of America.

- Lucas, Y., Luizao, F. J., Chauvel, A., Rouiller, J., & Nahon, D. (1993). The relation between biological activity of the rain forest and mineral composition of soils. *Science*, 260(5107), 521-523.
- Ludvigson, G. A., Jacobson, S. R., Witzke, B. J., & González, L. A. (1996). Carbonate component chemostratigraphy and depositional history of the Rocklandian Decorah formation. In B. J. Witzke (Ed.), *Paleozoic sequence stratigraphy: Views from the North American craton* (pp. 67-86). Boulder, CO.: Geological Society of America.
- Lueth, R. A. (1984). *Soil survey of Houston County, Minnesota*. Madison, WI: U.S. Department of Agriculture in cooperation with Minnesota Agricultural Experiment Station.
- Lusardi, B. A., Jennings, C. E., & Harris, K. L. (2011). Provenance of Des Moines lobe till records ice-stream catchment evolution during Laurentide deglaciation. *Boreas*, 40(4), 585-597.
- Ma, J. F. (2003). Functions of silicon in higher plants. In W. Müller (Ed.), *Silicon biomineralization* (pp. 127-148). Berlin: Springer Verlag.
- Ma, J. F., Miyake, Y., & Takahashi, E. (2001). Silicon as a beneficial element for crop plants. In L. E. Datnoff, G. H. Snyder & G. H. Korndörfer (Eds.), *Silicon in agriculture* (pp. 17-39). Amsterdam: Elsevier Science B.V.
- Maher Jr., L. J. (1982). The palynology of Devils Lake, Sauk County, Wisconsin. In J. C. Knox, L. Clayton & D. M. Mickelson (Eds.), *Quaternary history of the Driftless Area* (pp. 119-135). Madison, WI: Wisconsin Geological and Natural History Survey.

- Marin-Spiotta, E., Chadwick, O. A., Kramer, M., & Carbone, M. S. (2011). Carbon delivery to deep mineral horizons in Hawaiian rain forest soils. *Journal of Geophysical Research*, 116, 03011.
- Markewitz, D., & Richter, D. D. (1998). The bio in aluminum and silicon geochemistry. *Biogeochemistry*, 42(1/2), 235-252.
- Marschner, F. J. (1974). *The original vegetation of Minnesota. Compiled from U.S. General Land Office survey notes*. Washington, D.C.: U.S. Department of Agriculture, Office of Agricultural Economics, St. Paul, Minn.
- Mason, J. A. (1992). *Loess distribution and soil landscape evolution, southeastern Minnesota*. Unpublished M.S., University of Minnesota, Minneapolis, MN.
- Mason, J. A., & Jacobs, P. M. (1998). Chemical and particle-size evidence for the addition of fine dust to soils of the Midwestern United States. *Geology*, 26(12), 1135-1138.
- Mason, J. A., & Kuzila, M. S. (2000). Episodic Holocene loess deposition in central Nebraska. *Quaternary International*, 67, 119-131.
- Mason, J. A., & Nater, E. A. (1994). Soil morphology - Peoria Loess grain size relationships, southeastern Minnesota. *Soil Science Society of America Proceedings*, 58, 432-439.
- Mason, J. A. (2001). Transport direction of Peoria Loess in Nebraska and implications for loess sources on the central Great Plains. *Quaternary Research*, 56(1), 79-86.

- Mason, J. A. (1995). *Effects of glacial-interglacial climate change on mass wasting, southeastern Minnesota*. Unpublished Ph.D., University of Wisconsin-Madison, Madison, WI.
- Mason, J. A., Jacobs, P. M., Hanson, P. R., Miao, X., & Goble, R. J. (2003). Sources and paleoclimatic significance of Holocene Bignell Loess, central Great Plains, USA. *Quaternary Research*, 60(3), 330-339.
- Mason, J. A., Miao, X., Hanson, P. R., Johnson, W. C., Jacobs, P. M., & Goble, R. J. (2008). Loess record of the Pleistocene–Holocene transition on the northern and central Great Plains, USA. *Quaternary Science Reviews*, 27(17–18), 1772-1783.
- Mason, J. A., Nater, E. A., & Hobbs, H. C. (1994). Transport direction of Wisconsinan loess in southeastern Minnesota. *Quaternary Research*, 41(1), 44-51.
- McKeague, J. A., & Cline, M. G. (1963a). Silica in soil solutions. I. The form and concentration of dissolved silica in aqueous extracts of some soils. *Canadian Journal of Soil Science*, 43, 70-82.
- McKeague, J. A., & Cline, M. G. (1963b). Silica in soil solutions. II. The adsorption of monosilicic acid by soil and by other substances. *Canadian Journal of Soil Science*, 48, 83-96.
- McKeague, J. A., & Day, J. H. (1966). Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Canadian Journal of Soil Science*, 46, 13-22.

- McKnight, T. L., Hess, D., Aguado, E., & Burt, J. E. (2005). *Global physical environments, custom edition*. Boston, Massachusetts: Pearson Custom Printing.
- McKyes, E., Sethi, A., & Yong, R. N. (1974). Amorphous coatings on particles of sensitive clay soils. *Clays and Clay Minerals*, 22, 427-433.
- Melzer, S., Knapp, A., Kirkman, K., Smith, M., Blair, J., & Kelly, E. (2010). Fire and grazing impacts on silica production and storage in grass dominated ecosystems. *Biogeochemistry*, 97(2), 263-278.
- Menzies, J., Bowen, P., Ehret, D., & Glass, A. D. M. (1992). Foliar applications of potassium silicate reduce severity of powdery mildew on cucumber, muskmelon, and zucchini squash. *Journal of the American Society for Horticultural Science*, 112, 902-905.
- Meunier, J. -D., Colin, F., & Alarcon, C. (1999). Biogenic silica storage in soils. *Geology*, 27(9), 835-838.
- Miao, X., Wang, H., Mason, J. A., & Johnson, W. C. (2007). High-resolution proxy record of Holocene climate from a loess section in southwestern Nebraska, USA. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 245(3-4), 368-381.
- Michalopoulos, P., & Aller, R. C. (2004). Early diagenesis of biogenic silica in the amazon delta: Alteration, authigenic clay formation, and storage. *Geochimica et Cosmochimica Acta*, 68(5), 1061-1085.
- Minnesota DNR Staff. (2009). *Presettlement vegetation*., accessed 2009, from <http://deli.dnr.state.mn.us>

- Mortlock, R. A., & Froelich, P. N. (1989). A simple method for the rapid determination of biogenic opal in pelagic marine sediments. *Deep-Sea Research*, 36(9 A), 1415-1426.
- Mossler, J. H. (2008). *Paleozoic stratigraphic nomenclature for Minnesota: Minnesota geological survey report of investigations 65*. St. Paul, MN: Minnesota Geological Survey.
- Muhs, D. R., Bettis III, E. A., Aleinikoff, J. N., McGeehin, J. P., Beann, J., Skipp, G., et al. (2008). Origin and paleoclimatic significance of late Quaternary loess in Nebraska: Evidence from stratigraphy, chronology, sedimentology, and geochemistry. *Geological Society of America Bulletin*, 120(11-12), 1378-1407.
- Müller, W., & Schneider, R. (1993). An automated leaching method for the determination of opal in sediments and particulate matter. *Deep-Sea Research Part I-Oceanographic Research Papers*, 40(3), 425-444.
- Nelson, D. W., & Sommers, L. E. (1996). Total carbon, organic carbon, and organic matter. In D. L. Sparks, et al. (Eds.), *Methods of soil analysis, part 3. Chemical methods* (pp. 961-1010). Madison, WI: Soil Science Society of America.
- Nelson, D. M., Hu, F. S., Grimm, E. C., Curry, B. B., & Slate, J. E. (2006). The influence of aridity and fire on Holocene prairie communities in the eastern prairie peninsula. *Ecology*, 87(10), 2523-2536.
- Niewenhuyse, A., & van Breemen, N. (1997). Quantitative aspects of weathering and neoformation in selected Costa Rican volcanic soils. *Soil Science Society of America Journal*, 61, 1450-1458.

- NOAA Staff. (2002). Monthly station normals of temperature, precipitation, and heating and cooling degree days, 1971 - 2000. *Climatography of the United States* (pp. 1-36) US Department of Commerce.
- Ojakangas, R. W. (2009). *Roadside geology of Minnesota*. Missoula, MT: Mountain Press Publishing Company.
- Parr, J., Sullivan, L., Chen, B., & Zheng, W. (2010). Carbon bio-sequestration within the phytoliths of economic bamboo species. *Global Change Biology*, 16(10), 2661-2667.
- Parr, J., Sullivan, L., & Quirk, R. (2009). Sugarcane phytoliths: Encapsulation and sequestration of a long-lived carbon fraction. *Sugar Tech*, 11(1), 17-21.
- Parr, J. F., & Sullivan, L. A. (2005). Soil carbon sequestration in phytoliths. *Soil Biology and Biochemistry*, 37(1), 117-124.
- Parr, J., & Sullivan, L. (2011). Phytolith occluded carbon and silica variability in wheat cultivars. *Plant and Soil*, 342(1), 165-171.
- Parsons, R. B., Scholtes, W. H., & Riecken, F. F. (1962). Soils of Indian mounds in northeastern Iowa as benchmarks for studies of soil genesis. *Soil Science Society of America Journal*, 26(5), 491-496.
- Pearsall, D. M. (1989). *Paleoethnobotany: A handbook of procedures*. San Diego: Academic Press.
- Piperno, D. R. (2006). *Phytoliths*. Lanham, MD: AltaMira Press.

- Pye, K. (1995). The nature, origin and accumulation of loess. *Quaternary Science Reviews*, 14, 653-667.
- Raven, J. A. (2003). Cycling silicon: The role of accumulation in plants. *New Phytologist*, 158(3), 419-421.
- Reyerson, P. E. (2004). *Phytolith indicators of paleo-vegetation composition and density in eastern Washington state, USA*. Unpublished M.S., St. Cloud State University, St. Cloud, MN.
- Richter, D., & Markewitz, D. (2001). *Understanding soil change: Soil sustainability over millennia, centuries, and decades*. Cambridge, NY: Cambridge University Press.
- Rippey, B. (1983). A laboratory study of the silicon release process from a lake sediment (Lough Neagh, Northern Ireland). *Archiv Fuer Hydrobiologie*, 96(4), 417-433.
- Rosén, P., Vogel, H., Cunningham, L., Reuss, N., Conley, D. J., & Persson, P. (2010). Fourier transform infrared spectroscopy, a new method for rapid determination of total organic and inorganic carbon and biogenic silica concentration in lake sediments. *Journal of Paleolimnology*, 43, 247-259.
- Rousseau, D. -D., & Kukla, G. (1994). Late Pleistocene climate record in the Eustis loess section, Nebraska, based on land snail assemblages and magnetic susceptibility. *Quaternary Research*, 42(2), 176-187.
- Rückert, E. (1992). Naßbleichung und tonzerstörung durch ferrolysis in stauwasserböden baden-württembergs? *Hohenheimer Bodenkundliche Hefte*, 3, 1-178.

- Ruhe, R. V. (1969). *Quaternary landscapes in Iowa* (1st ed.). Ames, IA: Iowa State University Press.
- Saccone, L., Conley, D. J., Likens, G. E., Bailey, S. W., Busoc, D. C., & Johnson, C. E. (2008). Factors that control the range and variability of amorphous silica in soils in the Hubbard Brook Experimental Forest. *Soil Science Society of America Journal*, 72, 1637-1644.
- Saccone, L., Conley, D. J., & Sauer, D. (2006). Methodologies for amorphous silica analysis. *Journal of Geochemical Exploration*, 88(1-3), 235-238.
- Saccone, L., Conley, D. J., Koning, E., Sauer, D., Sommer, M., Kaczorek, D., et al. (2007). Assessing the extraction and quantification of amorphous silica in soils of forest and grassland ecosystems. *European Journal of Soil Science*, 58(6), 1446-1459.
- Santos, G. M., Alexandre, A., Southon, J. R., Treseder, K. K., Corbinau, R., & Reyerson, P. E. (2012). Possible source of ancient carbon in phytolith concentrates from harvested grasses. *Biogeosciences*, 9(5), 1873-1884.
- Santos, G. M., Alexandre, A., Coe, H. H. G., Reyerson, P. E., Southon, J. R., & De Carvalho, C. N. (2010). The phytolith ^{14}C puzzle: A tale of background determinations and accuracy tests. *Radiocarbon*, 52(1), 113-128.
- Sauer, D., Saccone, L., Conley, D. J., Herrmann, L., & Sommer, M. (2006). Review of methodologies for extracting plant-available and amorphous Si from soils and aquatic sediments. *Biogeochemistry*, 80(1), 89-108.

- Schaetzl, R., & Anderson, S. (2005). *Soils: Genesis and geomorphology*. Cambridge: Cambridge University Press.
- Schlüter, M., & Rickert, D. (1998). Effect of pH on the measurement of biogenic silica. *Marine Chemistry*, 63(1-2), 81-92.
- Schulte, E. E., & Hopkins, B. G. (1996). Estimation of organic matter by weight loss-on-ignition. In F.R. Magdoff et al (Eds.), *Soil organic matter: Analysis and interpretation* (pp. 21-31). Madison, WI: Soil Science Society of America.
- Schultz, C. B., & Stout, T. M. (1945). Pleistocene loess deposits of Nebraska. *American Journal of Science*, 243, 231-244.
- Schwertmann, U. (1964). Differenzierung der eisenoxide des bodens durch extraktion mit ammoniumoxalat losung. *Zeitschrift Für Pflanzenernährung Und Bodenkunde*, 105, 194-202.
- Segalen, P. (1968). Note sur une method de determination des produits minéraux amorphes dans certains sols à hydroxides tropicaux. *Cahiers Orstom Série Pédologie*, 6, 105-126.
- Shuman, B., Henderson, A. K., Plank, C., Stefanova, I., & Ziegler, S. S. (2009). Woodland-to-forest transition during prolonged drought in Minnesota after ca. AD 1300. *Ecology*, 90(10), 2792-2807.
- Snyder, G. H. (2001). Methods for silicon analysis in plants, soils, and fertilizers. In L. E. Datnoff, G. H. Snyder & G. H. Korndörfer (Eds.), *Silicon in agriculture* (pp. 185-196). Amsterdam: Elsevier Science B.V.

- Soil Survey Staff. (1993). *Soil survey manual*. Washington, D.C.: U.S. Government Printing Office.
- Soil Survey Staff. (1999). *Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys*. Washington, D.C.: U.S. Government Printing Office.
- Sommer, M., Kaczorek, D., Kuzyakov, Y., & Breuer, J. (2006). Silicon pools and fluxes in soils and landscapes - a review. *Journal of Plant Nutrition and Soil Science*, 169, 310-329.
- Song, Z., Wang, H., Strong, P. J., Li, Z., & Jiang, P. (2012). Plant impact on the coupled terrestrial biogeochemical cycles of silicon and carbon: Implications for biogeochemical carbon sequestration. *Earth-Science Reviews*, 115(4), 319-331.
- Stonestrom, D. A., White, A. F., & C. Akstin, K. (1998). Determining rates of chemical weathering in soils - solute transport versus profile evolution. *Journal of Hydrology*, 209(1-4), 331-345.
- Street-Perrott, F. A., & Barker, P. A. (2008). Biogenic silica: A neglected component of the coupled global continental biogeochemical cycles of carbon and silicon. *Earth Surface Processes and Landforms*, 33(9), 1436-1457.
- Strickland, J. D. H., & Parsons, T. R. (1968). *A practical handbook of seawater analysis*. Ottawa: Queen's Printer.
- Struyf, E., & Conley, D. J. (2009). Silica: An essential nutrient in wetland biogeochemistry. *Frontiers in Ecology and the Environment*, 7(2), 88-94.

- Struyf, E., Smis, A., Van Damme, S., Garnier, J., Govers, G., Van Wesemael, B., et al. (2010). Historical land use change has lowered terrestrial silica mobilization. *Nature Communications*, 1, 129.
- Stumm, W., & Morgan, J. J. *Aquatic chemistry: Chemical equilibria and rates in natural waters*. New York: Wiley.
- Sullivan, L. A., & Parr, J. F. (2007). 'Green' geosequestration: Secure carbon sequestration via plant silica biomineralisation. *Geochimica et Cosmochimica Acta*, 71(15), A985-A985.
- Swann, G. E. A. (2010). A comparison of the Si/Al and Si/time wet-alkaline digestion methods for measurement of biogenic silica in lake sediments. *Journal of Paleolimnology*, 44, 375-385.
- Swinehart, J. B., Souders, V. L., DeGraw, H. M., & Diffendal Jr., R. F. (1985). Cenozoic paleogeography of the western Nebraska. In R. M. Flores, & S. S. Kaplan (Eds.), *Cenozoic paleogeography of west-central United States* (pp. 209-229). Denver, CO: Rocky Mountain Section, Society of Economic Paleontologists and Mineralogists.
- Tanner, C. B., & Jackson, M. L. (1947). Nomographs of sedimentation times for soil particles under gravity or centrifugal acceleration. *Soil Science Society of America Proceedings*, 11, 60-65.
- Tavakkoli, E., Lyons, G., English, P., & Guppy, C. N. (2011). Silicon nutrition of rice is affected by soil pH, weathering and silicon fertilisation. *Journal of Plant Nutrition and Soil Science*, 174(3), 437-446.

Thiel, G. A. (1935). Sedimentary and petrographic analysis of the Saint Peter Sandstone.

Geological Society of America Bulletin, 46(4), 559-614.

Torn, M. S., Trumbore, S. E., Chadwick, O. A., Vitousek, P. M., & Hendricks, D. M. (1997).

Mineral control of soil organic carbon storage and turnover. *Nature*, 389(6647), 170-173.

Tréuger, P., Nelson, D. M., Van Bennekom, A. J., DeMaster, D. J., Leynaert, A. L., &

Quéguiner, B. (1995). The silica balance in the world ocean: A reestimate. *Science*, 268(5209), 375-379.

Truesdale, V. W., & Smith, C. J. (1975). Formation of molybdosilicic acids from mixed

solutions of molybdate and silicate. *Analyst*, 100(1188), 203-212.

Ugolini, F. C., & Sletten, R. S. (1991). The role of proton donors in pedogenesis as revealed by

soil solution studies. *Soil Science*, 151(1), 59-75.

Umbanhowar Jr., C. E. (2004). Interaction of fire, climate and vegetation change at a large

landscape scale in the big woods of Minnesota, USA. *Holocene*, 14(5), 661-676.

van Breemen, N. (1993). Soils as biotic constructs favouring net primary productivity.

Geoderma, 42(1), 183-211.

Verma, S. D., & Rust, R. H. (1969). Observations on opal phytoliths in a soil biosequence in

southeastern Minnesota. *Soil Science Society of America Proceedings*, 33, 749-751.

- Vogel, H., Rosén, P., Wagner, B., Melles, M., & Persson, P. (2008). Fourier transform infrared spectroscopy, a new cost-effective tool for quantitative analysis of biogeochemical properties in long sediment records. *Journal of Paleolimnology*, 40, 689-702.
- Wada, K. (1989). Allophane and imogolite. In J. B. Dixon, & S. D. Weed (Eds.), *Minerals in soil environments* (pp. 1051-1087). Madison, WI: Soil Science Society of America.
- Wada, K., & Greenland, D. J. (1970). Selective dissolution and differential infrared spectroscopy for characterization of 'amorphous' constituents in soil clays. *Clay Minerals*, 8, 241-254.
- Watteau, F., & Villemin, G. (2001). Ultrastructural study of the biogeochemical cycle of silicon in the soil and litter of a temperate forest. *European Journal of Soil Science*, 52(3), 385-396.
- Watts, W. A., & Wright Jr., H. E. (1966). Late-Wisconsin pollen and seed analysis from the Nebraska Sandhills. *Ecology*, 47(2), pp. 202-210.
- Wedepohl, K. (1995). The composition of the continental crust. *Geochimica et Cosmochimica Acta*, 59(7), 1217-1232.
- White, A. F., & Blum, A. E. (1995). Effects of climate on chemical weathering in watersheds. *Geochimica et Cosmochimica Acta*, 59(9), 1729-1747.
- White, A. F., Schulz, M. S., Vivit, D. V., Bullen, T. D., & Fitzpatrick, J. (2012). The impact of biotic/abiotic interfaces in mineral nutrient cycling: A study of soils of the Santa Cruz chronosequence, California. *Geochimica et Cosmochimica Acta*, 77(0), 62-85.

- Whittig, L. D. (1954). *Crystalline and x-amorphous mineral weathering products in some soils of temperate and tropical origin*. Unpublished Ph.D., University of Wisconsin - Madison, Madison, WI.
- Wilding, L. P., & Drees, L. R. (1971). Biogenic opal in Ohio soils. *Soil Science Society of America Journal*, 35, 1004-1010.
- Wilding, L. P., & Drees, L. R. (1974). Contributions of forest opal and associated crystalline phases to fine silt and clay fractions of soils. *Clays and Clay Minerals*, 22, 295-306.
- Williams, J. W. (2002). Variations in tree cover in North America since the last glacial maximum. *Global and Planetary Change*, 35, 1-23.
- Williams, J. W., Shuman, B. N., Webb III, T., Bartlein, P. J., & Leduc, P. L. (2004). Late-quaternary vegetation dynamics in North America: Scaling from taxa to biomes. *Ecological Monographs*, 74(2), 309-334.
- Willman, H. B., Frye, J. C. (1970). *Pleistocene stratigraphy of Illinois*. Urbana, IL: State of Illinois Dept. of Registration and Education.
- Winkler, M. G., Swain, A. M., & Kutzbach, J. E. (1986). Middle Holocene dry period in the northern Midwestern United States - lake levels and pollen stratigraphy. *Quaternary Research*, 25(2), 235-250.
- Winkler, M. G. (1988). Effect of climate on development of two sphagnum bogs in south-central Wisconsin. *Ecology*, 69(4), 1032-1043.

- Woodburn, T. L., Johnson, W. C., & Bozarth, S. R. (2011). High-resolution biosilicate analysis of the Pleistocene-Holocene transition: The Brady Soil, southwestern Nebraska [Abstract]. *8th International Meeting of Phytolith Researchers*, 59.
- Wright Jr., H. E., Winter, T. C., & Patten, H., L. (1963). Two pollen diagrams from southeastern Minnesota: Problems in the regional late-glacial and postglacial vegetational history. *Geological Society of America Bulletin*, 74(11), 1371-1396.
- Yamada, I., & Shoji, S. (1990). Heavy solution method for determination of volcanic glass content in tephra and tephra-derived soils. *Japanese Society of Soil Science and Plant Nutrition*, 36(3), 505-509.
- Zawacki, A. A., & Hausfater, G. (1969). *Early vegetation of the lower Illinois valley; a study of the distribution of floral resources with reference to prehistoric cultural-ecological adaptations*. Springfield, IL: Illinois Valley Archaeological Program.
- Zehetner, F. (2010). Does organic carbon sequestration in volcanic soils offset volcanic CO₂ emissions? *Quaternary Science Reviews*, 29(11-12), 1313-1316.
- Ziegler, K., Chadwick, O. A., Brzezinski, M. A., & Kelly, E. F. (2005). Natural variations of $\delta^{30}\text{Si}$ ratios during progressive basalt weathering, Hawaiian Islands. *Geochimica et Cosmochimica Acta*, 69(19), 4597-4610.
- Ziegler, S. S., Larson, E. R., Rauchfuss, J., & Elliott, G. P. (2008). Tree establishment during dry spells at an oak savanna in Minnesota. *Tree-Ring Research*, 64(1), 47-54.

APPENDIX 1. CHAPTER 2 SEDIMENT SAMPLE SEQUENTIAL LEACHING DATA.

Soil sample labels are depths in cm. WRG is White River Group. Concentrations are expressed as mg SiO₂ g⁻¹ dry sample weight. Data for diatomite and soil surface samples are the means, standard deviations (±), and coefficients of variation percentages (in parentheses) of three replicates.

		Time, Minutes									
Sample		30	60	90	120	150	180	210	240	270	300
<u>Sediments</u>	Silica gel	1043.34	1025.57	1017.68	1029.63	1021.75	1013.85	1010.46	1025.93	1014.52	1016.53
	Diatomite	444.08	623.38	717.02	756.00	784.98	797.53	798.81	790.25	791.02	800.68
		±5.63	±20.63	±35.23	±27.33	±23.15	±26.53	±21.69	±29.58	±9.87	±17.85
		(1.27)	(3.31)	(4.91)	(3.61)	(2.95)	(3.33)	(2.72)	(3.74)	(1.25)	(2.23)
	WRG	82.76	103.83	125.11	139.96	148.28	168.85	182.83	190.20	217.60	218.43
	Illite clay	21.10	32.28	41.42	50.58	61.16	76.04	84.45	97.03	106.85	116.68
<u>Soil 1</u>	Quartz sand	2.15	3.59	5.04	5.79	6.89	7.98	9.06	9.79	10.88	11.98
	5-10	63.98	83.14	96.12	103.96	110.31	117.65	125.01	133.28	136.93	141.00
		±1.47	±1.81	±1.11	±2.33	±2.53	±1.31	±2.29	±4.35	±1.11	±5.51
		(2.29)	(2.18)	(1.15)	(2.24)	(2.29)	(1.11)	(1.83)	(3.26)	(0.81)	(3.91)
	10-20	55.95	76.76	91.24	102.57	112.33	118.92	127.11	132.14	140.36	143.82
	20-30	59.40	83.19	101.12	110.20	119.29	128.41	134.58	140.77	146.96	147.25
	40-50	62.00	85.02	103.51	117.46	125.71	137.41	144.55	152.86	155.45	159.19
	0-10	43.36	57.84	67.62	74.73	81.04	86.33	90.43	95.76	98.67	101.61
		±0.63	±2.27	±1.09	±1.38	±2.43	±1.75	±2.32	±2.51	±2.54	±1.20
		(1.45)	(3.92)	(1.61)	(1.84)	(2.99)	(2.03)	(2.56)	(2.62)	(2.57)	(1.18)
	10-22	39.23	55.49	63.84	72.23	78.38	84.24	86.69	92.58	96.19	98.66
	22-35	39.00	54.68	65.81	73.93	80.54	88.40	93.20	99.55	101.28	106.10
	44-58	36.02	53.27	62.87	69.45	79.15	87.03	90.30	95.11	99.93	100.13
<u>Soil 2</u>	0-13	23.03	33.05	39.57	44.69	49.13	53.59	57.81	62.30	65.85	68.49
		±0.99	±1.70	±1.55	±1.44	±1.34	±1.14	±1.87	±1.17	±1.37	±0.58
		(4.27)	(5.14)	(3.93)	(3.22)	(2.74)	(2.13)	(3.23)	(1.88)	(2.07)	(0.85)
	13-20	23.34	35.65	43.89	49.42	56.33	60.52	64.73	70.30	75.89	78.76
	20-28	29.57	41.13	50.15	59.20	65.70	70.94	74.92	78.90	84.16	86.88
	28-50	46.72	67.34	82.53	92.27	102.03	107.71	114.77	121.84	124.81	127.80

APPENDIX 2. CHAPTER 2 SOIL SAMPLE [R_{rem}]_t DATA.

Data expressed as mg SiO₂ g⁻¹ dry soil weight. Precision data for surface samples are standard deviations (±), and coefficient of variation percentages (in parentheses) of three replicates.

	Depth, cm.	Time, Minutes									
		30	60	90	120	150	180	210	240	270	300
Soil 1	5-10	56.58 ±2.47 (4.37)	73.50 ±2.89 (3.94)	78.56 ±2.96 (3.76)	80.08 ±2.96 (3.70)	80.53 ±2.96 (3.68)	80.67 ±2.96 (3.67)	80.71 ±2.96 (3.66)	80.72 ±2.96 (3.66)	80.72 ±2.96 (3.66)	80.72 ±2.96 (3.66)
	10-20	46.29	65.81	74.03	77.50	78.96	79.58	79.84	79.95	80.00	80.02
	20-30	51.06	74.79	85.82	90.94	93.32	94.43	94.94	95.18	95.29	95.34
	40-50	51.78	76.88	89.04	94.94	97.80	99.19	99.86	100.18	100.34	100.42
Soil 2	0-10	37.01 ±0.55 (1.49)	50.88 ±1.18 (2.32)	56.08 ±1.76 (3.15)	58.04 ±2.10 (3.62)	58.78 ±2.27 (3.87)	59.06 ±2.35 (3.99)	59.17 ±2.39 (4.04)	59.21 ±2.41 (4.06)	59.22 ±2.41 (4.07)	59.23 ±2.41 (4.08)
	10-22	33.40	47.42	53.31	55.78	56.82	57.26	57.44	57.52	57.55	57.56
	22-35	32.08	46.31	52.62	55.41	56.65	57.20	57.44	57.55	57.60	57.62
	44-58	31.11	46.26	53.63	57.22	58.96	59.81	60.23	60.43	60.53	60.57
Soil 3	0-13	18.44 ±1.28 (6.96)	25.84 ±1.75 (6.78)	28.81 ±2.01 (6.99)	30.01 ±2.16 (7.20)	30.50 ±2.24 (7.33)	30.70 ±2.27 (7.40)	30.78 ±2.29 (7.44)	30.81 ±2.30 (7.45)	30.83 ±2.30 (7.46)	30.83 ±2.30 (7.46)
	13-20	18.53	26.70	30.31	31.91	32.61	32.92	33.06	33.12	33.15	33.16
	20-28	23.45	35.01	40.72	43.53	44.91	45.60	45.94	46.10	46.18	46.22
	28-50	39.24	59.20	69.34	74.50	77.12	78.45	79.13	79.47	79.65	79.74

APPENDIX 3. CHAPTER 2 SOIL SAMPLE RSi ESTIMATES.

Estimates are expressed as mg SiO₂ g⁻¹ dry soil weight. LE is linear extrapolation, while PM is power model. Precision data for surface samples are standard deviations ($\pm$), and coefficient of variation percentages (in parentheses) of three replicates.

	Depth, cm.	LE	PM
<u>Soil 1</u>	0-5	80.33 $\pm$ 2.52 (3.14)	80.73 $\pm$ 2.96 (3.66)
	10-20	80.5	80.03
	20-30	93	95.39
	40-50	96.62	100.49
<u>Soil 2</u>	0-10	61.18 $\pm$ 3.15 (5.15)	59.23 $\pm$ 2.42 (4.08)
	20-30	58.79	57.57
	22-35	57.82	57.64
	44-58	60.15	60.62
<u>Soil 3</u>	0-13	29.94 $\pm$ 2.04 (6.82)	30.84 $\pm$ 2.30 (7.47)
	13-20	32.65	33.17
	20-28	44.87	46.26
	28-50	76.38	79.83

APPENDIX 4. CHAPTER 2 DATA POINT EXPERIMENT RESULTS.

RSi data is expressed mg SiO₂ g⁻¹ dry soil weight. Data are the means, standard deviations ($\pm$), and coefficient of variation percentages (in parentheses) of 500 bootstrap iterations.

Bootstrap relations.

		Number of Data Points			
Depth, cm.		6	5	4	3
Soil 1	5-10 R1	78.80 ±6.29 (7.99)	79.43 ±7.50 (9.45)	79.79 ±11.90 (14.91)	82.27 ±18.23 (22.16)
	5-10 R2	83.81 ±3.67 (4.38)	83.59 ±4.35 (5.21)	83.60 ±5.75 (6.88)	85.85 ±11.05 (12.88)
	5-10 R3	83.60 ±7.60 (9.09)	78.80 ±6.29 (7.99)	84.77 ±10.87 (12.83)	86.81 ±17.43 (20.08)
	10-20	82.04 ±3.53 (4.30)	81.68 ±3.09 (3.78)	82.57 ±5.32 (6.45)	84.30 ±10.83 (12.85)
	20-30	95.10 ±6.88 (7.24)	94.47 ±7.85 (8.31)	95.53 ±10.19 (10.66)	96.79 ±14.22 (14.69)
	40-50	99.57 ±8.52 (8.56)	98.52 ±9.85 (10.00)	99.53 ±12.26 (12.32)	102.05 ±17.54 (17.19)
Soil 2	0-10 R1	58.12 ±4.63 (7.97)	58.83 ±6.31 (10.72)	58.99 ±7.38 (12.51)	60.12 ±10.38 (17.27)
	0-10 R2	61.38 ±0.97 (1.57)	61.40 ±1.30 (2.11)	61.51 ±2.71 (4.40)	62.18 ±5.75 (9.24)
	0-10 R3	64.32 ±3.70 (5.75)	64.29 ±3.56 (5.54)	64.78 ±5.41 (8.35)	65.65 ±8.40 (12.80)
	10-22	58.75 ±2.32 (3.95)	58.91 ±3.10 (5.26)	58.97 ±4.44 (7.52)	59.64 ±7.05 (11.81)
	22-35	58.28 ±4.29 (7.36)	59.02 ±5.72 (9.68)	58.68 ±7.23 (12.32)	60.12 ±10.68 (17.76)
	44-58	60.30 ±4.95 (8.21)	60.23 ±5.36 (8.90)	60.63 ±7.30 (12.04)	61.38 ±10.62 (17.31)
Soil 3	0-13 R1	29.97 ±2.08 (6.94)	30.04 ±2.20 (7.32)	30.43 ±3.94 (12.96)	31.06 ±6.34 (20.41)
	0-13 R2	29.82 ±1.20 (4.04)	30.13 ±2.77 (9.19)	30.29 ±3.59 (11.87)	29.61 ±5.64 (19.05)
	0-13 R3	33.67 ±2.76 (8.19)	33.79 ±3.42 (10.12)	34.16 ±4.69 (13.73)	35.26 ±7.02 (19.90)
	13-20	33.05 ±1.49 (4.52)	33.23 ±2.13 (6.41)	33.24 ±3.71 (11.16)	34.32 ±6.63 (19.32)
	20-28	45.72 ±1.35 (2.96)	45.86 ±2.43 (5.30)	45.93 ±3.11 (6.76)	46.67 ±5.79 (12.40)
	28-50	78.03 ±4.85 (6.21)	77.95 ±6.27 (8.04)	78.95 ±8.40 (10.64)	79.02 ±10.86 (13.75)

5a. 8G00 soil description.**Date Collected:** 2000**Location:** 41.51386°N, 99.45303°W**Topography:** Upland, flat**Land Use/Vegetation:** Mixed grass steppe, used as pasture, never plowed**Method:** Hydraulic push corer

Horizon	Depth, cm	Description
A1	0-24	7.5YR 3/1, sil, 1 f sbk ptg. to 1 f gr, ns, c, eo.
A2	24-45	7.5YR 3/1, sil, 1 f sbk ptg. to 2 f gr, ns, c, eo.
A1b	56-55	7.5YR 2/1, sicl, 2 f sbk, ns, c, eo.
A2b	55-71	10YR 2/1, sil, 3 f sbk, ns, c, eo.
ABb	71-81	10YR 4/2, sil, 2 f sbk, ns, c, eo. Common thin patchy 10YR 3/1 coatings on ped faces.
Bt1b	81-90	10YR 4/2, sicl, 2 f pr ptg. to 2 f sbk, ns, c, eo. Common thin patchy 10YR 3/2 coatings on ped faces.
Bt2b	90-100	2.5Y 5/3, sil, 1 m pr ptg. to 2 m sbk, ns, c, eo. Common 2.5Y 4/2 coatings on ped faces.
BCb	100-132	2.5Y 5/3, sil, 1 m sbk, ns, c, eo. Few fine 10YR 5/6 primary mottles. Few fine 2.5YR 5/2 secondary mottles.
BCKb	132-197	2.5Y 5/3, sil, 1 m sbk, ns, c, e. Common fine carbonate threads. Common fine 10 YR 5/6 primary mottles. Few fine 2.5Y 5/2 secondary mottles.
CKb	197-305	2.5Y 5/3, sil, 1 m sbk, ns, c, e. Few medium carbonate threads. Common fine 2.5Y 5/2 primary mottles. Common fine 7.5YR 5/6 secondary mottles.

5b. 5G00 soil description.**Date Collected:** 2000**Location:** 40.36506°N, 98.69125°W**Topography:** Upland, flat**Land Use/Vegetation:** Mixed grass steppe, used as pasture, never plowed**Method:** Hydraulic push corer

Horizon	Depth, cm	Description
A	0-53	10YR 2/1, sil, 1 m sbk ptg. to 3 f gr, ns, g, eo.
AB	53-64	10YR 3/1, sil, 2 f sbk ptg. to 2 f gr, ns, c, eo.
A1b	64-76	10YR 3/1, siel, 2 c sbk, ptg. to 2 f sbk, ns, g, eo.
A2b	76-90	2.5Y 4/1, sic, 2 f pr ptg. to 3 f sbk, ns, c, eo.
ABb	90-99	2.5Y 4/2, sic, 2 m sbk, ns, c, eo. Many thin patchy 2.5Y 4/1 coatings on ped faces.
Btb	99-112	5Y 5/2, siel, 2 m sbk, ns, a, eo. Common thin patchy 2.5Y 4/1 coatings on ped faces.
Bk1b	112-135	5Y 5/2, sil, 2 f pr ptg. to 2 f sbk, ns, c, e. Many coarse carbonates.
Bk2b	135-159	5Y 5/2, sil, 2 m sbk, ns, c, e. Few thick continuous 5Y 5/2 coatings on ped faces. Common fine carbonate threads. Few fine 10YR 4/6 mottles.
C	159-207	5Y 5/2, sil, 1 m sbk, ns, c, e. Few fine carbonate threads. Few fine 7.5YR 4/6 mottles.

5c. 3GOO soil description.

Date Collected: 2000

Location: 40.88703°N, 97.00947°W

Topography: Upland, flat

Land Use/Vegetation: Alfalfa field, 100-140 yr of cultivation

Method: Hydraulic push corer

Horizon	Depth, cm	Description
Ap	0-16	7.5YR 2/1, sicl, 1 m sbk ptg. to 1 f sbk, ns, c, eo.
Ap	16-27	10YR 2/1, sicl, 2 f sbk ptg. to 2 f gr, ns, c, eo.
AB	27-43	10YR 4/2, sicl, 2 f sbk ptg. to 2 f gr, ns, c, eo. Many thin continuous 2.5Y 3/1 coatings on ped faces.
Bt1	43-64	2.5Y 4/2, ,sic, 2 f pr ptg. to 3 f sbk, ns, g, eo. Many thin continuous 2.5Y 3/1 coatings on ped faces. Few fine 7.5YR 5/6 mottles.
Bt2	64-93	2.5Y 5/2, sic, 3 f pr ptg. to 3 m sbk, ns, g, eo. Many thin continuous 2.5Y 4/2 coatings on ped faces. Few fine 7.5YR 4/6 mottles.
Bt3	93-106	2.5Y 5/2, sic, 2 m pr ptg. to 2 m sbk, ns, c, eo. Many thin patchy 2.5Y 4/2 coatings on ped faces. Common medium 5YR 4/4 mottles.
BC1	106-133	5Y 5/2, sicl, 2 m pr ptg. to 1 m sbk, ns, g, eo. Few thin patchy 2.5Y 5/2 coatings on ped faces. Common medium 5YR 4/6 mottles.
BC2	133-195	5Y 6/1, sil, 1 m pr ptg. to 1 m sbk, ns, c, eo. Few thick patchy 5Y 5/1 coatings on ped faces. Many fine 7.5YR 4/6 mottles.
Ck	195-256	5Y 6/1, sil, 1 m sbk, ns, c, e. Few thin patchy 5Y 5/1 coatings on ped faces. Common fine carbonate threads. Many fine 7.5YR 4/6 mottles.

5d. AL2 soil description.**Date Collected:** September 13, 2009**Location:** 43.67595°N, 91.42888°W**Topography:** Upland, flat**Land Use/Vegetation:** Hardwood forest, selective harvesting in 1960s**Method:** Soil pit

Horizon	Depth, cm	Description
A	0-9	10YR 3/1, si, 1 f gr, ns, c, eo.
E/A	9-20	10YR 5/2 & 10YR 3/1, si, 1 f pl ptg. to 1 f gr, ns, g, eo.
E	20-33	10YR 5/2, sil, 1 f pl, ns, g, eo.
BE	33-47	10YR 4/3, sil, 1 m sbk & 1 f pl, ns, g, eo.
Bt1	47-57	10YR 4/4, sicl, 1 m sbk, ns, g, eo. Common mod. thick patchy 10YR 4/3 5/6 coatings on ped faces.
Bt2	57-73	10YR 4/4, sil, 1 m sbk, ns, g, eo. Common mod. thick 10YR 5/6 coatings on ped faces. Few fine 10YR 4/3 coatings in pores.
Bt3	73-94	10YR 4/4, sil, 1 m sbk, ns, g, eo. Common mod. thick 10YR 6/4 coatings on ped faces. Few moderate 7.5YR 5/6 mottles.
Bt4	94-114	10YR 4/3, sicl, 2 c sbk, ns, g, eo. Common mod. thick continuous 10YR 6/4 coatings on ped faces. Few thin 10YR 2/1, pore infillings. Few moderate 7.5YR 4/6 mottles.
Bt5	114-135	10YR 4/4, sil, 1 m-c sbk, ns, g, eo. Few mod. thin patchy 10YR 6/4 coatings on ped faces. Few mod. thin patchy 10YR 4/3 coating on ped faces and pores. Few moderate 7.5YR 4/6 mottles.
BC	135-161	10YR 4/4, sil, 1 m-c sbk, ns, a, eo. Few thin mod. patchy 10YR 4/3 coatings on ped faces. Common moderate 7.5YR 5/6 mottles.
C1	161-345	10YR 4/4, sil, 1 m-c sbk, ns, g, eo (above 200 cm). Common moderate layering of 7.5YR 5/6 & 10YR 7/2 mottles/masses. Few fine 10YR 3/1 masses.

5e. KO1 soil description.

Date Collected: November 5, 2009

Location: 43.54874°N, 91.49104°W

Topography: Upland, flat

Land Use/Vegetation: Corn field, harvested

Method: Soil pit

Horizon	Depth, cm	Description
Ap	0-17	10YR 2/1, sil, 1 c sbk ptg. to 1 f gr, ns, c, eo. Sand and manure applied by landowner.
A	17-31	10YR 2/1, sil, 1-2 c sbk ptg. to 1 fgr, ns, c, eo.
A/B	31-41	10YR 2/1 & 4/3, 1 c sbk ptg. to 1 fgr, ns, g, eo.
BA	41-52	10YR 4/3, few 10YR 2/1 aggregates, siel, 1 c sbk ptg. to 1 f gr, ns, g, eo. Few faint patchy 10YR 6/4 coating on ped faces.
Bt1	52-72	10YR 4/3, siel, 1 m-c sbk ptg. to 1 fgr, ns, g, eo. Common mod. thick patchy 10YR 6/4 coating on ped faces & pores. Few 10YR 3/1 root fillings.
Bt2	72-91	10YR 4/3, siel, 1 m-c sbk ptg. to 1 fgr, ns, g, eo. Common thick nearly continuous 10YR 6/4 coating on ped faces & pores. Few moderate patchy 10YR 4/3 coatings on ped faces. Few 10YR 3/1 root fillings.
Bt3	91-118	10YR 4/4, sil, 1 c sbk, ns, g, eo. Many thick nearly continuous 10YR 6/4 coating on ped faces & pores. Few moderate patchy 10YR 4/3 coatings on ped faces. Few 10YR 3/1 root fillings.
Bt4	118-140	10YR 4/4, sil, 1 m-c sbk, ns, g, eo. Common thick patchy 10YR 7/3 coatings on ped faces. Common moderate thin nearly continuous 10YR 3/2 coatings on ped faces. Few faint 7.5YR 5/6 mottles (near bottom of horizon).
BC	140-154	10YR 4/4, sil, 1 m-c sbk, ns, g, eo. Common moderate thin nearly discontinuous 10YR 3/2 coatings on ped faces. Few thin 10YR 4/3 coatings in pores. Few fine 7.5YR 5/6 mottles.
C1	154-200	10YR 4/4, sil, 1 m-c sbk ptg. to ma, ns, g, eo. Few thin patchy 10YR 5/4 coatings on ped faces. Few 10YR 4/3 coatings in pores. Common moderate layered 7.5YR 6/4 masses.

5F. KA soil description.**Date Collected:** 2008**Location:** 43.17276°N, 89.18855°W**Topography:** Upland, flat, loess over till**Land Use/Vegetation:** Corn field, harvested**Method:** Hydraulic push corer

Horizon	Depth, cm	Description
Ap	0-20	10YR 2/1, sil, 1 f sbk ptg. to 2 f gr, ns, c, eo.
A	20-29	10YR 3/1, sil, 1 f pl ptg. to 2 f gr, ns, g, eo.
AB	29-35	10YR 3/2, sil, 2 f sbk, ns, c, eo. Many thin patchy 10YR 3/1 coatings on ped faces.
Bt1	35-54	10YR 4/4, sil, 2 f sbk, ns, g, eo. Many thin patchy 10YR 4/3 coatings on ped faces. Few burrow fills.
Bt2	54-92	10YR 4/4, sil, 1 m sbk ptg. to 2 f sbk, ns, g, eo. Common moderate thick patchy 10YR 4/3 coatings on ped faces.
Bt3	92-112	10YR 5/4, sil, 1 m sbk ptg. to 1 f sbk, ns, g, eo. Common thin patchy 10YR 4/3 coatings on ped faces.
BC	112-146	10YR 5/4, sil, 1 m sbk, ns, c, eo. Few thin patchy 10YR 4/4 coatings on ped faces.
C	146-184	10YR 6/4, sil, 1 m sbk, ns, c, e.

5g. TQ soil description.**Date Collected:** 1996**Location:** 39.52555°N, 90.51361°W**Topography:** Upland, flat**Land Use/Vegetation:** Hardwood forest, possibly logged**Method:** Hydraulic push corer

Horizon	Depth, cm	Description
A	0-13	10YR 4/2-3/2, sil, 1 f sbk ptg. to 1 vf gr, vfr, a, eo.
E	13-20	10YR 5/3, sil, 2 f & m sbk, fr, c, eo.
BE	20-28	9YR 5/4, sil, 2 f & m sbk, fr, c, eo. 10YR 5/3 silans.
Bt1	28-50	10YR 4/4, siel, 3 m & f sbk, fi, g, eo. Many thin continuous 10YR 4/4 coatings on ped faces.
Bt2	50-80	10YR 4/4, siel, 2 f pr ptg. to 2 m sbk, fi, g, eo. Many thin continuous 9YR 4/4 coatings on ped faces. Few fine distinct mangans.
Bt3	80-114	10YR 5/6, sil, 1 f pr ptg. to 2 m sbk, fr, g, eo. Many thick patchy 9YR 4/4 coatings on ped faces.
Bt4	114-134	10YR 5/6, sil, 1-2 m sbk, fr, c, eo. Common thin patchy 9YR 4/4 coatings on ped faces.
BC	134-172	10YR 5/6, sil, 1 m-c sbk, fr, a, eo. Few thin patchy 9YR 4/4 coatings on ped faces.
C1	172-208	10YR 6/4, sil, v1 c sbk, fr, c, eo. Few fine carbonate nodules.

APPENDIX 6. CHAPTER 3 DATA SETS

6a. 8G00 data set. All measurements expressed as mg g⁻¹ except pH.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extract. RSi	Particle Size		Organic Carbon	pH
	<i>Total</i>	<i>Clay- Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
0-5	78.50	26.74	51.77	34.67	17.10	0.21	-	-	-	5.36
5-10	82.39	-	-	-	-	-	205.23	794.80	15.35	5.77
	83.25	-	-	-	-	-	-	-	-	-
	84.04	-	-	-	-	-	-	-	-	-
10-20	85.88	-	-	-	-	-	-	-	-	-
20-30	93.24	73.57	19.67	14.08	5.58	0.19	250.90	749.10	13.60	5.96
30-40	103.01	-	-	-	-	-	290.91	709.10	10.78	-
40-50	95.55	44.24	51.31	13.26	38.05	0.25	330.30	669.70	9.70	6.46
50-60	-	-	-	-	-	-	321.44	678.60	6.35	-
60-70	96.93	-	-	-	-	-	-	-	-	6.72
70-80	82.42	66.00	16.42	6.66	9.77	0.33	290.79	709.20	5.14	6.24
80-90	86.23	-	-	-	-	-	270.67	729.30	3.32	6.46
90-100	93.33	77.64	15.68	6.77	8.91	0.79	260.87	739.10	3.79	6.35
100-110	-	-	-	-	-	-	-	-	-	6.24
110-120	69.39	-	-	-	-	-	210.64	789.40	3.32	8.12
120-130	-	-	-	-	-	-	-	-	-	8.11
130-140	68.45	-	-	-	-	-	164.04	836.00	3.93	-
150-160	64.11	-	-	-	-	0.55	168.81	831.20	2.58	8.38
160-170	68.09	-	-	-	-	-	-	-	-	-
180-190	-	-	-	-	-	-	175.98	824.00	3.32	8.16
190-200	80.25	61.29	18.96	8.66	10.30	0.43	-	-	-	8.54

¹Data collected by J. Mason and P. Jacobs.

6b. 5G00 data set. All measurements expressed as mg g⁻¹ except pH.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extract. RSi	Particle Size ¹		Organic Carbon ¹	pH
	<i>Total</i>	<i>Clay-Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
0-5	71.32	20.44	50.88	29.99	20.89	0.23	-	-	-	5.45
5-10	65.36	-	-	-	-	-	-	-	-	-
10-20	65.32	-	-	-	-	-	209.62	790.40	11.79	6.25
20-30	76.29	49.66	26.62	12.65	13.97	0.32	223.44 ²	762.73 ²	10.49 ²	6.27
30-40	78.24	-	-	-	-	-	-	-	-	-
40-50	72.99	53.04	19.94	13.38	6.56	0.45	251.07	748.90	9.84	6.35
50-60	77.67	-	-	-	-	-	289.28	710.70	6.14	6.45
60-70	87.28	-	-	-	-	-	-	-	-	-
70-80	80.22	76.88	3.35	1.44	1.91	0.82	430.84	569.20	6.95	6.64
80-90	77.89	-	-	-	-	-	380.57	619.40	4.60	6.76
90-100	86.35	79.16	7.20	3.50	3.69	0.75	357.22	642.80	3.86	6.78
100-110	-	-	-	-	-	-	355.97	644.00	2.32	6.85
110-120	83.33	-	-	-	-	-	-	-	-	-
120-130	-	-	-	-	-	-	313.00	687.00	1.58	7.08
130-140	72.70	-	-	-	-	-	-	-	-	-
140-150	-	-	-	-	-	-	291.68	708.30	1.24	-
150-160	71.43	-	-	-	-	0.44	-	-	-	-
170-180	79.88	-	-	-	-	-	280.18	719.80	0.43	8.06
190-200	74.93	59.26	15.68	6.37	9.30	0.45	267.86	732.10	0.70	7.55

¹Data collected by J. Mason and P. Jacobs.

²Interpolated.

6c. 3G00 data set. All measurements expressed as mg g⁻¹ except pH.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extract. RSi	Particle Size ¹		Organic Carbon ¹	pH
	<i>Total</i>	<i>Clay- Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
0-5	72.42	51.01	21.40	15.24	6.16	0.51	281.54	718.50	15.14	6.58
5-10	78.61	-	-	-	-	-	-	-	-	-
10-20	84.86	-	-	-	-	-	-	-	-	6.08
20-30	86.30	82.00	4.30	3.12	1.18	0.38	341.84	658.20	12.05	5.57
30-40	84.19	-	-	-	-	-	356.76	643.20	9.17	5.90
40-50	83.54	81.85	1.70	0.82	0.88	0.61	-	-	-	5.76
50-60	79.06	-	-	-	-	-	405.01	595.00	6.35	6.02
70-80	67.66	64.60	3.06	1.41	1.65	0.63	371.24	628.80	2.65	6.28
90-100	74.29	66.32	7.97	3.59	4.38	0.90	348.19	651.80	1.64	6.49
110-120	68.19	-	-	-	-	-	329.10	670.90	1.44	6.86
130-140	-	-	-	-	-	-	-	-	-	6.84
140-150	59.82	-	-	-	-	0.61	310.80	689.20	2.25	6.78
170-180	61.98	-	-	-	-	-	317.84	682.20	2.92	7.22
190-200	66.99	56.06	10.93	5.96	4.97	0.84	305.19	694.80	0.37	7.56

¹Data collected by J. Mason and P. Jacobs.

6d. AL2 data set. All measurements expressed as mg g⁻¹ except pH.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extract. RSi	Particle Size		Organic Carbon	pH
	<i>Total</i>	<i>Clay- Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
0-9	35.92	26.45	9.47	6.61	2.86	0.22	100.68	899.32	43.50	6.07
9-20	38.02	-	-	-	-	-	105.86	894.14	19.51	5.81
20-33	46.23	36.93	9.30	5.18	4.12	0.18	142.18	857.82	8.28	5.38
33-47	49.85	-	-	-	-	-	194.15	805.85	9.65	4.98
47-57	51.37	46.17	5.21	2.64	2.56	0.39	272.82	727.18	9.03	4.93
57-73	57.64	-	-	-	-	-	266.74	733.26	10.65	4.89
73-85	63.81	61.50	2.31	0.17	2.14	0.51	277.29	722.71	16.07	4.87
85-94	59.33	-	-	-	-	-	287.71	712.29	-	-
94-114	65.13	62.49	2.64	0.15	2.48	0.50	275.94	724.06	10.71	5.01
115-125	49.53	-	-	-	-	-	234.72	765.28	9.07	5.10
125-135	51.61	-	-	-	-	-	240.59	759.41	9.47	5.19
135-145	52.73	-	-	-	-	-	235.22	764.78	-	-
150-160	49.34	-	-	-	-	0.41	224.51	775.49	9.43	5.33
165-175	62.30	-	-	-	-	-	241.05	758.95	9.92	5.38
175-185	71.02	-	-	-	-	-	120.70	879.30	-	-
200-210	43.13	34.92	8.21	0.24	7.97	0.54	203.87	796.13	7.52	5.95

6e. KO1 data set. All measurements expressed as mg g⁻¹ except pH.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extract. RSi	Particle Size		Organic Carbon	pH
	<i>Total</i>	<i>Clay- Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
0-8	49.88	39.82	10.06	8.86	1.20	0.48	195.76	804.24	27.23	7.44
	48.37	36.43	11.93	9.85	2.09	0.52	-	-	-	-
	50.14	36.88	13.26	10.41	2.85	0.50	-	-	-	-
	-	-	-	-	-	0.52	-	-	-	-
	-	-	-	-	-	0.51	-	-	-	-
	-	-	-	-	-	0.52	-	-	-	-
	-	-	-	-	-	0.53	-	-	-	-
8-17	55.70	-	-	-	-	0.56	219.88	780.12	28.83	7.40
17-24	64.13	-	-	-	-	-	231.28	768.72	26.55	7.35
24-31	77.43	64.22	13.20	11.88	1.33	0.68	255.02	744.98	25.79	7.17
31-41	67.83	-	-	-	-	0.68	283.51	716.49	19.16	-
41-52	66.75	63.67	3.08	2.56	0.52	0.73	279.85	720.15	17.43	6.89
52-62	63.49	-	-	-	-	-	327.44	672.56	14.43	6.72
62-72	53.19	-	-	-	-	-	-	-	-	-
72-81	51.47	49.50	1.97	0.62	1.35	0.82	289.47	710.53	11.41	6.47
81-91	53.86	-	-	-	-	-	282.88	717.12	-	6.19
91-104	-	-	-	-	-	-	-	-	-	-
104-118	53.70	50.77	2.94	0.21	2.73	0.69	260.04	739.96	-	5.71
118-130	49.71	-	-	-	-	-	-	-	7.70	5.72
130-140	46.54	-	-	-	-	-	238.60	761.40	-	-
140-154	51.81	-	-	-	-	0.83	240.78	759.22	6.98	5.74
154-170	58.38	-	-	-	-	-	267.90	732.10	6.86	
170-188	74.80	-	-	-	-	-	265.17	734.83	9.12	5.72
188-200	-	-	-	-	-	-	-	-	-	
200-210	58.93	49.87	9.06	0.80	8.25	0.59	269.20	730.80	8.94	5.70

6f. KA data set. All measurements expressed as mg g⁻¹ except pH.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extract. RSi	Particle Size		Organic Carbon	pH
	<i>Total</i>	<i>Clay- Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
0-5	75.68	57.78	17.90	17.36	0.54	0.40	220.42	779.58	23.93	6.27
5-10	76.62	-	-	-	-	-	-	-	-	6.21
10-20	74.28	-	-	-	-	-	-	-	-	-
20-30	65.59	55.57	10.02	9.59	0.43	0.27	233.43	766.57	21.28	5.13
30-40	52.22	-	-	-	-	-	225.93	774.07	16.38	4.97
40-50	55.28	53.86	1.42	1.24	0.18	0.35	250.49	749.51	12.38	4.98
60-70	48.57	-	-	-	-	-	249.41	750.59	10.05	4.98
70-80	58.95	57.63	1.32	0.83	0.48	0.46	250.77	749.23	7.60	5.06
80-90	50.83	-	-	-	-	-	-	-	-	-
90-100	50.00	48.34	1.66	1.17	0.49	0.51	231.48	768.52	6.38	5.52
100-110	42.85	-	-	-	-	-	-	-	-	5.16
120-130	34.19	-	-	-	-	-	189.27	810.73	5.80	5.59
140-150	33.87	-	-	-	-	0.54	152.19	847.81	4.16	6.82
150-160	-	-	-	-	-	-	120.68	879.32	3.83	7.52
160-170	28.72	-	-	-	-	-	-	-	-	-
170-180	-	-	-	-	-	-	119.99	880.01	3.11	7.63
180-190	22.48	-	-	-	-	-	105.28	894.72	-	-
189	-	-	-	-	-	-	76.22	923.78	2.65	7.66
190-200	10.68	7.53	3.16	1.96	1.19	0.55	58.66	941.34	-	7.82

6g. TQ data set. All measurements expressed as mg g⁻¹ except pH.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extract. RSi	Particle Size		Organic Carbon	pH
	<i>Total</i>	<i>Clay- Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
0-13	35.75	21.33	14.43	13.72	0.71	0.38	155.45	844.55	24.65	6.30
	30.42	-	-	-	-	-	-	-	-	-
	32.77	-	-	-	-	-	-	-	-	-
13-20	34.56	-	-	-	-	-	183.89	816.11	11.21	6.20
20-28	46.45	34.96	11.48	10.87	0.61	0.30	235.07	764.93	10.44	6.06
28-50	79.91	76.59	3.32	2.89	0.42	0.44	385.37	614.63	13.17	5.21
50-80	63.37	61.91	1.46	1.26	0.20	0.56	357.27	642.73	12.64	5.09
80-114	49.44	46.71	2.72	1.70	1.02	0.53	273.15	726.85	11.95	5.18
114-134	32.00	-	-	-	-	-	232.11	767.89	10.30	5.38
134-172	22.41	-	-	-	-	0.43	153.02	846.98	8.35	5.59
172	11.14	-	-	-	-	-	82.71	917.29	5.96	7.59
185	12.60	10.92	1.68	0.51	1.17	0.56	82.25	917.75	5.73	8.40

Texture		Structure		Moist Consistence	
si	Silt	1	Weak	ns	Not specified
sicl	Silty clay loam	2	Moderate	fr	Friable
sil	Silt loam	3	Firm	vfr	Very friable
		f	Fine		
		m	Medium		
		c	Coarse	a	Abrupt
		gr	Granular	c	Clear
		pl	Platy	g	Gradual
		pr	Prismatic		
		sbk	Subangular blocky		
				Effervescence	
				eo	No effervescence

7a. KL1 soil description.**Date Collected:** November 6, 2009**Location:** 43.65828°N, 91.50847°W**Topography:** Upland, flat**Land Use/Vegetation:** Corn field, not harvested**Method:** 30 mm soil probe

Horizon	Depth, cm	Description
Ap	0-17	10YR 3/1, sil, 1 f gr, ns, a, eo.
A	17-27	10YR 3/1, few 10YR 4/3 aggregates, sil, 1 m sbk ptg. to 1 f gr, ns, c, eo. Few thin v. patchy 10YR 6/4 coatings on ped faces.
AB	27-44	10YR 3/1 & 4/3, sil, 1 m sbk ptg. To 1 f gr, ns, g, eo. Few thin faint v. patchy 10YR 6/4 coatings on ped faces.
Bt1	44-55	10YR 4/3, sil, 1 c sbk ptg. to 1 f gr, ns, g, eo. Few mod. thin patchy 10YR 6/4 on ped faces.
Bt2	55-75	10YR 4/3, siel, 1 c sbk ptg. to 1 m gr, ns, g, eo. Common mod. thick 10YR 7/3 coatings on ped faces.
Bt3	75-101	10YR 4/3, siel, 1-2 c sbk, ns, g, eo. Many thick continuous 10YR 7/3 coatings on ped faces. Few fine 7.5YR 4/4 mottles.

7b. KL3 soil description.**Date Collected:** November 7, 2009**Location:** 43.66176°N, 91.50729°W**Topography:** Upland, nearly flat**Land Use/Vegetation:** Edge of corn field, not harvested**Method:** 30 mm soil probe

Horizon	Depth, cm	Description
Ap1	0-5	10YR 3/2 sil, 1 f gr, c, ns, eo.
Ap2	5-25	10YR 3/2 sil, 1 f gr, ns, c, eo.
B/A	25-32	10YR 4/3 & 3/2, sil, 1 f sbk ptg. to 1 f gr, ns, a, eo. Common mod. thick discontinuous 10YR 6/4 coatings on ped faces.
BA	32-39	10YR 4/3, few 10YR 3/2 aggregates, sil, 1 m-c sbk ptg. to 1 f gr, ns, g, eo. Thick discontinuous 10YR 6/4 coatings on ped faces.
Bt1	39-56	10YR 4/3, sil, 1 m-c sbk ptg. to 1 f gr, ns, g, eo. Common mod. thick patchy 10YR 7/3 coatings on ped faces.
Bt2	56-74	10YR 4/3, sil, 1 m sbk ptg. to 1 f gr, ns, g, eo. Common thick discontinuous 10YR 7/3 coatings on ped faces and pores.
Bt3	74-82	10YR 4/3, siel, 1-2 c sbk, ns, g, eo. Common thick discontinuous 10YR 7/3 & 10YR 3/2 coatings on ped faces and pores. Few fine 7.5YR 4/6 mottles.
Bt4	82-102	10YR 4/3, siel, 1 c sbk, ns, g, eo. Common mod. thick discontinuous 10YR 7/3 & 3/2 coatings on ped faces. Few-common fine 7.5YR 4/6 mottles.

7c. KO1 soil description.**Date Collected:** November 5, 2009**Location:** 43.54874°N, 91.49104°W**Topography:** Upland, flat**Land Use/Vegetation:** Corn field, harvested**Method:** Soil pit

Horizon	Depth, cm	Description
Ap	0-17	10YR 2/1, sil, 1 c sbk ptg. to 1 f gr, ns, c, eo.
A	17-31	10YR 2/1, sil, 1-2 c sbk ptg. to 1 fgr, ns, c, eo.
A/B	31-41	10YR 2/1 & 4/3, 1 c sbk ptg. to 1 fgr, ns, g, eo.
BA	41-52	10YR 4/3, few 10YR 2/1 aggregates, sicl, 1 c sbk ptg. to 1 f gr, ns, g, eo. Few faint patchy 10YR 6/4 coating on ped faces.
Bt1	52-72	10YR 4/3, sicl, 1 m-c sbk ptg. to 1 fgr, ns, g, eo. Common mod. thick patchy 10YR 6/4 coating on ped faces & pores. Few 10YR 3/1 root fillings.
Bt2	72-91	10YR 4/3, sicl, 1 m-c sbk ptg. to 1 fgr, ns, g, eo. Common thick nearly continuous 10YR 6/4 coating on ped faces & pores. Few moderate patchy 10YR 4/3 coatings on ped faces. Few 10YR 3/1 root fillings.
Bt3	91-118	10YR 4/4, sil, 1 c sbk, ns, g, eo. Many thick nearly continuous 10YR 6/4 coating on ped faces & pores. Few moderate patchy 10YR 4/3 coatings on ped faces. Few 10YR 3/1 root fillings.

7d. NL soil description.**Date Collected:** September 8, 2008**Location:** 43.60153°N, 91.55448°W**Topography:** Upland, flat**Land Use/Vegetation:** Hay field, harvested**Method:** Hydraulic push corer

Horizon	Depth, cm	Description
Ap1	0-11	10YR 2/1, sil, 1 g gr, ns, c, eo.
Ap2	11-27	10YR 2/1, sil, 1 m sbk, ns, c, eo. Compacted.
A	27-37	10YR 3/1, sil, 1 f sbk, ptg. to 1 f gr, ns, g, eo.
BA	37-50	10YR 3/3, sil, 1 f sbk, ptg. to 1 f gr, ns, g, eo.
Bt1	50-70	10YR 4/4, sicl, 3 f sbk, ns, g, eo. Common mod. thick patchy 10YR 3/3 coatings on ped faces.
Bt2	70-93	10YR 4/4, sicl, 2 f sbk, ns, g, eo. Common mod. thick patchy 10YR 4/3 coatings on ped faces.
Bt3	93-110	10YR 4/4, sicl, 2 f sbk, ns, g, eo. Common thin patchy 10YR 4/3 coatings on ped faces.

7e. AL2 soil description.**Date Collected:** September 13, 2009**Location:** 43.67595°N, 91.42888°W**Topography:** Upland, flat**Land Use/Vegetation:** Hardwood forest, selective harvesting in 1960s**Method:** Soil pit

Horizon	Depth, cm	Description
A	0-9	10YR 3/1, si, 1 f gr, ns, c, eo.
E/A	9-20	10YR 5/2 & 10YR 3/1, si, 1 f pl ptg. to 1 f gr, ns, g, eo.
E	20-33	10YR 5/2, sil, 1 f pl, ns, g, eo.
BE	33-47	10YR 4/3, sil, 1 m sbk & 1 f pl, ns, g, eo.
Bt1	47-57	10YR 4/4, sicl, 1 m sbk, ns, g, eo. Common mod. thick patchy 10YR 4/3 & 5/6 coatings on ped faces.
Bt2	57-73	10YR 4/4, sil, 1 m sbk, ns, g, eo. Common mod. thick 10YR 5/6 coatings on ped faces. Few fine 10YR 4/3 coatings in pores.
Bt3	73-94	10YR 4/4, sil, 1 m sbk, ns, g, eo. Common mod. thick 10YR 6/4 coatings on ped faces. Few moderate 7.5YR 5/6 mottles.
Bt4	94-114	10YR 4/3, sicl, 2 c sbk, ns, g, eo. Common mod. thick continuous 10YR 6/4 coatings on ped faces. Few thin 10YR 2/1 coatings in pores. Few moderate 7.5YR 4/6 mottles.

7f. CA soil description.**Date Collected:** September 8, 2008**Location:** 43.71123°N, 91.44581°W**Topography:** Upland, flat**Land Use/Vegetation:** Pasture (previously tilled)**Method:** Hydraulic push corer

Horizon	Depth, cm	Description
Ap	0-16	10YR 4/2, sil, 1 f sbk ptg. to 1 f gr, ns, c, eo.
AB	16-26	10YR 4/2 & 4/3, sil, 2 f sbk, ns, c, eo.
Bt1	26-36	10YR 4/4, sicl, 2 f sbk, ns, c, eo. Many mod. thick to thick patchy 10YR 4/3 coatings on ped faces.
Bt2	36-56	10YR 4/4, sicl, 3 f sbk, ns, g, eo. Common mod. thick continuous 10YR 4/3 coatings on ped faces.
Bt3	56-73	10YR 5/4, sicl, 2 m sbk, ns, g, eo. Common mod. thick continuous 9YR 4/3 coatings on ped faces.
Bt4	73-98	10YR 5/4, sil, 2 c pr ptg. to 2 m sbk, ns, g, eo. Common thin continuous 10YR 4/3 coatings on ped faces.
Bt5	98-108	10YR 5/4, sil, 1 c pr ptg. To 2 m sbk, ns, g, eo. Few thin continuous 10YR 4/3 coatings on ped faces. Patchy silans on prisms.

7g. CAR soil description.**Date Collected:** October 26, 2009**Location:** 43.70187°N, 91.61784°W**Topography:** Upland, nearly flat**Land Use/Vegetation:** Hardwood forest, approx. 50 yr old (previously tilled)**Method:** 20 mm soil probe

Horizon	Depth, cm	Description
Ap1	0-11	10YR 3/1-2, sil, 1 f gr, ns, c, g, eo.
EA	11-21	10YR 4/4 & 3/2, sil, 1 f gr, ns, c eo.
BE	21-37	10YR 4/4, sil, 1 f sbk ptg. to 1 f gr, ns, c, eo.
Bt1	37-58	10YR 4/4. sil, 1 f sbk, ns, c, eo. Common mod. thick discontinuous 10YR 4/3 & 5/3 coatings on ped faces.
Bt2	58-95	10YR 4/4. siel, 1 f-m sbk, ns, g, eo. Common mod. thick discontinuous 10YR 4/3 & 5/3 coatings on ped faces.
Bt3	95-138	10YR 5/4, sil, 2 c pr ptg. to 2 m sbk, ns, g, eo. Common thin continuous 10YR 4/3 coatings on ped faces. Common mod. thick discontinuous 10YR 5/3 coatings on ped faces. Few fine 10YR 2/1 root infillings.

7h. OR soil description.**Date Collected:** 1997**Location:** 43.73803°N, 91.64418°W**Topography:** Upland, flat**Land Use/Vegetation:** Hay field**Method:** Hydraulic push corer

Horizon	Depth, cm	Description
A	0-12	10YR 3/2, sil, 1 f gr, vfr, c, eo.
E	12-30	10YR 4/2, sil, 1 f gr & 1 th pl, fr, c, eo.
Bt1	30-58	10YR 4/4, siel, 1 m sbk ptg. To 1 f sbk, fr, g, eo. Common thin patchy 10YR 4/3 coatings on ped faces.
Bt2	58-78	10YR 4/4, siel, 1 f-m pr ptg. To 2 m sbk, fr, g, eo. Common thin continuous 10YR 4/3 coatings on ped faces.
Bt3	78-102	10YR 5/4, sil, 1 m pr ptg. To 1 m sbk, fr, g, eo. Common thin patchy 10YR 4/4 coatings on ped faces.

APPENDIX 8. CHAPTER 4 DATA SETS.

8A. KL1 data set.

All measurements expressed as mg g⁻¹ except pH. Multiple measurements for a given depth represent replicates.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extractable RSi	Particle Size		Organic Carbon	pH
	<i>Total</i>	<i>Clay- Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
0-10	52.62	43.08	9.53	7.65	1.88	0.40	238.51	761.49	23.38	5.92
10-20	59.35	-	-	-	-	-	248.47	751.53	21.37	6.01
20-27	63.94	56.28	7.66	6.15	1.52	0.49	304.36	695.64	18.88	6.17
27-37	70.23	-	-	-	-	-	246.80	753.20	15.95	-
37-44	75.79	-	-	-	-	-	236.56	763.44	16.71	5.90
44-55	70.98	69.10	1.87	0.58	1.29	0.63	299.16	700.84	13.96	5.84
55-65	73.79	-	-	-	-	-	305.66	694.34	12.02	-
65-75	69.51	-	-	-	-	-	300.85	699.15	-	5.17
75-85	64.31	61.13	3.18	0.36	2.82	0.58	287.97	712.03	10.01	5.19
85-95	67.52	-	-	-	-	-	299.97	700.03	-	-
95-101	55.95	52.65	3.29	0.51	2.78	0.56	277.81	722.19	8.96	5.31

8b. KL3 data set.

All measurements expressed as mg g⁻¹ except pH. Multiple measurements for a given depth represent replicates.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extractable RSi	Particle Size		Organic Carbon	pH
	<i>Total</i>	<i>Clay- Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
0-5	46.73	39.66	7.07	5.05	2.03	0.79	199.41	800.59	23.35	6.61
5-15	61.03	-	-	-	-	-	168.20	831.80	24.13	6.58
15-25	62.42	-	-	-	-	-	188.96	811.04	16.99	6.51
25-32	71.58	67.56	4.02	2.24	1.78	0.62	235.57	764.43	13.09	6.25
32-39	69.66	-	-	-	-	-	-	-	11.17	-
39-46	49.93	-	-	-	-	-	246.25	753.75	-	5.93
46-56	49.35	46.69	2.66	0.32	2.34	0.53	256.59	743.41	11.09	5.59
56-66	50.19	-	-	-	-	-	274.79	725.21	-	-
66-74	51.70	-	-	-	-	-	248.66	751.34	10.35	5.29
74-82	61.83	57.53	4.30	0.14	4.16	0.50	286.96	713.04	10.72	5.27
82-92	63.89	-	-	-	-	-	277.57	722.43	-	-
92-102	49.80	45.47	4.33	0.16	4.17	0.33	245.22	754.78	9.63	5.43

8c. KO1 data set.

All measurements expressed as mg g⁻¹ except pH. Multiple measurements for a given depth represent replicates.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extractable RSi	Particle Size		Organic Carbon	pH
	<i>Total</i>	<i>Clay- Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
0-8	49.88	39.82	10.06	8.86	1.20	0.48	195.76	804.24	27.23	7.44
	48.37	36.43	11.93	9.85	2.09	0.52	-	-	-	-
	50.14	36.88	13.26	10.41	2.85	0.50	-	-	-	-
	-	-	-	-	-	0.52	-	-	-	-
	-	-	-	-	-	0.51	-	-	-	-
	-	-	-	-	-	0.52	-	-	-	-
	-	-	-	-	-	0.53	-	-	-	-
	-	-	-	-	-	0.54	-	-	-	-
8-17	55.70	-	-	-	-	0.56	219.88	780.12	28.83	7.40
17-24	64.13	-	-	-	-	0.68	231.28	768.72	26.55	7.35
24-31	77.43	64.22	13.20	11.88	1.33	0.68	255.02	744.98	25.79	7.17
31-41	67.83	-	-	-	-	-	283.51	716.49	19.16	-
41-52	66.75	63.67	3.08	2.56	0.52	0.73	279.85	720.15	17.43	6.89
52-62	63.49	-	-	-	-	-	327.44	672.56	14.43	6.72
62-72	53.19	-	-	-	-	-	-	-	-	-
72-81	51.47	49.50	1.97	0.62	1.35	0.82	289.47	710.53	11.41	6.47
81-91	53.86	-	-	-	-	-	282.88	717.12	-	6.19
91-104	-	-	-	-	-	-	-	-	-	-
104-118	53.70	50.77	2.94	0.21	2.73	0.69	260.04	739.96	-	5.71
118-130	-	-	-	-	-	-	-	-	0.00	-

8d. NL data set.

All measurements expressed as mg g⁻¹ except pH. Multiple measurements for a given depth represent replicates.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extractable RSi	Particle Size		Organic Carbon	pH
	<i>Total</i>	<i>Clay- Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
0-5	66.73	49.98	16.74	14.73	2.02	0.78	247.51	752.49	32.51	7.01
5-10	75.05	-	-	-	-	0.68	-	-	31.88	7.27
10-20	75.81	-	-	-	-	0.68	256.92	743.08	29.19	7.49
20-30	60.75	48.72	12.03	9.49	2.54	0.67	272.78	727.22	26.53	7.36
30-40	60.38	-	-	-	-	0.50	261.11	738.89	20.10	7.24
40-50	58.26	54.72	3.54	1.70	1.84	0.52	237.93	762.07	15.30	7.27
50-60	60.54	-	-	-	-	0.59	-	-	-	7.10
60-70	59.41	-	-	-	-	-	280.07	719.93	12.63	7.28
70-80	59.18	55.93	3.25	0.41	2.84	0.54	270.54 ¹	729.46 ¹	11.44	7.18
80-90	56.75	-	-	-	-	-	261.00	739.00	11.03	6.69
90-100	51.02	47.96	3.06	0.24	2.82	0.64	244.30	755.70	9.46	6.59

¹Interpolated.

8e. AL2 data set.

All measurements expressed as mg g⁻¹ except pH. Multiple measurements for a given depth represent replicates.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extractable RSi	Particle Size		Organic Carbon	pH
	<i>Total</i>	<i>Clay- Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
0-9	35.92	26.45	9.47	6.61	2.86	0.22	100.68	899.32	43.50	6.07
9-20	38.02	-	-	-	-	-	105.86	894.14	19.51	5.81
20-33	46.23	36.93	9.30	5.18	4.12	0.18	142.18	857.82	8.28	5.38
33-47	49.85	-	-	-	-	-	194.15	805.85	9.65	4.98
47-57	51.37	46.17	5.21	2.64	2.56	0.39	272.82	727.18	9.03	4.93
57-73	57.64	-	-	-	-	-	266.74	733.26	10.65	4.89
73-85	63.81	61.50	2.31	0.17	2.14	0.51	277.29	722.71	16.07	4.87
85-94	59.33	-	-	-	-	-	287.71	712.29	-	-
94-114	65.13	62.49	2.64	0.15	2.48	0.50	275.94	724.06	10.71	5.01

8f. CA data set.

All measurements expressed as mg g⁻¹ except pH. Multiple measurements for a given depth represent replicates.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extractable RSi	Particle Size		Organic Carbon	pH
	<i>Total</i>	<i>Clay- Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
0-5	45.98	37.48	8.49	7.29	1.20	0.37	162.39	837.61	38.97	6.75
5-10	45.25	-	-	-	-	-	-	-	22.40	6.62
10-20	46.01	-	-	-	-	-	157.10	842.90	15.82	-
20-30	60.62	56.85	3.78	2.33	1.45	0.41	237.50	762.50	10.70	6.57
30-40	62.38	-	-	-	-	-	-	-	-	-
40-50	69.68	68.16	1.52	0.47	1.04	0.62	266.67	733.33	10.09	6.73
50-60	72.42	-	-	-	-	-	-	-	-	-
60-70	71.04	-	-	-	-	-	257.40	742.60	10.54	6.55
70-80	74.66	72.37	2.29	0.30	1.99	0.56	247.42 ¹	752.58 ¹	11.58	6.50
80-90	66.42	-	-	-	-	-	247.42	752.58	9.88	6.33
90-100	43.85	41.33	2.53	0.16	2.37	0.46	242.62 ¹	757.38 ¹	9.40	6.03
100-110	-	-	-	-	-	-	237.43	762.57	-	-

¹Interpolated.

8g. CAR data set.

All measurements expressed as mg g⁻¹ except pH. Multiple measurements for a given depth represent replicates.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extractable RSi	Particle Size		Organic Carbon	pH
	<i>Total</i>	<i>Clay- Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
0-11	37.31	26.11	11.20	8.00	3.21	0.17	153.66	846.34	24.13	5.19
11-21	38.92	-	-	-	-	-	172.34	827.66	12.84	5.04
21-37	49.80	43.92	5.88	3.99	1.89	0.28	227.17	772.83	11.26	5.16
37-47	67.77	65.66	2.11	1.07	1.05	0.69	270.22	729.78	11.64	5.08
47-58	54.12	-	-	-	-	-	-	-	11.65	4.99
58-68	56.84	-	-	-	-	-	287.43	712.57	10.66	4.96
68-78	53.36	51.58	1.78	0.25	1.53	0.39	274.17 ¹	725.83 ¹	11.60	4.97
78-88	56.30	-	-	-	-	-	274.17	725.83	10.77	-
88-95	55.52	-	-	-	-	-	-	-	-	-
95-105	56.40	53.04	3.36	0.20	3.16	0.49	260.90	739.10	9.46	5.14

¹Interpolated.

8h. OR data set.

All measurements expressed as mg g⁻¹ except pH. Multiple measurements for a given depth represent replicates.

Depth	SLLE Extractable RSi		Floatation Extractable RSi			Oxalate Extractable RSi	Particle Size		Organic Carbon	pH
	<i>Total</i>	<i>Clay- Sized</i>	<i>Total</i>	<i>BSi</i>	<i>NSi</i>		<i>Clay</i>	<i>Silt/ Sand</i>		
5	43.82	34.88	8.94	6.59	2.35	0.20	194.65	805.35	24.42	5.49
15	35.99	-	-	-	-	0.14	-	-	12.22	5.80
25	36.21	-	-	-	-	-	171.44	828.56	11.44	5.74
35	61.09	60.05	1.04	0.64	0.40	0.36	224.12 ¹	775.88 ¹	8.13	5.68
45	50.00	48.65	1.35	0.68	0.68	0.30	224.12	775.88	7.57	5.55
55	55.24	-	-	-	-	-	-	-	6.92	-
65	53.49	-	-	-	-	-	276.80	723.20	7.62	5.00
75	55.70	54.64	1.05	0.13	0.93	0.36	266.06 ¹	733.94 ¹	6.47	5.21
85	58.74	-	-	-	-	-	264.55	735.45	7.20	-
95	51.90	50.23	1.67	0.10	1.57	0.40	267.22 ¹	732.78 ¹	8.13	5.35

¹Interpolated.