

DISSERTATION

PEDOLOGICAL AND ECOLOGICAL CONTROLS ON BIOGENIC  
SILICA CYCLING IN GRASS DOMINATED ECOSYSTEMS

Submitted by

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In partial fulfillment of the requirements

for the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

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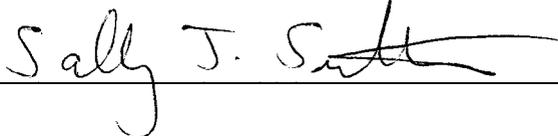
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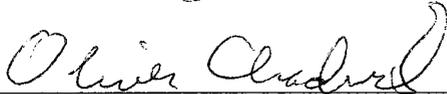
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## ABSTRACT OF DISSERTATION

### PEDOLOGICAL AND ECOLOGICAL CONTROLS ON BIOGENIC SILICA CYCLING IN GRASS DOMINATED ECOSYSTEMS

The biogeochemical behavior of silica is closely linked to the carbon cycle as marine Si-based diatoms are a major control on the distribution of silica in oceans, and play a major role in controlling atmospheric pCO<sub>2</sub> via the “biological pump.” The importance of biological controls on silica cycling in the terrestrial environment has only recently been known and our studies point to grasslands and grass dominated ecosystems as important repositories. Although the structure and ecological functioning of these ecosystems are strongly influenced by fire and grazing, the role of these key ecological drivers in the production and storage of Si represents a significant knowledge gap. Additionally, the effect of biogenic silica dissolution on the weathering of rock with different mineral assemblages is also insufficiently understood. I evaluated the effects of fire, grazing and parent material on the range and variability of plant derived biogenic silica stored in plant biomass and soils by sampling plants and soils in the mesic grasslands of North America and savannas of South Africa. Using these and other intensive study sites, along with extant productivity and soil texture data I estimated the global Si storage based on two approaches: “*measure and multiply*” and “*paint by numbers*”.

Overall, our results indicate that South African plants and soils responded differently to ecological drivers with respect to Si cycling, and these are likely linked to differences in the age and evolutionary history of these ecosystems. Plants and soils from the grazed sites in the older South African ecosystems had up to 76% and 54% greater BSi totals, respectively, than grazed North American sites. In the North American soils, grazing and fire combined resulted in the greatest abundance of BSi, whereas South African soils had the highest biogenic silica in burned plots in the absence of grazing.

Our results also indicate that the cycling of Si is strongly influenced by parent material (and therefore, texture and soil hydrology). Fine textured basaltic soils had less total and dissolved Si with a greater proportion of the total Si made up of biogenic silica relative to coarse textured granitic soils. Additionally, plants and soils overlying basaltic parent material had greater abundance of biogenic silica and slower turnover times than those overlying granitic parent materials. While both basaltic and granitic soils were strongly regulated by biologic uptake, the former showed a “tighter cycle” with less loss of Si and the latter a “leakier cycle” which, although more dependent on biogenic silica dissolution, had greater losses of total Si.

A first order estimate of biogenic silica storage in the vegetation and underlying soils of grass dominated ecosystems worldwide indicated that Africa and Asia had the greatest stores of biogenic silica in both plant and soil which, was reflective of their larger grassland area. Europe had the lowest stores of plant and soil biogenic silica. Global average biogenic silica content for grassland aboveground biomass was  $\sim 8 \text{ Tmole Si yr}^{-1}$ . Aboveground biomass BSi estimates for non-woody grasslands in North America alone was  $0.315 (\pm 0.002) \text{ Tmole Si yr}^{-1}$ . Global average biogenic silica content for

grassland soils was  $\sim 23,000 \text{ Tmole Si yr}^{-1}$  which, was approximately 100-400 times greater than biogenic silica in all terrestrial aboveground biomass and approximately 3,000 times greater than global estimates for grasslands alone. Nonwoody North American grasslands had a biogenic silica content of  $\sim 1,476 (\pm 164) \text{ Tmol Si yr}^{-1}$ ; however, 87% of this total resided within the fine size fraction and only 13% in the coarse size fraction. To extrapolate our results to continental scales we used simple regression models to predict plant and soil BSi using remotely sensed estimates of ANPP for the grass dominated ecosystems.

Overall, my data suggests that grass dominated ecosystems worldwide have the potential to accumulate high levels of biogenic silica due to the large quantities found in the dominant vegetation and soils and the lack of significant and continuous ground and stream water export pathways in these systems. These data were further utilized in conjunction with paleoenvironmental studies and ocean records to assess how major periods of grassland expansion and contraction may have influenced the terrestrial storage, mobilization and delivery of biogenic silica to the oceans. Although I was inconclusive in linking my data to the long-term temporal record in marine opal deposits, which is critical in interpreting the paleoclimate, I do speculate that during the late Miocene and onward, phytoliths contributed regularly to seawater chemistry, particularly during sea level falls as they are more labile sources of Si than mineral quartz.

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# C HAPTER ONE

## Introduction

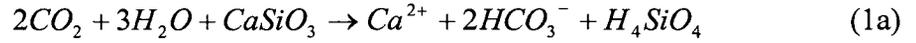
## **Introduction**

Silicon (Si) is the second most abundant element in the Earth's crust and, according to Ittekkot et al. (2006), is "probably the only element that clearly shows the link between rock and life." Si commonly occurs as silicon dioxide ( $\text{SiO}_2$ ) in crystalline and amorphous minerals and its abundance and role in terrestrial weathering has overshadowed its biological and biogeochemical importance. Across many disciplines in the earth and biological sciences scientists are no longer treating Si as "inert". They have recognized Si as fundamentally important in biological systems and are now interested in the processes that regulate the biogeochemical cycling of Si.

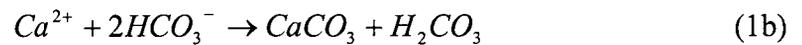
Much like the global carbon cycle, the biogeochemical behavior of silica is strongly regulated by photosynthetic organisms (Raven 2003). In silica-rich oceans (e.g. southern oceans and northwest Pacific), diatoms play a major role in sequestering atmospheric  $\text{CO}_2$  since they remove it from the surface ocean and convert it into organic carbon particles that settle out of the euphotic zone rapidly. The silica-ocean type of "biological pump" works most efficiently to absorb the atmospheric  $\text{CO}_2$  and transport it to the deep ocean sink as opposed to carbonate rich oceans where the  $\text{CO}_2$  is "consumed" during the weathering of silicate minerals and the by-product contributes to the deposition of carbonate in the oceans (Froelich et al. 1992).

### *Silicate Mineral Weathering in Terrestrial Ecosystems*

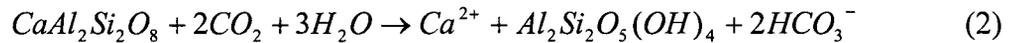
The weathering of rock and soil minerals is the primary process controlling the release of Si and its concentrations and fluxes in soils. The chemical weathering of primary silicate minerals may be represented as,



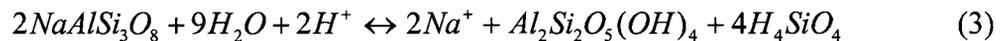
which is considered a key process that has regulated global concentrations of atmospheric CO<sub>2</sub> over geologic timescales and thus, plays a role in global climate change scenarios (Berner & Berner 1996). The ultimate storage of C in oceanic systems is represented as:



The formation of secondary minerals by incongruent dissolution of primary minerals is a more likely reaction involving the consumption of CO<sub>2</sub> and is represented as:



where the primary mineral anorthite, in the presence of CO<sub>2</sub> and H<sub>2</sub>O, weathers to form kaolinite and bicarbonate. Additionally, the common mineral albite will weather to form kaolinite and monosilicic acid as:



Equations 1, 2 and 3 above demonstrate that carbon is stored as carbonate and Si is available for transport in the form of monosilicic acid. Transported Si to oceans plays an additional role in C sequestration as a pivotal part of the “biological pump” since

photosynthetic diatoms which consume C need Si for their skeletons. Studies have found that 5 Tmol Si y<sup>-1</sup> or 80% of the total annual Si flux into oceans is supplied by rivers whose ultimate Si source is mineral weathering in terrestrial systems (Treguer et al. 1995; Conley 2002).

In general, mineral weathering rates depend on temperature, precipitation (White & Blum 1995) and are closely coupled to areas of active tectonic uplift (Rea 1994; 1998). Biologically mediated weathering by plants is closely coupled to changes in temperature and precipitation (Kelly et al. 1998). Plants have been shown to significantly accelerate mineral weathering by producing weathering agents like CO<sub>2</sub>, and organic acids and ligands, increasing soil water holding capacity and mineral-water contact time, and cation biocycling (Kelly et al. 1998; Lucas 2001). Most assessments of the controls on Si export from the terrestrial environment have largely ignored or minimized the role of plants in the biocycling of Si by assuming that mineral weathering reactions alone control Si fluxes into riverine systems (Berner & Berner, 1996). Recent studies now suggest that the biocycling of Si by plants can exert important controls on the storage and mobilization of Si in terrestrial ecosystems (Alexandre 1997; Blecker 2006; Conley 2002).

### *Plant and Soil Biogenic Silica*

The importance of Si in higher plants has been studied for decades and is well understood (Jones & Handreck 1967; Raven 1983; Epstein 1999). Plants can be characterized as either Si accumulators or nonaccumulators as they take up Si either actively or passively. Early literature supported that plants generally take up silicon

passively as monosilicic acid via transpiration and excrete the silica into amorphous silica bodies known as *opal phytoliths* ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ) in cell walls, cell lumina, and intercellular spaces near evaporating surfaces (Raven 1983; Epstein 1999). More recently, a Si-transporter gene was identified in rice suggesting that active uptake was the key mechanism in certain plants (Ma et al. 2004). Plants accumulate Si from <0.5 to 15 wt. % (Epstein 1994). Though more mechanical than physiological, the functions of Si in plants often manifest themselves under environmental stress (Ma et al. 2001) and benefit plants by increasing mechanical strength, salt tolerance, enzyme activity, and resistance to disease and pests (Epstein 1999). Ecologically, Si accumulates in many plants as a defense against herbivory and generally increases as grazing intensifies (McNaughton et al. 1985).

Plants which accumulate more Si consequently supply more Si to soil as plants die and decompose. Phytolith content in soil ranges from <0.5 to 50 wt. % (Jones & Beavers 1964; Alexandre et al. 1997; Clarke 2003). Once in the soil phytoliths may have several fates such as, 1) being translocated and stored within the soil body, 2) undergoing dissolution to be available for uptake again, or 3) being removed by leaching or eroded and transported to rivers and eventually oceans. The ultimate fate is determined by environmental conditions that regulate soil development and the inherent solubility of phytoliths in soil which is a function of particle size, chemical composition, and the co-existing minerals (Drees et al. 1989). Silicon concentrations in soil solutions would be regulated by the most soluble silica bearing minerals. The biologically derived phytoliths maintain solubilities close to  $10^{-2.74}$  and, in co-existence with quartz (solubility  $\sim 10^{-4.0}$ ), contribute more to the plant available reservoir of  $\text{H}_4\text{SiO}_4$ .

## *The Biogeochemical Cycle of Silicon*

The major terrestrial pools of Si are parent material (geologic substrates), aboveground biomass and minerals that comprise the soil matrix. Soils are the medium in which biogeochemical processes that transform Si take place and biotic and abiotic components of terrestrial ecosystems are coupled. The majority of Si available to plants is originally derived from mineral weathering (Kelly et al. 1998). Indeed, the importance of primary mineral dissolution and formation of secondary minerals has been recognized as a primary control on silicon concentrations and fluxes in soil solution and stream waters and is generally linked to climate and weathering intensity (White & Blum 1995; Gaillardet et al. 1999). Transfers (fluxes) within the soil environment are regulated by soil phytolith and silicate mineral dissolution, and secondary mineral formation. Exports or fluxes out of the soil include plant uptake and stream- and groundwater outputs. Inputs or fluxes into the soils include litterfall and atmospheric inputs.

Recent research supports the importance of plant uptake and cycling on silica activity and mineral stability in soils subjected to high amounts of chemical weathering (Lucas et al. 1993; Alexandre et al. 1997; Markewitz & Richter 1998; Meunier et al. 1999). Lucas et al. (1993) found that silica inputs from vegetation in a study in the Congo was 4 times greater than the silica that was leached from the soil system; a contribution that has maintained a soil mineralogical profile more siliceous (kaolinitic) in the upper horizons versus more aluminous (gibbsitic) in the lower horizons, which is in opposition to geochemical model predictions. Meunier et al. (1999) noted that a significant proportion of silica dissolved from parent rock can be stored in the soil as

phytolith, slowing the transfer of silica from soils to surface and ground waters. Hence, silicate mineral dissolution does not always control dissolved silica contents in surficial water in systems with high rates of biological silica turnover. In temperate forest systems, where biogenic silica turnover can be much lower than in the tropics, Markewitz and Richter (1998) demonstrated that increasing the biogenic silica sink lowered soil solution silica concentrations and consequently increased silica released by mineral weathering by an estimated 82%. Studies suggest that the most important flux of Si to the soil is from litterfall. Litterfall fluxes have primarily been obtained from forest ecosystems such as the 116 mmol Si m<sup>-2</sup> y<sup>-1</sup> in a rainforest from Amazonia (Lucas et al. 1993) and the 207-271 Si m<sup>-2</sup> y<sup>-1</sup> in a rainforest from the Congo (Alexandre et al. 1997). The greatest litterfall flux (3500-4900 Si m<sup>-2</sup> y<sup>-1</sup>) reported is from Reunion Island on soils derived from trachytic ash (Meunier et al. 1999). Higher values of Si flux have been documented in grasslands than in forests as grasses accumulate more Si per unit biomass than trees.

In grassland ecosystems, Si accumulates to high levels due to (1) the relatively high concentrations found in the dominant vegetation, and (2) the lack of significant ground- and stream-water export pathways in these more water limited biomes. Blecker et al. (2006) were the first to quantify BSi pools and fluxes within grassland ecosystems. Their study was along a precipitation and productivity gradient in the central Great Plains of North America which spanned arid to semiarid to mesic grasslands. Results indicated that short grass steppe ecosystems have the greatest accumulations of BSi in soil and the lowest storage in biomass, whereas, tall grass systems have greatest biomass silica and lowest BSi accumulation in soils (Blecker et al. 2006). Additionally, biocycling of Si

within grasslands may have significant implications regarding global Si flux from terrestrial to oceanic systems and the global expansion of grasslands during the late Neogene.

The role of terrestrial biomass in the global biogeochemical Si cycle was estimated in terms of biomass storage in terrestrial systems. Conley (2002) found annual Si storage in global biomass to be 60-200 Tmol Si which was estimated on the basis of total net primary production and average BSi content of global terrestrial vegetation. Blecker et al. (2006) estimated North American BSi stores for grasslands alone and found 0.3 Tmol Si in aboveground biomass and 130 Tmol Si in the soil which, rival Conley's (2002) global terrestrial estimates and total marine BSi production and terrestrial biomass estimates of 240 and 200 Tmol Si, respectively.

### *Research Objectives*

This research intends to broaden the current knowledge of the range and variability of BSi production and storage in grass dominated ecosystems by addressing two questions, (1) what is the variability of BSi pools, and (2) what are the important pedological and ecological controls that regulate the size of these BSi pools? North American grasslands and South African savannas were intensively sampled. Although these sites share many similarities, they also have unique attributes that make them valuable for assessing potential controls on BSi.

The specific objectives for this research were:

- (1) to evaluate the range and variability of BSi production in plant biomass and storage in grassland and savanna soils as a function of fire frequency and grazing,
- (2) to evaluate the importance of parent material in establishing the range and variability of BSi production and storage in plants and soils overlying granitic versus basaltic rocks,
- (3) to evaluate climatic controls on annual net primary production and BSi levels in three grass types to help constrain global estimates of biogenic Si mobilization and storage in grass dominated systems.

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# C HAPTER TWO

## Fire and Grazing Impacts on Silica Production and Storage in Grass Dominated Ecosystems

## Introduction

Silicon is the second most abundant element in the Earth's crust after oxygen and its biogeochemical coupling with the global carbon cycle makes knowledge of Si cycling particularly important (Treguer et al. 1995; Ragueneau et al. 2000; Treguer & Pondaven 2000; Yool & Tyrell 2003; Struyf & Conley 2008). The weathering of primary silicate minerals (e.g. anorthite) to secondary forms (e.g. kaolinite) is a process whereby carbon dioxide reacts with silicate minerals in the presence of water to yield bicarbonate. In other cases the weathering of primary and secondary minerals also yields silicic acid. Such chemical weathering reactions play an important role in C sequestration as CO<sub>2</sub> is consumed. Additionally, these weathering processes are an important Si source for marine diatoms that remove silicic acid from estuaries and oceans for long term storage as skeletal biogenic silica (BSi) sediments (Berner & Berner 1996; DeMaster 2002; Yool & Tyrell 2003). Diatoms are Si-limited in some ocean basins and are, therefore, critical CO<sub>2</sub> regulators (Dugdale et al. 1995). Together, mineral weathering and diatom production processes link not only the Si and C cycles, but also the terrestrial and oceanic biogeochemical systems.

The role of terrestrial land plants on Si cycling is a key contributor to this continental- to- oceanic relationship as they are well known for producing weathering agents (Kelly et al. 1998) and mobilizing Si through plant uptake from the soil (Conley 2002; Blecker et al 2006). Similar to diatoms in aquatic ecosystems, terrestrial plants also transform silicic acid into BSi (Raven 1983; Datnoff et al. 2001). Grasses, in particular, take up monosilicic acid (Si(OH)<sub>4</sub>) from the soil solution and deposit it as BSi, or phytoliths on cell walls, in lumina and in intercellular spaces (Siever & Scott 1963;

Raven 1983; Epstein 1999). When plants die, their BSi is returned to the soil where its amorphous form is more soluble than quartz and less soluble than other siliceous crystalline minerals (Lindsay 1979). These solubility differences distinguish various Si pools (Figure 2.1) that determine the release of Si from the soil environment and into riverine and oceanic systems. For example, the higher solubility of BSi relative to quartz makes it more readily available for cycling into the soil Si pool where it is either available for biotic uptake or leached from the system.

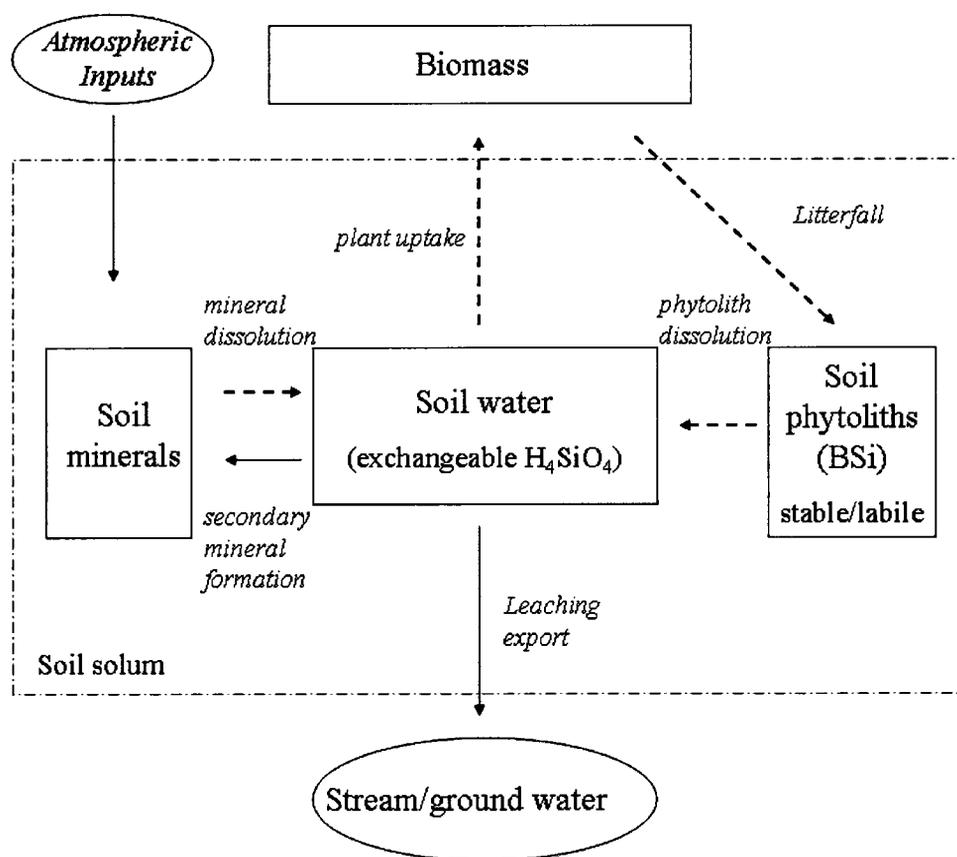


Figure 2.1. Conceptual model of the terrestrial silica cycle used in this study. Boxes represent pools and arrows represent fluxes. Dashed arrows emphasize the area of the cycle that was of particular interest for measurements in this study. (Adapted from Blecker et al. 2006)

Recent estimates have shown that rivers transport approximately 5 Tmol Si y<sup>-1</sup> globally or 80% of the total annual fluxes from continents to oceans (Treguer et al. 1995; Conley 2002). Although silicate mineral weathering is a primary source of this flux, the terrestrial production of BSi also controls Si mobility, and its role has been largely underestimated in Si export models (Berner & Berner 1996). The underestimation of this important biogenic component (BSi) is particularly apparent in grassland systems where recent estimates indicate that North American grasslands alone yield 0.3 Tmol Si in aboveground biomass and 130 Tmol Si in the soil (Blecker et al. 2006). Thus, the BSi stored in the soils of temperate grassland ecosystems alone rivals the estimated storage in global biomass determined by Conley (2002) to be at 60-200 Tmol Si y<sup>-1</sup>. In addition, Blecker et al. (2006) suggested that the geochemical behavior as well as the variability of BSi within grassland ecosystems is linked closely to climate and ANPP. However, other ecological processes, namely fire and grazing, have not been assessed with regard to their impact on the production and cycling of silica.

Fire and grazing, whether natural or managed, play an important role in the structure and function of grassland and savanna ecosystems worldwide (Hulbert 1969; Old 1969; Vogl 1974; Axelrod 1985). Fire and grazing in grass dominated systems prevents the invasion of woody species and strongly impacts plant species composition (Bragg & Hulbert 1976; Knapp et al. 1999; Uys et al. 2004; Briggs et al. 2005). The mesic grasslands of North America and the savannas of South Africa are two examples of ecosystems where both fire and grazing play a key role in virtually all ecological processes (Knapp et al. 1998, Du Toit et al. 2003).

Although functioning as management tools (Tainton 1999), fire and grazing are considered to be “natural disturbances” to the ecosystem as they remove biomass and alter resource availability (Pickett & White 1985). The frequency at which an ecosystem experiences burning throughout its evolutionary history can strongly influence the plant community (Freeman 1998; Lunt & Morgan 2002) and can alter the chemical composition (Gillon 1983; Cass et al. 1984; Gill et al. 1990) and development of the soil (Powers et al. 1990; Huggett 1998; Neary et al. 1999). Given that precipitation, fire and grazing regimes are being impacted directly and indirectly by human activities in grasslands and savannas worldwide, an understanding of the influence of fire and grazing on biogenic silica (BSi) production and storage is needed, particularly with the potential link between Si and C cycles.

In a bioclimatic study across the Great Plains, Blecker et al. (2006) found productivity to be an important control over Si storage as BSi content in aboveground biomass increased with increased precipitation. Their results suggest that fire and grazing, two additional drivers of productivity are thus, also likely to be important. Indeed, the turnover time of grasses and the release of BSi into the soil may be largely controlled by fire and grazing. Based on these regional-scale observations, a study was conducted with the following objectives: (1) to evaluate the range and variability of BSi production in plant biomass and storage in grassland and savanna soils as a function of fire frequency and grazing pressures (2) to determine whether the older and more highly weathered soils of South African savannas exhibit similar patterns in Si production and storage as the younger and more nutrient rich soils of North American grasslands under similar fire regimes and grazing pressures.

## Methods

### *Study Areas*

Research was conducted within the framework of three long-term field experiments in North America and South Africa (Figure 2.2) to specifically examine the effects of fire and grazing on BSi (Table 2.1). The North American and two South African sites allow for comparative studies because key aspects of their experimental designs are virtually identical.

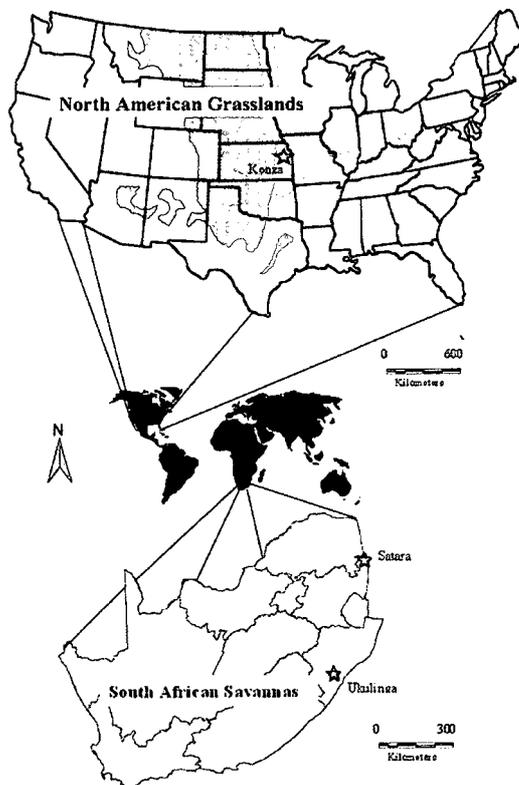


Figure 2.2. The burn experiment site locations in North America at the Konza Prairie Biological Station and in South Africa at the Satara Kruger National Park and Ukulinga Research Farm used in this study.

Table 2.1. Climatic and site property data of three grassland fire treatments

| Site Properties <sup>‡</sup>         | Konza |                               |     | Satara                      |  |     | Ukulinga |   |     |
|--------------------------------------|-------|-------------------------------|-----|-----------------------------|--|-----|----------|---|-----|
|                                      | UB    | IB                            | AB  | Burn Treatment <sup>†</sup> |  |     | UB       | IB  | AB  |
| ANPP, g m <sup>-2</sup> <sup>§</sup> |       |                               |     |                             |  |     |          |   |     |
| Grazed                               | 270   | 235                           | 285 | 478                         | 523  | 496 |          |   |     |
| Ungrazed                             | 296   | 286                           | 285 |                             |  |     | 511      | 464   | 537 |
| MAP, mm                              |       | 835 <sup>¶</sup>              |     |                             | 544 <sup>#</sup>   |     |          | 844 <sup>#</sup>  |     |
| MAT, °C                              |       | 12.7 <sup>¶</sup>             |     |                             | 21.2-23.3 <sup>#</sup>                                   |     |          | 17.6 <sup>#</sup>   |     |
| MMT, °C                              |       | -2.7-26.6 <sup>††</sup>       |     |                             | 16-28 <sup>#</sup>                                       |     |          | 13.2-21.4 <sup>#</sup>  |     |
| Latitude/Longitude                   |       | 39° 05.48 N/<br>96° 34.12 W   |     |                             | 23-25°S/<br>30-31°E                                      |     |          | 29°40'S/<br>30°20'E   |     |
| Elevation range, m                   |       | 320-444                       |     |                             | 240-320  |     |          | 840   |     |
| Underlying geology                   |       | Cherty limestone<br>and shale |     |                             | Basalt   |     |          | Marine shales and<br>dolerite colluvium                       |     |
| Soil type                            |       | Udic argiustolls              |     |                             | Rhodic nitisols,<br>Haplic luvisols,<br>Leptic phaeozems |     |          | Dystric leptosols,<br>Chromic luvisols,<br>Haplic plinthisols |     |
| Vegetation type                      |       | Tall grass                    |     |                             | Mixed lowveld<br>bushveld                                |     |          | Tall grassveld  |     |
| Biome type                           |       | Mesic grassland,<br>temperate |     |                             | Savanna,<br>subtropical                                  |     |          | Savanna,<br>subtropical                                       |     |

<sup>†</sup> UB=Unburned, IB=Intermediately burned, AB=Annually burned

<sup>‡</sup> ANPP=Aboveground annual net primary productivity, MAP=Mean annual precipitation, MAT=Mean annual temperature, MMT=Mean monthly temperature range

<sup>§</sup> Greg Buis et al. (2009)

<sup>¶</sup> Data from Bark (1987)

<sup>#</sup> Data from Mills and Fey (2004a)

<sup>††</sup> Data from Hayden (1998)

The North American site is located on the 3,487 ha Konza Prairie Biological Station (KPBS) which lies in the northern Flint Hills region of northeastern Kansas and has been a participant in the Long Term Ecological Research (LTER) network since the program's inception in 1981 (Callahan 1984). The silty clay loam- to clay loam soil textures at KPBS are derived from parent materials of cherty limestone and shale (Jantz et al. 1975; Ransom et al. 1998). Morphologically the soils are typical of North American grassland Mollisols with high concentrations of organic carbon in the surface A horizons and high base saturation (Blecker et al. 2006). Konza Prairie Biological Station is a tallgrass prairie dominated by native perennial C<sub>4</sub> grasses such as big bluestem (*Andropogon gerardii*) and indian grass (*Sorghastrum nutans*) (Knapp et al. 1998). The climate is continental with mean monthly temperature ranges from -2.7 °C in January to 26.6 °C in July (Hayden 1998). Annual precipitation averages 835 mm with 75% falling during the growing season between April to September (Bark 1987).

Konza Prairie Biological Station is divided into 60 experimental units where the unit of study is the watershed. Each watershed is associated with a fire treatment where natural fire is replicated with burning intervals of 1-, 2-, 4-, 10- and 20- years. Additionally, bison are included in a subset of the watersheds to address the role of native grazers and fire-grazing interactions (Knapp et al. 1999; Johnson & Matchett 2001). Data for this study are from plots (ca. 250 m<sup>2</sup>) replicated three times in watersheds that have been grazed by bison or ungrazed and burned annually (AB), quadrennially, and every twenty years (UB).

The continental comparison with the North American tallgrass prairie was made with experimental fire plots in South Africa. Like the North American grasslands, the

South African savanna grasslands are dominated by C<sub>4</sub> grass species such as red grass (*Themeda triandra*). According to Sage et al. (1999), the grasslands of southern Australia, the steppe of south-east Asia, the pampas of South America and the tallgrass prairie of North America are all structurally analogous to the grasslands of South Africa.

One of the two South African sites was located near Satara in the approximately two million ha Kruger National Park (KNP) of north-eastern South Africa. The fine textured soils at Satara are derived from basalt and are classified as rhodic nitisols, haplic luvisols and leptic phaeozems (WRB) (Mills & Fey 2004a, b). The savanna biome is populated with scattered marula (*Sclerocarya birrea*) and knobthorn (*Acacia nigrescens*) trees (Mills & Fey 2004a, b) in a mix of grasses (Table 2.2). The climate is semi-arid with mean monthly temperature ranges from 16 to 28 °C (Mills & Fey 2004a) and with a mean annual precipitation of 544 mm (Govender et al. 2006).

The experimental fire plots on the KNP cover approximately seven ha each and similar to Konza are AB, triennially burned, and UB. A diverse suite of large grazers have unrestricted access to the fire plots at KNP.

The other of the two South African sites is on the Ukulinga Research Farm (URF) located in KwaZulu-Natal within the Coast Hinterland Bushveld (Low & Rebelo 1996). The clay loam to sandy clay loam textured soils at Ukulinga are derived from parent materials of shales and dolerite and are classified as chromic luvisols and haplic plinthosols (WRB) (Mills & Fey 2004a). Although characterized as savanna where the dominant non-graminoid species is *Asteraceae* (Mills & Fey 2004a), the regular burning at Ukulinga has maintained it as an open grassland (Tainton & Mentis 1983) (Table 2.2).

The climate is sub-humid with mean monthly temperature ranges from 13.2 to 21.4 °C (Mills & Fey 2004a) and with a mean annual precipitation of 710 mm (Tainton 1981).

Table 2.2. Satara and Ukulinga dominant plant species across burn frequency.

| Site     | Burn Frequency <sup>†</sup>    |                               |   |
|----------|--------------------------------|-------------------------------|---|
|          | AB                             | IB                            | UB  |
| Satara   | <i>Bothriochloa radicans</i>   | <i>Bothriochloa radicans</i>  | <i>Bothriochloa radicans</i>  |
|          | <i>Eragrostis nindensis</i>    | <i>Panicum coloratum</i>      | <i>Chloris virgata</i>  |
|          | <i>Panicum coloratum</i>       | <i>Themeda triandra</i>       | <i>Digitaria eriantha</i>   |
|          | <i>Urochloa mosambicensis</i>  | <i>Urochloa mosambicensis</i> | <i>Panicum coloratum</i><br><i>Panicum maximum</i><br><i>Themeda triandra</i> |
| Ukulinga | <i>Cymbopogon validus</i>      | <i>Aristida junciformis</i>   | <i>Aristida junciformis</i>   |
|          | <i>Diheteropogon amplexans</i> | <i>Cymbopogon excavatus</i>   | <i>Cymbopogon excavatus</i>   |
|          | <i>Heteropogon contortus</i>   | <i>Eragrostis curvula</i>     | <i>Eragrostis curvula</i>   |
|          | <i>Hyparrhenia hirta</i>       | <i>Tristachya leucothrix</i>  | <i>Panicum maximum</i>  |
|          | <i>Themeda triandra</i>        |                               |   |
|          | <i>Tristachya leucothrix</i>   |                               |   |

<sup>†</sup> UB=Unburned, IB=Intermediately burned, AB=Annually burned

The experimental fire plots on the URF cover approximately 14 x 18 m each are AB, triennially burned, and UB. Each treatment was replicated three times. There are no large grazers at URF. Thus, in South Africa, the effects of varying fire frequency alone (Ukulinga) or fire frequency combined with grazing (Kruger) can be assessed, but interactions between fire and grazing at the same site are not available. At Konza, the fully factorial design allows for assessment of the main and interactive effects of fire and grazing.

## *Field Sampling*

The sampling scheme and terminology used in this study and applied to the Konza, Satara and Ukulinga sites are defined as follows. The plot is the smallest enclosed unit that is experimentally burned at each site. The treatments are the fire frequency prescribed to each plot. For the purposes of this study, only annually, triennially (quadrennially at Konza) and twenty year burn plots were considered. For the remainder of this paper, the Konza quadrennially burned plots and the Satara and Ukulinga triennially burned plots will be referred to as intermediate (IB) burned plots and those plots burned only once in 20 years (and not during this study) will be termed unburned. There were three replicates of each plot with the same treatment. Each replicate plot was sampled at two depth intervals, 0-10 cm and 10-20 cm using a tile spade shovel. These depths were sampled because there is generally a sharp decline in soil phytolith with depth where the highest amounts are typically in the A horizon and less abundant in other genetic horizons. Konza plots were sampled in both ungrazed and bison grazed watersheds. This allowed us to compare the KPBS plots to both the KNP plots, which are grazed by large herbivores and the URF plots, which are ungrazed. A total of 36 plots with fire-grazing interactions in both North America and South Africa were assessed; 18 plots are from KPBS (3 plots x 3 fire regimes x 2 grazing pressures), 9 plots are from KNP (3 plots x 3 grazed fire regimes) and 9 plots are from URF (3 plots x 3 ungrazed fire regimes). A total of 216 samples from all sites were returned to the laboratory in plastic bags kept in coolers, air dried and then sieved. Replicate samples from each site at each depth were kept separate throughout all analytical procedures. The

3-4 dominant grass species that were actively grazed or ungrazed at each experimental fire plot were sampled adjacent to the soil sampling area and grouped together for analyses. Estimates of productivity ( $\text{g m}^{-2} \text{ yr}^{-1}$ ) for all sites (including historically grazed/ungrazed sites from exclosures) were made by harvesting aboveground biomass at the end of the growing season, drying the biomass, and determining the mass of current year's production (Buis et al. 2009). Although scattered trees and shrubs were found at most sites, particularly in unburned plots, these were not sampled for BSi or included in productivity estimates.

### *Analytical Methods*

Soil samples were air dried, sieved through a 2 mm (#10 mesh) sieve, ground in a ball mill and oven dried in preparation to be analyzed for carbon and nitrogen. Total carbon and total nitrogen were analyzed on a LECO-TruSpec CN analyzer. Subsamples of the prepared oven dried soils were also used to analyze for inorganic carbon by pressure transducer (Harris et al. 2001), in which the samples were exposed to 6N hydrochloric acid (HCl) in a capped and sealed glass bottle. The soil reacted with the HCl to evolve  $\text{CO}_2$  during a 2 h period at which time the pressure inside the bottle was measured. Measured values were converted to concentrations using a calibration curve generated from known concentrations of  $\text{CaCO}_3$  standards. Percent organic carbon was determined by taking the difference of the results found from each carbon analysis (total C – inorganic C = organic C). Soil pH on air-dried soil using the soil:water (1:1) method was measured with an Orion Model 420A pH meter.

Due to the inability to acquire soil clods from the organic rich upper 20 cm of the Konza and Ukulinga soils, bulk density was calculated empirically from particle size and organic matter content (organic matter is determined from organic carbon, LECO data) (Adams 1973; Rawls 1983). Bulk density for the Satara soils was determined using the Blake and Hartge (1986) clod method in which natural soil peds were coated in paraffin wax and weighed first in air and then again in water.

### Biogenic Silica

Biogenic silica was recovered from dominant plant species using a gravimetric approach (Blecker et al. 2006) adapted from Piperno (1988), Kelly (1990), and Parr et al. (2001) in which samples were washed, ashed, chemically treated, filtered and weighed. Approximately 10 g of 2-3 cm length oven dried plant material were cleaned with a solution of 5% sodium hexametaphosphate, 10% HCl and de-ionized water (DI) in a 1:1:8 ratio respectively. Samples were then thoroughly rinsed with DI, treated with 80 °C, 70% ethanol to strip them from their waxy coatings, and rinsed with DI water again. They were dried at 65 °C in preparation for dry ashing. Pre-weighed subsamples of washed and dried plant material were placed in ceramic crucibles and ashed for 2 h in a muffle furnace at 500 °C after which they were allowed to cool in a dessicator and weighed. The resultant ash was then treated with 10% HCl at a temperature of 65 °C, filtered through pre-weighed 0.2 µm polycarbonate membranes, treated with 30% H<sub>2</sub>O<sub>2</sub> at a temperature of 65 °C and filtered again through pre-weighed 0.2 µm polycarbonate membranes. Finally, samples were rinsed thoroughly with DI water then oven dried at 60 °C and weighed.

The alkaline wet chemical dissolution method using the weak base  $\text{Na}_2\text{CO}_3$  was used to analyze for BSi in soils. Although this  $\text{Na}_2\text{CO}_3$  method has been primarily used by aquatic scientists studying aquatic systems (DeMaster 1981; Conley 1998), we along with our colleagues found it suitable for recovery of BSi from soils of terrestrial ecosystems (Saccone et al. 2006, 2007; Sauer et al. 2006).

Approximately 30 ( $\pm 0.05$ ) mg of hand-ground freeze-dried soil were measured into 60 mL polypropylene round flat-bottom bottles with 40.0 mL of 1%  $\text{Na}_2\text{CO}_3$ . Bottles were placed in an 85 °C shaking water bath for a total of 3, 4 and 5 h at which times 1.0 mL aliquots were removed for analysis. Analysis for dissolved Si was conducted using the molybdate blue spectrophotometric method where the spectrophotometer was set at 812 nm (Mortlock & Froelich 1989), a modification from the reduced molybdosilicic acid spectrophotometric method (Strickland & Parsons 1968; Fanning & Pilson 1973). Disodium hexafluorosilicate, 99+%  $\text{Na}_2\text{SiF}_6$  from Alfa Aesar (Ward Hill, MA), was dissolved in high purity water to make a stock standard solution. The solubility differences between BSi and mineral Si cause them to go into solution (of  $\text{Na}_2\text{CO}_3$ ) at different rates. Dissolution of BSi occurs within the initial 2 h, whereas mineral Si (specifically clay minerals) dissolves at a constant rate for a much longer period of time (DeMaster 1981; Koning et al. 2002; Saccone et al. 2006). Thus, BSi is calculated from the intercept of the linear portion of the mineral Si dissolution curve (DeMaster 1981; Koning et al. 2002).

## *Statistics*

Data were analyzed by an analysis of variance (ANOVA) in SAS (version 9.1) (Cary, NC). A two-way ANOVA was used at Konza with main effects for fire treatment (UB, IB, AB) and grazing condition (G, UG) and a one-way ANOVA was used at Satara and Ukulinga with only fire treatment as a main effect. Comparisons were also made across continents (North America and South Africa) where fire treatment, grazing conditions and continent were main effects. Sites were analyzed separately as a randomized complete block design. Replicate samples were averaged for each treatment site. Depth (0-10 cm and 10-20 cm) were added together and not considered as a separate effect as the focus of the study was on the total amount of BSi and not its depth distribution. Additionally, the two depth intervals were combined as no significant differences in phytolith abundance was observed between these intervals. Pairwise comparisons were made using the Bonferroni adjustment method with an  $\alpha = 0.05$ .

## **Results**

### *Plant Biogenic Silica*

Using the amount of BSi in the dominant grasses of Konza and aboveground productivity data, we estimated that BSi in the vegetation aboveground ranged from 87 to 140 kg ha<sup>-1</sup> (3.2 - 5.0 wt. % in the grasses) in grazed plots and 124 to 215 kg ha<sup>-1</sup> (4.2-6.4 wt. % in the grasses) in ungrazed plots. The greatest BSi values under grazed and ungrazed conditions were from annually burned and unburned sites, respectively. There was no significant ( $P < 0.05$ ) fire or grazing effects (Figure 2.3).

Dominant grasses of the grazed Satara and ungrazed Ukulinga sites (Table 2.2) yielded BSi values ranging from 305 to 552 kg ha<sup>-1</sup> (5.8-10.6 wt. % in the grasses) and 98 to 363 kg ha<sup>-1</sup> (2.1-6.8 wt. % in the grasses), respectively. The greatest BSi values from both Satara and Ukulinga were from burned sites but there was no significant fire effect at the grazed Satara sites. Biogenic silica content in the dominant grasses were significantly greater ( $P < 0.05$ ) in annually burned treatments as compared to unburned and intermediately burned treatments at the ungrazed Ukulinga sites (Figure 2.4). Biogenic silica content in the grasses at grazed Satara sites were significantly greater ( $P < 0.05$ ) in unburned (by 52%) and intermediately burned (by 59%) plots than in their ungrazed Ukulinga counterparts.

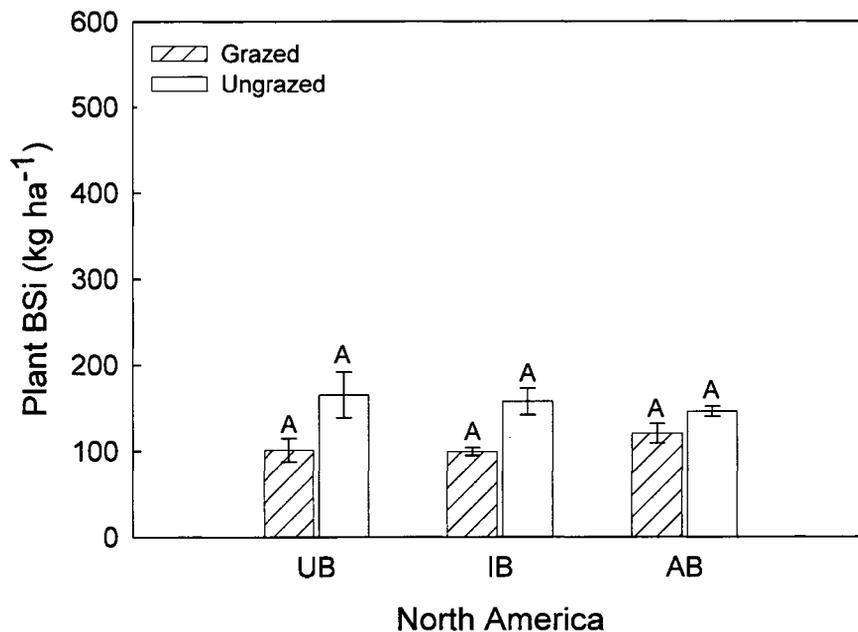


Figure 2.3. Mean plant biogenic silica (BSi) amounts (kg ha<sup>-1</sup>) ( $\pm 1$  standard error of the mean) for the dominant grass species at unburned (UB), intermediately burned (IB), and annually burned (AB) plots that are grazed or ungrazed in North America. A letter change indicates significant differences in means across grazed-ungrazed paired plots and across fire treatments at  $\alpha = 0.05$ . Main effects were for fire treatment ( $P < 0.05$ ), grazing ( $P < 0.05$ ), and fire treatment  $\times$  grazing ( $P < 0.05$ ).

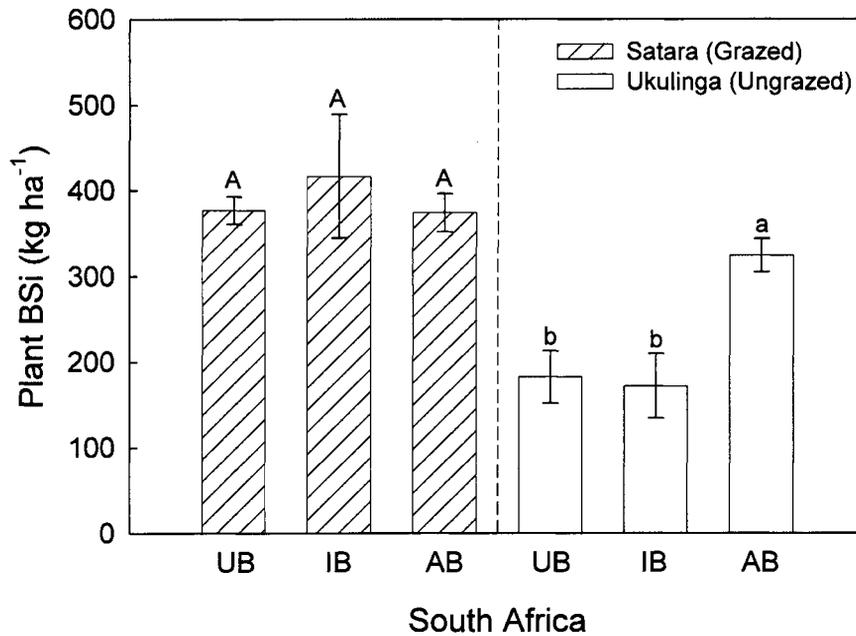


Figure 2.4. Mean biogenic silica (BSi) amounts ( $\text{kg ha}^{-1}$ ) ( $\pm 1$  standard error of the mean) for the dominant grass species at unburned (UB), intermediately burned (IB), and annually burned (AB) plots that are grazed (Satara) or ungrazed (Ukulinga) in South Africa. Capital- and lower- case letters are designated for grazed (Satara) and ungrazed (Ukulinga) plots respectively. A letter change indicates significant differences in means across fire treatments at  $\alpha = 0.05$ . Main effects were for fire treatment ( $P < 0.05$ ).

A continental comparison between North America (Figure 2.3) and South Africa (Figure 2.4) revealed that the South African sites had significantly greater ( $P < 0.05$ ) BSi content (by 73% in UB, 76% in IB and 68% in AB plots) than the North American sites in all fire treatment plots under grazed conditions. The North American and South African sites with the highest BSi content were those with the highest ANPP (Table 2.1).

Plant analyses were also conducted across grazed and ungrazed burn treatments using BSi *concentration* data (in contrast to total BSi amounts) to address the question of whether uptake and storage of BSi was a direct response to fire and grazing or whether total BSi content was a direct reflection of ANPP and thus, an indirect response to fire and grazing. Results suggest that there was no significant ( $P < 0.05$ ) fire or grazing effect at Konza, Satara, or Ukulinga sites in plant BSi concentration.

In summary, the total BSi amounts in vegetation were not affected by grazing or fire in North America, just annual fire in South Africa whereas BSi concentrations in the vegetation were not affected by grazing or fire. The largest differences were found when comparing North America and South Africa where grazing has a greater affect on total BSi amounts in South Africa across fire treatments.

### *Soil Biogenic Silica*

The amount of BSi in the soil (0-20 cm) was three orders of magnitude greater than plant BSi, a ratio similar to other terrestrial grassland systems (Blecker et al. 2006). Biogenic silica amounts within the top 20 cm of the soil surface at Konza ranged from 22,000 to 78,100 kg ha<sup>-1</sup> (2.0-7.1 wt. %) at grazed sites and 18,700 to 81,400 kg ha<sup>-1</sup> (1.7-7.4 wt. %) at ungrazed sites. Biogenic silica contents were significantly greater ( $P < 0.05$ ) in burned treatment plots as compared to unburned treatment plots under grazed conditions (Figure 2.5). There was no fire effect at ungrazed sites. Biogenic silica content in grazed Konza sites were significantly greater (by 25%) in annually burned plots than their ungrazed counterparts.

Biogenic silica content within the top 20 cm of the soil surface at the grazed Satara and ungrazed Ukulinga sites ranged from 22,400 to 176,400 kg ha<sup>-1</sup> (1.6-12.6 wt. %) and 24,000 to 88,800 kg ha<sup>-1</sup> (2.0-7.4 wt. %), respectively. The greatest BSi content at Satara were from unburned treatment plots and the greatest BSi content at Ukulinga were from annually burned treatment plots (Figure 2.6). Biogenic silica contents were significantly greater in unburned and annually burned treatments as compared to intermediately burned treatments at Satara sites. Biogenic silica content at grazed Satara

were significantly greater in unburned (by 52%) and annually burned (by 34%) plots than their ungrazed Ukulinga counterparts.

A continental comparison between North America (Figure 2.5) and South Africa (Figure 2.6) revealed that under grazed conditions, South African soils had significantly greater BSi content than North American soils in unburned (by 54%) and annually burned (by 34%) treatment plots and in annually burned (by 26%) plots under ungrazed conditions.

In summary, the total BSi amounts in soil were only affected by grazing with annual fire in North America and only affected by fire when grazed in South Africa. Similar to the findings for vegetation, the greatest differences in total BSi amounts in soil were found when comparing North America and South Africa where grazing has a greater affect on BSi totals in South Africa.

Soil to plant ratios were calculated to gain information about Si cycling between the plants and soils to a depth of 20 cm. Across all treatments and on both continents the ratio was on the same order of magnitude, and on the basis of kg/ha ranged from 251:1 at Satara intermediately burned sites to 930:1 at Konza annually burned and grazed sites. Soil and plant concentration data yielded soil:plant BSi ratios ranging from 1:1 to 3:1 with most sites having a ratio of 2:1 (Figure 2.7). Approximately 50% of the variance in soil BSi was explained by plant BSi. A continental comparison, however, showed that, when analyzed separately, South African sites contributed most to this positive correlation as approximately 75% of the variance in soil BSi was explained by plant BSi in South African sites alone.

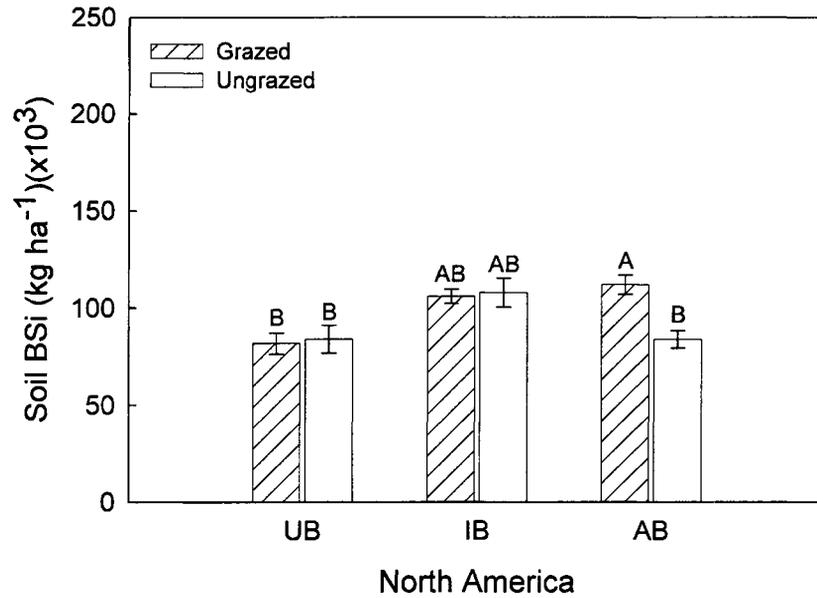


Figure 2.5. Mean soil biogenic silica (BSi) amounts (kg ha<sup>-1</sup>)(x10<sup>3</sup>) ( $\pm$  1 standard error of the mean.) at depths up to 20 cm at unburned (UB), intermediately burned (IB), and annually burned (AB) plots that are grazed or ungrazed in North America. A letter change indicates significant differences in means across grazed-ungrazed paired plots and across fire treatments at  $\alpha = 0.05$ . Main effects were for fire treatment ( $P < 0.05$ ), grazing ( $P < 0.05$ ), and fire treatment x grazing ( $P < 0.05$ ).

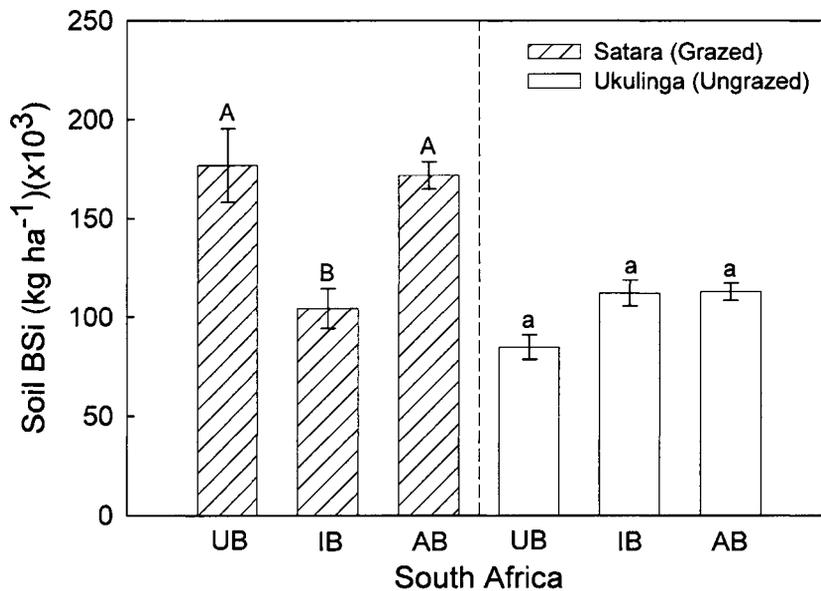


Figure 2.6. Mean soil biogenic silica (BSi) amounts (kg ha<sup>-1</sup>)(x10<sup>3</sup>) ( $\pm$  1 standard error of the mean.) at depths up to 20 cm at unburned (UB), intermediately burned (IB), and annually burned (AB) plots that are grazed (Satara) or ungrazed (Ukulinga) in South Africa. Capital- and lower- case letters are designated for grazed (Satara) and ungrazed (Ukulinga) plots respectively. A letter change indicates significant differences in means across fire treatments at  $\alpha = 0.05$ . Main effects were for fire treatment ( $P < 0.05$ ).

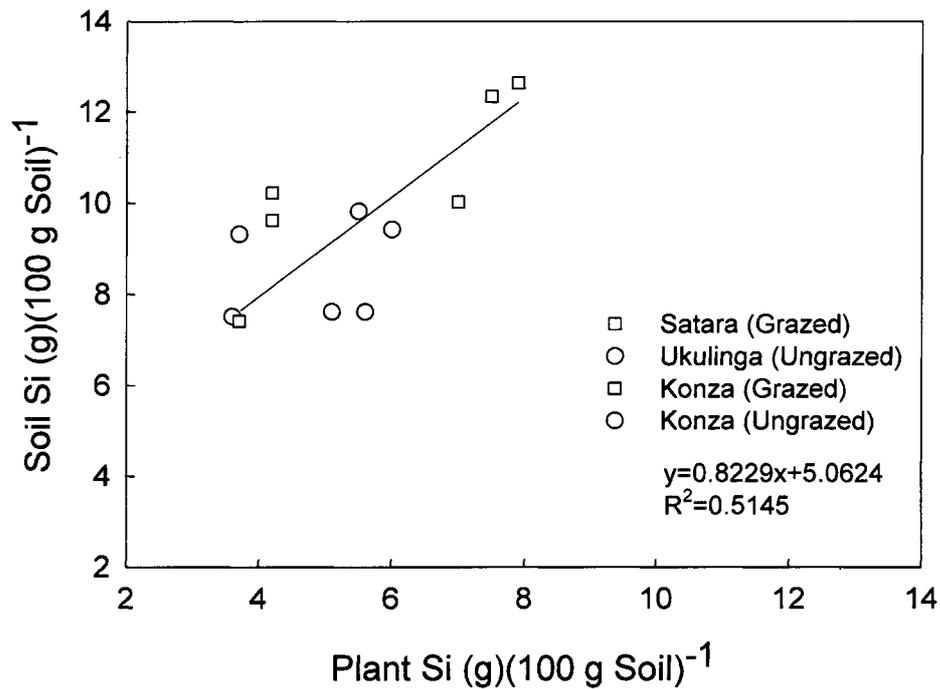
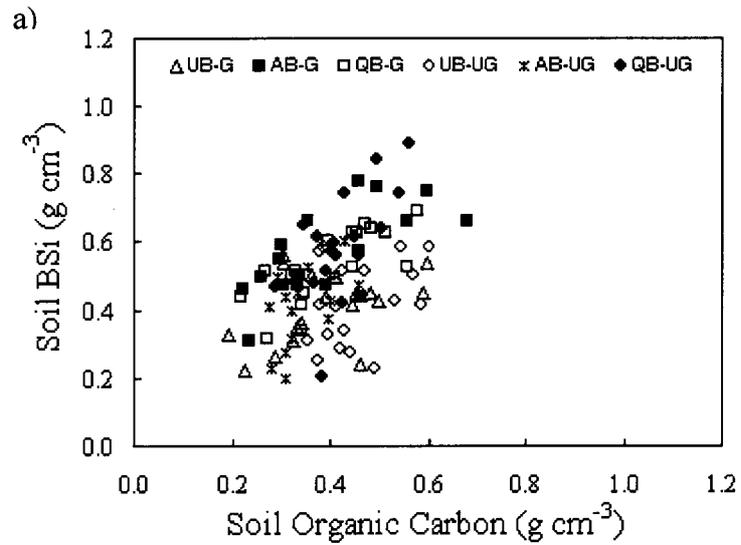
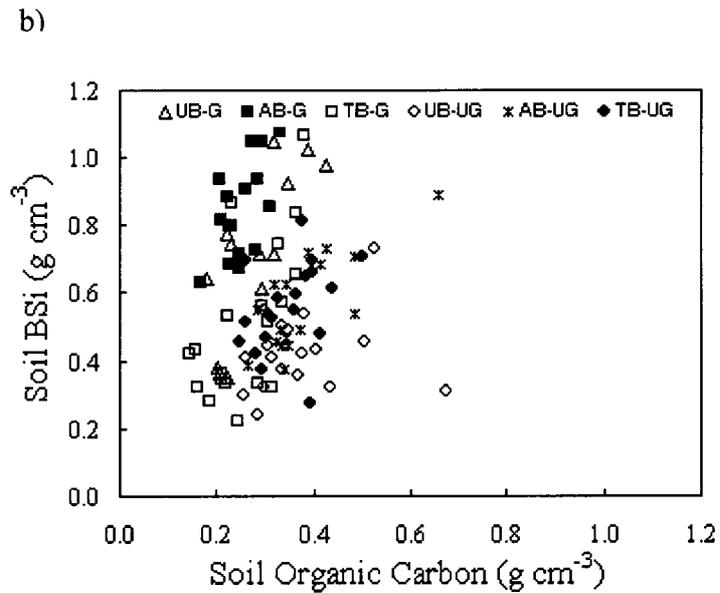


Figure 2.7. Relationship between plant and soil biogenic silica (BSi) wt. percent at grazed and ungrazed North American (Konza) and South African (Satara and Ukulinga) sites, regardless of burn treatment.

Both soil BSi and soil organic carbon (SOC) are plant mediated and thus data were regressed against each other to determine whether SOC content could be used as a general predictor of BSi content. A general relationship ( $r^2 = 0.65$ ) existed between SOC and soil BSi across North American sites (Figure 2.8a). The North American burned and grazed sites contributed most, and the unburned ungrazed sites least, to this positive correlation. A similar trend was not evident ( $r^2 = 0.30$ ) for South African samples (Figure 2.8b).



North America



South Africa

Figure 2.8. Relationship between two biologically mediated soil constituents, soil organic carbon and biogenic silica (BSi), across interactive burning and grazing regimes in a) North American grasslands and b) South African savannas. Unburned (UB), intermediately burned (IB), and annually burned (AB) treatments make up the fire regime, and grazed (G) and ungrazed (UG) treatments make up the grazing regime.

## Discussion

This study contrasted the response of BSi in plants and soils with grazing and fire frequency in North American grasslands and South African savannas. Globally, grasslands share their reliance upon fire and grazing to maintain community structure and function as they influence vegetation composition, annual aboveground net primary productivity (ANPP) and nutrient cycling. However, grasslands may respond differently to fire and grazing depending on the limitations from the above- and belowground processes and the feedbacks between plant and soil systems. For example, although higher rates of precipitation are largely responsible for the gradients in ANPP across the Great Plains, this is not always the case in the tallgrass prairie where other factors such as light and N are often limiting due to different fire frequencies (Knapp et al. 1998b).

The effects of fire and grazing have been more thoroughly examined in the Great Plains of North America than in other regions. The strongest reported ecological response to greater fire frequency has been greater ANPP (Knapp et al. 1998a) and belowground net primary productivity (BNPP) in the North American tallgrass prairie. Frequent fire results in greater light competition and N limitation allowing C<sub>4</sub> grasses to dominate over forbs in abundance (Collins et al. 1998; Briggs & Knapp 2001). Grazing also has been shown to have positive effects on ANPP in some North American grasslands (Frank et al. 2002).

The relationship of ANPP to BSi is important as previous studies show that plant BSi distribution in North American grasslands is largely driven by ANPP (Blecker et al. 2006). They found that plant BSi content increases with increasing ANPP along a bioclimate sequence. Although fire affects ANPP directly and BSi indirectly, we

hypothesized that fire would have a negative effect on soil BSi content as a direct physical vector of loss by wind driven removal of ash after fire; therefore we expected to see less soil BSi accumulation from burned plots. Grazing was hypothesized to have a positive effect on soil BSi content because grasses were expected to take up greater amounts of BSi at higher concentrations as a response to, and protection against, herbivory. Consumption of Si rich grasses by grazers was expected to increase turnover and return of Si back into soil through deposition of fecal material. We therefore expected to see more BSi accumulation in these grazed soils.

In the present study, plant and soil BSi content from Konza exhibited similar general responses to fire and grazing: both plant and soil BSi content were, 1) greater in grazed burned vs. unburned fire treatments and 2) less in grazed vs. ungrazed sites across treatments with exception of the annually burned soils. More significantly, however, are the interactive affects that fire and grazing have on soil BSi content where soils from annually burned grazed sites had greater storage of Si than unburned grazed sites.

Although our results did not support our hypothesis regarding the direct loss of soil BSi content after fire, fire may have an indirect effect at Konza because of greater ANPP in grazed annually burned sites and in ungrazed unburned sites, as compared to other respective fire treatments. The decrease in forb abundance and the increase in grasses at frequently burned sites likely resulted in greater BSi uptake because, according to Blecker et al. (2006), forbs take up less Si on a dry weight basis. Specifically, forbs at Konza only averaged  $0.29 \pm 0.07\%$  Si (Blecker et al 2006). We found that although many ecological variables respond oppositely to grazing than fire, together they promoted Si uptake and storage. The effects of fire and grazing as interactive factors have been

minimally studied; however, Archibald et al. (2005) found that fire affects grazing by altering large-scale foraging patterns and suggested that the new growth after fire attracts grazers onto frequently burned sites. Additionally, they found that grazers affect fire by reducing fuel loads and altering fire spread in a landscape which may ultimately reduce the amount of material susceptible to fire derived wind erosion.

Although the interactions between fire and grazing cannot be assessed directly in South Africa, we can speculate about interactive factors based on their independent relationships and on their comparisons to Konza. Like the plants and soils at grazed Konza sites, those from Satara and Ukulinga exhibited similar general relationships to fire and grazing in that burned sites had greater BSi amounts in plants and soils than unburned sites. Unlike the Konza sites, the grazed Satara sites had greater BSi amounts than the ungrazed Ukulinga sites; however, this difference may be attributed to other site factors and not directly a grazing effect. In the plants and soils of Satara and Ukulinga, the effects of fire and grazing on Si production and storage appear to have been independent. Biogenic silica content in plants at the ungrazed Ukulinga sites were greater when burned annually, but BSi was predominantly greater at the grazed Satara sites in plants and soils.

South African plants and soils take up and store significantly greater ( $P < 0.05$ ) amounts of BSi than North American plants and soils when compared in the end-member fire treatments with grazing, indicating that North American and South African systems respond differently to the combined effects of the key ecological drivers, with respect to Si production and storage. This difference in BSi production and storage between North American and South African sites is likely linked to differences in their age and

evolutionary history. The results suggest that the dominant South African plants sampled may have developed a defense mechanism against herbivory in response to its long history of grazing. Grazing activity often enhances the cycling of other nutrients (McNaughton 1983) and may increase Si concentrations in grasses (McNaughton et al. 1985; Gali-Muhtasib et al. 1992).

Although our BSi concentration data suggest that there is not a requirement of plants to take up greater concentrations of Si in response to fire or grazing, we did not sample identical plant species across sites. Changes in species composition as a result of fire or grazing may indeed cause differences in overall BSi storage as different species take up different concentrations of Si; however, this direct physiological response needs to be addressed in subsequent studies. We suggest that mass differences of BSi in plants among treatments result from differences in ANPP and are indirectly affected by fire and grazing in their individual instances.

Soil to plant BSi ratios imply that South African plant BSi values are better predictors of BSi soil storage than North American plants. Generalized soil storage estimations may be made from plant BSi data using  $y=0.8229x+5.0624$ ; however, this equation was best suited for South African sites and only considered plant and soil components of the Si cycle. The other approximate 50% of the variability in soil BSi concentration that was not accounted for by plant BSi concentration may be influenced by primary mineral dissolution, secondary mineral formation, atmospheric deposition, and leaching outputs (Figure 2.1). South African soils may stockpile greater proportions of BSi in the soil from what is provided by plant decomposition than North American systems.

Unlike the North American soils, the South African soils did not show a trend between soil BSi and organic carbon. The soils of South Africa are older and more weathered than the North American soils and therefore South African systems may cycle soil BSi more rapidly. Silicon from mineral/nonbiogenic pools may be an additional and perhaps a greater Si source than in North America. This combination of Si supply from biogenic and nonbiogenic sources would diminish the direct correlation with SOC because it is biologically mediated. Evolutionarily, the North American plants may not have adapted the need for additional Si uptake and their Si source may be solely from the soil BSi pool.

### **Summary and Conclusions**

In this study, it appears that quantities of BSi aboveground are coupled to quantities found in the soil, suggesting that fire and grazing do not negatively affect the total BSi pool size in these grassland systems. Leaching of BSi was not considered a major vector of loss because in water limited ecosystems such as grassland and savanna environments silica precipitates in the soil and leaching loss is probably more important over pedogenic scales (Schaetzl & Anderson 2005). Plant and soil BSi values appear to be influenced directly by ANPP and thus, indirectly by fire and grazing. However, on a mass per area basis, BSi cycling between South African plants and soils may be more responsive to grazing than North American sites, and may promote Si release via chemical weathering as Si supplied by soil labile BSi reservoirs are transported. The additional source of Si from mineral dissolution may make South African sites less correlative with SOC and biologic turnover compared to North American sites.

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# C HAPTER THREE

## Lithologic Controls on Biogenic Silica Cycling in South African Savanna Ecosystems

## **Introduction**

Growing evidence exists for a major role of biologically mediated silica cycling in regulating silica storage and mobility in the terrestrial environment (Conely 2002; Blecker et al. 2006). In some ecosystems, this biogenic silica (BSi) can comprise up to 80% of the soluble silica pool (Derry et al. 2005) that is readily mobile through leaching or erosional loss. It is generally more labile than mineral silica and is likely an important source of silica export from terrestrial ecosystems to rivers and estuaries (Conley et al. 2002).

Grassland ecosystems are a particularly large reservoir of BSi (due to dominance by grasses with relatively high silica content) where the relationship between BSi production and storage has been linked to climate (Kelly et al. 1998; Blecker et al. 2006), plant type and productivity (Blecker et al. 2006; Saccone et al. 2007), and key ecological drivers such as fire and grazing (Melzer et al. in review). In general, increased chemical weathering and biological activity in grassland ecosystems will result in increased BSi production by plants and storage in soils.

The literature is replete with studies that focus on the influence of parent material on weathering rates, soil nutrients (Hamdan & Burnham 1996) and the physical properties that influence the hydrologic regime of soils (Osher & Buol 1998). However, little is known about the importance of parent material on the biogeochemical cycling of silica. Identifying the key geologic controls on the mobilization of BSi would further constrain estimates of the range and variability of silica that is released through biologically mediated weathering processes.

The most common rock types used as “weathering endpoints” in the majority of studies are of granitic and basaltic composition. These lithologies are widespread in a variety of terrestrial ecosystems and their compositional and structural differences set the range and variability of soil properties found within a single ecosystem (Stephen 1952; Plaster & Sherwood 1971). In general, mafic basalts are more easily weathered than other silicate rocks (Maybeck 1986; Amoitte-Suchet & Probst 1993) like felsic granites, and contribute nutrients more readily to the system that are essential to maintain soil fertility and ecosystem productivity. Continental basalts make up a surface area of  $6.8 \times 10^6$  km<sup>2</sup> which represents ~ 4.6% of the continental surface or 8.4% of the global silicate area (Amiotte-Suchet et al. 2003; Dessert et al. 2003). The weathering of continental basalts alone contributes to  $4.08 \times 10^{12}$  mol/yr C consumption which represents ~ 30% of the C sequestered by chemical weathering of continental silicates (Milliman & Syvitski 1992; Dessert et al. 2003). The remaining C flux is derived from the weathering of granitic and sedimentary rocks. Although granitic rocks weather at a slower rate and contribute less to carbon sequestration during weathering, they contain more silica for a longer-term supply to both diatoms and terrestrial plants

Although the geochemical weathering of silicate minerals is a slow process (Lerman 1988), it is accelerated by the effects of plant growth (Richter & Markewitz 1995). Meunier (2003) demonstrated that the inclusion of plants increased estimates of geochemical weathering by a factor of up to eight. Several key mechanisms are identified as directly influencing weathering, namely, production of CO<sub>2</sub> and organic acids (Berner 1992), and biocycling of metals (Drever 1994) and silica (Kelly et al.

1998). The identification of the key underlying mechanisms, however, vary as a function of climate and ecosystem (Berner 1992).

The transformation of inorganic Si to BSi is driven by plants as they take up Si in the form of monosilicic acid ( $\text{Si}(\text{OH})_4$ ) and transform it into BSi, (e.g. phytolith or more soluble forms of  $\text{SiO}_4 \times n\text{H}_2\text{O}$ ) (Raven 1983; Piperno 1988; Datnoff et al. 2001). In general, plants accumulate Si from <0.5 to 15 wt. % (Epstein 1994). Biogenic silica is found in the greatest quantities in grasses, comprising up to ~10% of their dry weight (Lovering 1959; Kelly 1989; Kelly et al. 1991). When plants die and decompose, BSi enters the soil system where it may be distributed throughout the profile by physical translocation and chemical dissolution (Bartoli 1981, 1983). Soil BSi typically makes up ~3-5% by weight on a total soil basis (Drees et al. 1989; Kelly 1989), but may range from <0.5 to 5 wt. % (Jones & Beavers 1964; Alexandre et al. 1997; Clarke 2003). In comparing BSi to mineral silicate dissolution, BSi dissolution is 5 orders of magnitude faster because of its greater solubility (Lindsay 1979; Hurd 1983). The degree to which BSi is translocated within soils is dependent on temperature, particle size, chemical composition and the presence of disrupted layers (Drees et al. 1989). In general, BSi accumulates in soils when its production rate exceeds its dissolution and physical removal rate (Kelly et al. 1991; Meunier 2003; Blecker et al. 2006).

The takeup of Si by plants has been shown by Kelly et al. (1998) and others to significantly affect weathering processes and soil formation. Estimates of silicate weathering rates and contributions to the riverine Si flux are variable. Most studies agree that as much as 80% of the total Si inputs to oceans are from rivers (Treguer et al. 1995) and others have estimated that as much as 16% of the total Si is biogenically derived

(Conley 1997). Other detailed studies in tropical ecosystems have suggested that BSi inputs into soil solution and subsequent delivery to riverine systems can be much higher depending on local edaphic conditions (Alexandre et al. 1997; Derry et al. 2005). Although silicate mineral weathering is the primary source of Si to soil solution, the short term source to plants and the retention in terrestrial ecosystems is strongly influenced by the amounts and chemical mobility of BSi (Farmer et al. 2005). The effect of labile BSi dissolution with regard to positive or negative feedbacks on the weathering of rocks with different primary mineral assemblages is not completely understood and should contribute necessary information to determine the fate and mobility of Si in soils of terrestrial ecosystems.

The primary goal of this study was to examine mineral Si and plant and soil BSi pools in a savanna ecosystem and to determine the effect of differing soil parent material on BSi cycling. Soils forming in parent materials that compositionally fall within the range of basalts and granites are analyzed under two different climatic regimes in South Africa.

## **Methods**

### *Study Area*

Kruger National Park (KNP) is located in the ~2 million ha area situated in the continental interior, lowveld region of the Limpopo and Mpumalanga provinces of northeastern South Africa (Figure 3.1). The north-south trending park extends ~350 km and covers two climatic zones: the lowveld bushveld zone in the south (rainfall of 500-700 mm/y) and the arid bushveld zone in the north (rainfall of 300-500 mm/y) (Venter

2003). Both climatic zones are classified as dry, low latitude steppe by the Koppen climate classification. Seven major rivers flow across the savanna biome and dissect the granitic and basaltic substrate from west to east, respectively.

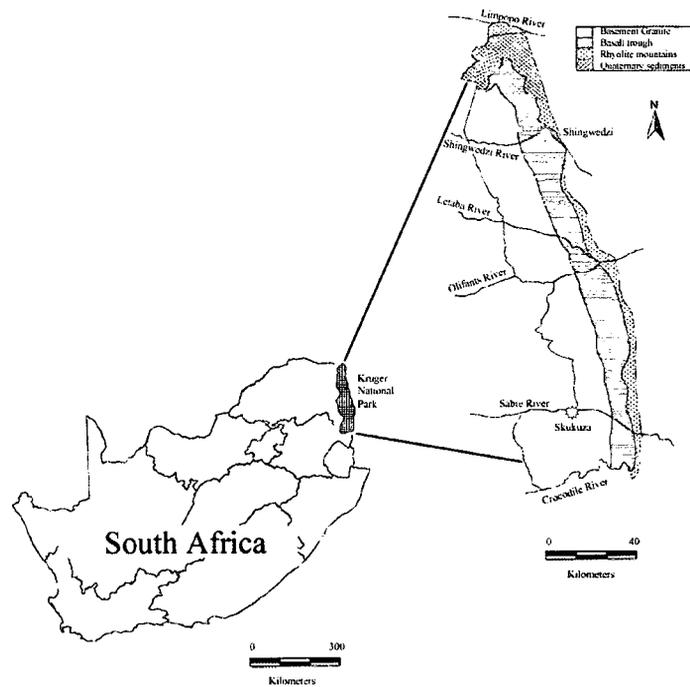


Figure 3.1. The site locations in Kruger National Park in South Africa at Shingwedzi and Skukuza. (Adapted from Van Reit and Cooks 1990)

The rocks in KNP display a long geologic history which has been described in detail by Schutte (1974), Bristow (1980), Bristow & Venter (1986) and Venter (1990). The oldest material exposed at KNP is part of the granitic and gneissic basement complex, ~3.5 Ga in age (Barton et al. 1986), which forms most of the gently rolling western portion of the park. The flatter eastern portion of the park is of the Karoo Sequence which is primarily basaltic and rhyolitic rocks (Van Riet & Cooks 1990), ~300 Ma in age. This study was conducted on soils developed from a complex suite of rocks

that are compositionally similar to basalts (pedons 1 & 3) and granites (pedons 2 & 4) in both climatic regions of the park near Shingwedzi, along the Shingwedzi River in the north and near Skukuza along the Sabie River in the south (Figure 3.1). Slight compositional variations exist between typical basalts and granites and the rocks of this study. However, for the purpose of this study, the rocks are referred to as basalts and granites and their overlying soils are referred to as basaltic and granitic soils respectively. Khomo (2009) recognized a distinction between the Skukuza and Shingwedzi granitic lithologies in which, the latter exhibited migmatization and migmatite fractionation during weathering. Migmatite and its fractionation was less prevalent at Skukuza as was shown by their average Ti and Zr concentrations. The climatic and lithologic differences among the sites allowed us to study the effects of soil parent material on BSi cycling under two semiarid climatic regimes (Table 3.1).

### *Field Sampling*

Soil pit locations were selected based on their topographic positioning, substrate and vegetation, and accessibility. Hand-dug pits were excavated on broad level upland crest positions to minimize the effects of run-on/run-off and climatic impacts on weathering. Four full pedons, representing each lithologic-climatic pair, were described and sampled based on genetic horizons according to procedures of the USDA Natural Resources Conservation Service (Schoeneberger et al. 1998). Samples were shipped from the field to the laboratory in quart-sized plastic bags in coolers. Rock parent material samples were obtained from rock underneath soils. However, due to the migmatite fractionation during weathering, parent material data for granitic sites were

obtained from published data in the literature for outcrop rocks (Vorster 1979; Khomo et al. 2009). Unlike the rocks under soil, these outcrop rocks retain the geochemical composition of unfractionated migmatite (Robb 1977). The dominant grass species were sampled adjacent to the soil pits (Table 3.1) and combined into a bulk sample for analyses.

Table 3.1. Climatic and site property data for four locations within Kruger National Park

| Site Properties                     | Site Location                |                              |
|-------------------------------------|------------------------------|------------------------------|
|                                     | Shingwedzi                   | Skukuza                      |
| Latitude/Longitude                  |                              |                              |
| Granite                             | 7451196N, 0322428E           | 7231971N, 0348678E           |
| Basalt                              | 7443514N, 0342778E           | 7224605N, 0394825E           |
| MAP, mm <sup>†</sup>                | 454                          | 599                          |
| MAT, °C <sup>‡</sup>                | 23                           | 22                           |
| ANPP, g/m <sup>2</sup> <sup>§</sup> |                              |                              |
| Granite                             | 445                          | 329                          |
| Basalt                              | 473                          | 417                          |
| Climate <sup>¶</sup>                | BSh                          | BSh                          |
| Biome                               | Savanna                      | Savanna                      |
| Grass Species                       |                              |                              |
| Granite                             | <i>Cedrus ciliaris</i>       | <i>Eragrostis rigidior</i> , |
| Basalt                              | <i>Bothriochloa radicans</i> | <i>Cymbopogon plurinodis</i> |
|                                     |                              | <i>Themeda triandra</i> ,    |
|                                     |                              | <i>Heteropogon contortus</i> |

<sup>†</sup> MAP= Mean annual precipitation (Codron et al. 2005)

<sup>‡</sup> MAT= Mean annual temperature (Ventor 1990)

<sup>§</sup> ANPP= Aboveground annual net primary productivity

<sup>¶</sup> Based on Koppen Climate Classification System; BSh= Dry low latitude steppe

### *Soil and Water Analyses*

Soil samples were air dried and sieved through a 2 mm (#10 mesh) sieve. Samples for C analysis were ground in a ball mill and oven dried. Total C were analyzed on a LECO-TruSpec CN analyzer at the Natural Resource Ecology Laboratory at Colorado State University. Subsamples of the ground oven dried soils were also used for

inorganic carbon analysis by Pressure Transducer (Harris et al. 2001). Samples were exposed to 6N HCl in a capped and sealed glass bottle. The soil reacted with the HCl to evolve CO<sub>2</sub> during a 2 hr period at which time the pressure inside the bottle was measured. Measured values were converted to concentrations using a calibration curve generated from known concentrations of CaCO<sub>3</sub> standards. Organic carbon concentrations were determined by subtracting inorganic carbon from total carbon concentrations.

Soil texture on <2 mm unground soil was determined using the hydrometer method (Gee & Bauder 1986). Bulk density was determined by the clod method (Blake & Hartge 1986). Clods from pedon 3 were extremely fragile and were not useable upon their return to the laboratory. Pedon 3 bulk density was therefore estimated using the linear equation  $y=0.6961x+0.2873$  which, compared empirically derived bulk density (Adams 1973; Rawls 1983) with the clod values. Parent material bulk densities were 2.9 for basalts and 2.8 for granites (Mussett & Khan 2000). Soil pH was determined on air-dried soil using the soil:water (1:1) method and Orion Model 420A pH meter.

Mineral Services of SGS Canada Inc., Toronto, conducted total elemental analysis on pulverized soil samples. Inductively coupled plasma atomic emission spectroscopy (ICP-OES) analyzed pulverized samples for Al, Ca, Cr, Fe, K, Mg, Mn, Na, P, Si, Ti, Ba, Nb, Sr, Y, Zn, and Zr after Li-metaborate fusion.

Mineralogy was determined on a Scintag PADV from 2° to 65° 2θ at 2° per minute with Cu-radiation (University of Colorado, Boulder). Clay samples were additionally exposed to ethylene glycol and scanned at 2° to 20° 2θ at 2° per minute to

identify the 2:1 expandable clays from the 1:1 clays. Rock thin section analysis was also conducted for mineralogical composition.

Si content of the soil solution (dissolved silica, DSi pool) was determined using a saturation paste extraction method (Lajtha et al. 1999). The pre-weighed, 2 mm sieved soils were saturated with DI water and well mixed to form glistening pastes. The pastes were then left to equilibrate for 48 h. After 48 h, the saturated pastes were filtered through Whatman no. 42 filter paper in a 10 cm Buchner funnel. The filtrates were then filtered a second time through a 0.2  $\mu\text{m}$  polycarbonate membrane in preparation for ICP-Si analysis.

### *Biogenic Silica Analyses*

Biogenic silica was recovered from dominant plant species using a gravimetric approach (Blecker et al. 2006) adapted from Piperno (1988), Kelly (1990), and Parr et al. (2001) in which samples were washed, ashed, chemically treated, filtered and weighed. Approximately 10 g of 2-3 cm length oven dried plant material were cleaned with a solution of 5% sodium hexametaphosphate, 10% HCl and de-ionized water (DI) in a 1:1:8 ratio, respectively. Samples were then thoroughly rinsed with DI, treated with 80°C, 70% ethanol to strip them from their waxy coatings, and rinsed with DI water again. They were dried at 65°C in preparation for dry ashing. Pre-weighed subsamples of washed and dried plant material were placed in ceramic crucibles and ashed for 2 h in a muffle furnace at 500°C after which they were allowed to cool in a dessicator and weighed. The resultant ash was then treated at a temperature of 65°C with 10% HCl, filtered through pre-weighed 0.2  $\mu\text{m}$  polycarbonate membranes, treated at a temperature

of 65°C with 30% H<sub>2</sub>O<sub>2</sub> and filtered again through pre-weighed 0.2 µm polycarbonate membranes. Samples were oven dried at 60°C and weighed, after having been rinsed thoroughly with DI water. Plant biogenic silica concentrations were converted to a mass/volume by incorporating aboveground net primary productivity. Only standing crop biomass data was available for the study sites; aboveground net primary productivity data was limited in KNP and, thus, a correction was applied to the study sites using data from Satara, KNP in which both standing crop data and ANPP data exist (Greg Buis, unpublished data, personal communication).

Soil BSi was extracted by the alkaline wet chemical dissolution method using the weak base Na<sub>2</sub>CO<sub>3</sub>. Although the Na<sub>2</sub>CO<sub>3</sub> method has primarily been used by scientists studying aquatic systems (DeMaster 1981; Conley 1998), we, along with our colleagues, found it suitable for recovery of BSi from soils of terrestrial ecosystems (Saconne et al. 2006, 2007; Sauer et al. 2006). Approximately 30 (± 0.05) mg of hand-ground freeze-dried soil were measured into 60 mL polypropylene round flat-bottom bottles with 40.0 mL of 1% Na<sub>2</sub>CO<sub>3</sub>. Bottles were placed in an 85°C shaking water bath for a total of 3, 4 and 5 h at which times 1.0 mL aliquots were removed for analysis. Analysis for dissolved Si was conducted using the molybdate blue spectrophotometric method where the spectrophotometer was set at 812 nm (Mortlock & Froelich 1989), a modification from the reduced molybdosilicic acid spectrophotometric method (Strickland & Parsons 1968; Fanning & Pilson 1973). Disodium hexafluorosilicate, 99+% Na<sub>2</sub>SiF<sub>6</sub> from Alfa Aesar (Ward Hill, MA), was dissolved in high purity water to make a stock standard solution. The solubility differences between BSi and mineral Si cause them to go into solution (of Na<sub>2</sub>CO<sub>3</sub>) at different rates. The dissolution of BSi has been shown to occur

within the first 2 h, whereas mineral Si (specifically clay minerals) continues to go into dissolution at a constant rate long after (DeMaster 1981; Koning et al. 2002; Saccone et al. 2006). Thus, BSi can be calculated from the intercept of the linear portion of the mineral Si dissolution curve (DeMaster 1981; Koning et al. 2002). Soil Si concentrations were converted to a mass/volume by incorporating depth and bulk density data. The total mass/volume value for a particular pedon is found from the sum of its horizons.

### *Mass Balance*

Geochemical mass balance is a tool used to quantify weathering on the basis of volume change and parent material composition. Specifically, it uses the amounts of stable constituents to quantify the gains and losses of less stable material during pedogenesis. The products of primary mineral weathering can be partitioned into three major groups: 1) release of ions or molecules into solution, 2) the production of new secondary minerals and 3) the residual accumulation of insoluble material (Bland & Rolls 1998). The relative partitioning of elements among the solution, secondary minerals and residual mineral fractions is dependent on the rate of weathering, the composition of minerals in the parent material and the mobilities of the ions in the soil geochemical environment. The mass balance approach allows us to assess the degree of weathering by calculating the volume changes associated with the mass fluxes (gains and losses) within soil horizons and among soils.

Strain,  $\epsilon_{i,w}$ , is a volumetric change in the soil that is facilitated by mass flux. It is calculated by comparing volumes of parent material and soil (Brimhall & Dietrich 1987; Chadwick et al. 1990; Brimhall et al. 1992) as follows:

$$\varepsilon_{i,w} = \frac{(\rho_p C_{i,p})}{(\rho_w C_{i,w})} - 1$$

where  $\rho$  is soil bulk density,  $w$  is the soil horizon,  $p$  is parent material and  $C_i$  is the concentration of an immobile element. Positive strain denoted dilation or volume gain and negative strain denoted collapse or volume loss. Conservative elements defined above may include Zr, Ti, Nb, and Y.

Element mobility within the soil is characterized by the mass transfer coefficient,  $\tau_{j,w}$ , to examine weathering and Si flux. Mass transfer was computed from density, chemical composition data and volume change (Brimhall & Dietrich 1987; Chadwick et al. 1990; Brimhall et al. 1992) as follows:

$$\tau_{j,w} = \frac{(\rho_w C_{j,w})}{(\rho_p C_{j,p})} (\varepsilon_{i,w} + 1) - 1$$

where  $C_j$  is the concentration of a chemical species and  $\varepsilon_{i,w}$  is the volumetric strain. Zirconium was used as the conservative element or reference point for this study and its selection was based on transported mass fraction vs. strain comparisons (with Zr and Ti immobile elements) as well as comparisons with clay and sand abundances. Bedrock was the parent material for all pedons. The bedrock basalt from pedon 1 was applied to pedon 3 because no exposure to bedrock existed for the latter. All mass balance calculations were conducted to a soil depth of 100 cm.

## Results

### *Physical, Chemical and Mineralogical Composition of the Soils*

Regardless of parent material and precipitation regimes, soils possess similar morphological features (Table 3.2). In general, all pedons have thin A horizons and multiple Bw horizons with fine to medium subangular blocky structure. Basaltic soils, however, have larger and more stable soil aggregates relative to the granitic soils. This more advanced structural morphology is likely due to the accompanying greater contents of organic carbon and clay. At both Shingwedzi and Skukuza sites, the basaltic soils had greater amounts of clay and lower sand content, lower bulk density, and greater organic carbon than their granitic counterparts (Table 3.2).

Within each of the climatic zones, the pH values of basaltic soils were generally higher than their granite counterparts. Variations in pH among soils of similar parent materials were greater, as more acidic (lower) pH values were obtained in the higher precipitation zone (Skukuza) (Table 3.2).

Table 3.2. Morphological descriptions for each of the four pedons within Kruger National Park

| Site location/<br>lithology | Pedon | Diagnostic<br>Horizon | Depth<br>(cm) | Bulk<br>Density<br>(g/cm <sup>3</sup> ) | Texture | pH  | Organic<br>Carbon<br>(%) | Color<br>moist/dry         | Structure            |
|-----------------------------|-------|-----------------------|---------------|---|---------|-----|--------------------------|----------------------------|----------------------|
| Shingwedzi/<br>Basalt       | 1     | A                     | 0-5           | 1.4                                     | C       | 7.1 | 2.4                      | 10YR 2/1<br>10YR 3/1       | 1 f sbk              |
|                             |       | BA                    | 5-31          | 1.7                                     | C       | 6.6 | 2.0                      | 10YR 2/1<br>10YR 3/1       | 3 f sbk              |
|                             |       | Bw1                   | 31-75         | 1.4                                     | c       | 7.3 | 1.9                      | 10YR 2/1<br>10YR 3/1       | 2 f sbk              |
|                             |       | Bw2                   | 75-100        | 1.6                                     | C       | 7.6 | 1.4                      | 10YR 2/1<br>10YR 3/1       | 1 f sbk              |
| Shingwedzi/<br>Granite      | 2     | A                     | 0-1           | 1.4                                     | SI      | 6.7 | 1.1                      | 10YR 3/3<br>10YR 4/4       | 0 sg                 |
|                             |       | Bw1                   | 1-13          | 1.5                                     | SI      | 6.6 | 0.6                      | 10YR 2/2<br>10YR 4/3       | 1 vf sbk             |
|                             |       | Bw2                   | 13-22         | 1.7                                     | SI      | 6.8 | 0.4                      | 10YR 3/3<br>10YR 4/4       | 2 m sbk              |
|                             |       | Bw3                   | 22-45         | 1.7                                     | SI      | 6.6 | 0.4                      | 7.5YR 3/3<br>7.5YR 4/4     | 2 f sbk              |
| Skukuza/<br>Basalt          | 3     | A                     | 0-8           | 1.5                                     | Cl      | 5.9 | 2.22                     | 5YR 2.5/2<br>5YR 3/3       | 2 m gr/<br>2 m sbk   |
|                             |       | Bw1                   | 8-19          | 1.3                                     | Cl      | 6.0 | 1.91                     | 5YR 2.5/2<br>5YR 3/3       | 1 m f gr/<br>1 f sbk |
|                             |       | Bw2                   | 19-32         | 1.6                                     | Cl      | 6.3 | 1.01                     | 2.5YR 2.5/3<br>2.5YR 2.5/4 | 1 m sbk              |
|                             |       | C1                    | 32-46         | 1.7                                     | Scl     | 6.6 | 0.53                     | 7.5YR 3/4<br>7.5YR 4/4     | 0 ma                 |
|                             |       | C2                    | 46+           | 1.7                                     | Scl     | 6.4 | 0.36                     | 7.5YR 3/4<br>7.5YR 4/4     | 0 ma                 |
| Skukuza/<br>Granite         | 4     | A                     | 0-15          | 1.7                                     | SI      | 5.0 | 0.48                     | 7.5YR 2.5/3<br>7.5YR 5/4   | 1 f-m sbk            |
|                             |       | Bw1                   | 15-41         | 1.8                                     | SI      | 4.7 | 0.33                     | 7.5YR 3/4<br>7.5YR 4/4     | 1 f-m-co<br>sbk      |
|                             |       | Bw2                   | 41-62         | 1.8                                     | SI      | 4.7 | 0.26                     | 5YR 4/4<br>7.5YR 5/4       | 1 f sbk/<br>1 f-m gr |
|                             |       | Bw3                   | 62-95         | 1.9                                     | SI      | 5.0 | 0.24                     | 7.5YR 4/4<br>7.5YR 6/4     | 1 vff gr/<br>Sg      |
|                             |       | C                     | 95-105        | 1.9                                     | SI      | 4.7 | 0.20                     | 10YR 4/3<br>10YR 6/4       | 0 ma                 |

The chemical composition of the granites and basalts used for our mass balance determinations are presented in Table 3.3. Granites at Shingwedzi and Skukuza were uniform with a < 3% difference in elemental concentration in the major and less than 4% in the intermediately abundant elements Si and Al, and Ca, Na, K and Fe respectively (Table 3.3). The minor granitic constituents Mg and P were less than 0.3% different and

Zr and Ti were less than 0.02% different from Shingwedzi to Skukuza. Basalt was not exposed at Skukuza so data used was derived from Shingwedzi basalt samples.

Table 3.3. Chemical composition of rock parent material for each of the four pedons within Kruger National Park

|                                | Shingwedzi  |         | Skukuza |         |
|--------------------------------|-------------|---------|---------|---------|
|                                | Basalt      | Granite | Basalt  | Granite |
|                                | -----%----- |         |         |         |
| SiO <sub>2</sub>               | 53.05       | 70.59   | 53.05   | 68.45   |
| Al <sub>2</sub> O <sub>3</sub> | 13.23       | 15.68   | 13.23   | 14.74   |
| Fe <sub>2</sub> O <sub>3</sub> | 9.01        | 1.86    | 9.01    | 3.00    |
| CaO                            | 5.04        | 2.10    | 5.04    | 3.08    |
| MgO                            | 3.81        | 0.50    | 3.81    | 0.78    |
| Na <sub>2</sub> O              | 2.29        | 5.53    | 2.29    | 2.43    |
| K <sub>2</sub> O               | 4.46        | 1.93    | 4.46    | 5.06    |
| TiO <sub>2</sub>               | 3.84        | 0.28    | 3.84    | 0.30    |
| P <sub>2</sub> O <sub>5</sub>  | 0.69        | 0.14    | 0.69    | 0.05    |
| Zr                             | 0.06        | 0.01    | 0.06    | 0.01    |

The granites are primarily composed of quartz and plagioclase with some microcline and minor amounts of ferromagnesian minerals (Table 3.4). Kaolinite and mica make up a majority of the clay fraction. Textural evidence from petrographic analysis suggests a metamorphic overprint on the granitic rocks (Figure 3.2). Evidence of low temperature alteration or weathering is apparent in altered biotite grains, the replacement of epidote for plagioclase and the in filling of faults and fractures by epidote. The basalts are made up of a fine groundmass of plagioclase with minor phenocrysts of olivine and opaques. Kaolinite and mica make up the majority of the clay mineralogy in the Skukuza basaltic soils, but mica and smectite make up the majority of the clay mineralogy in the Shingwedzi basaltic soils.

Table 3.4. Primary and secondary mineralogical composition in basaltic and granitic soils within Kruger National Park

| Lithology      | Major primary mineral constituents | Minor primary mineral constituents | Clay mineral constituents |
|----------------|------------------------------------|------------------------------------|---------------------------|
| Basaltic soils | plagioclase                        | olivine, opaques                   | smectite, kaolinite, mica |
| Granitic soils | quartz, plagioclase, microcline    | biotite, epidote                   | kaolinite, mica           |

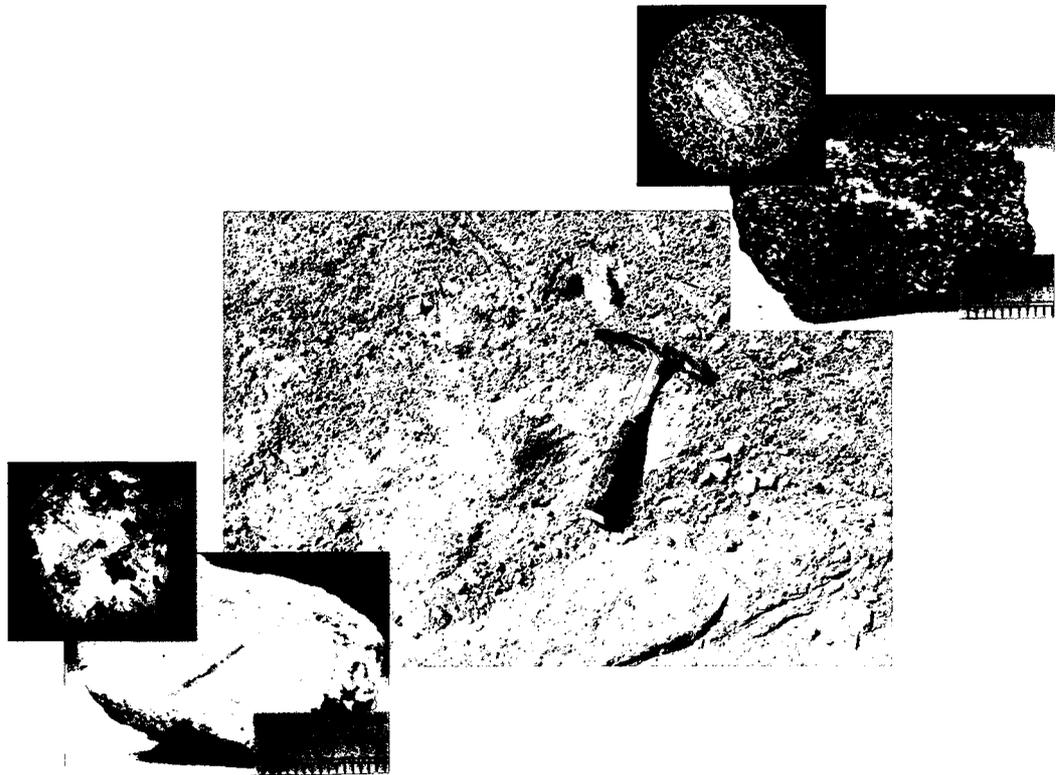


Figure 3.2. Outcrop, hand sample, and thin section photos of granitic (lower left) and basaltic (upper right) rock parent materials.

### *Pedon Transformation and Elemental Transfers*

Granitic soils exhibited up to 5% collapse and up to 27% dilation at the drier Shingwedzi site and up to 36% collapse at the wetter Skukuza site (Figure 3.3). Both granitic soils exhibited consistent strain with depth. Although the granitic Shingwedzi soils do not show significant collapse, these soils have net elemental loss in each horizon for each element which suggests isovolumetric weathering and alteration of these soils. Silicon and Al show consistent losses with depth where the greatest losses are at the surface (Table 3.5). Base cations do not show a clear depth distribution in terms of their transport. The granitic Skukuza soils show greater loss in all cations except Na than at Shingwedzi. They also exhibit a depth distribution for Si, Al and Mg. The greater losses at Skukuza are likely due to the increased precipitation experienced by this site and the depth distributions likely are a result of more intense weathering experienced at the surface of all soils. The base cations do not show this depth distribution as they are biocycled and greater losses of these with depth would indicate active mining by plant roots from deeper horizons.

The basaltic soils exhibited dilation which varied with depth at both sites. Dilation increased with depth in the basaltic Skukuza soils to nearly three times its original volume and increased in the A and Bw1 horizons in the basaltic Shingwedzi soils to nearly double its original volume (Figure 3.3). Similar to the granitic soils, the base cations from basaltic Shingwedzi soils showed a net loss throughout their depths; however, only Mg had a trend with depth. Silicon and Al showed net gains and their depth distributions may indicate their incorporations into secondary mineral formations. Skukuza basaltic soils exhibit cation loss at the surface and gains with depth (Si, Al and

Mg) or continued loss with depth with greatest losses at the surface (Ca and Na). In both granitic and basaltic soils, mass transport calculations suggest that strain is primarily attributed to base cation transfers within the pedons (Table 3.5). The incorporation of water and carbon may also contribute to dilation, especially in the basaltic soils.

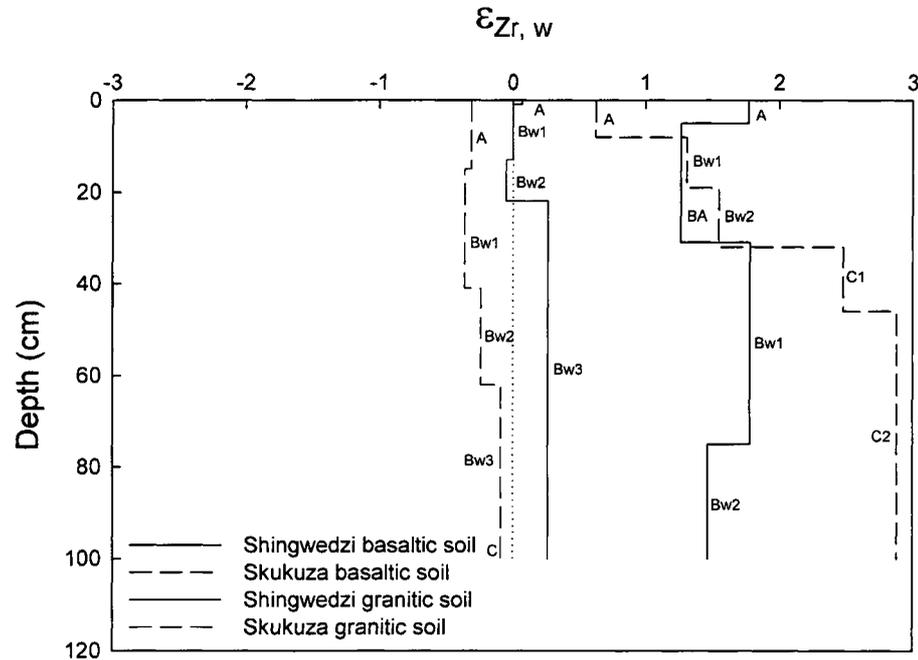


Figure 3.3. Strain ( $\epsilon_{zr,w}$ ) as a function of a depth to 100 cm for soils derived from basalt and granite at Shingwedzi and Skukuza. Dotted horizontal line represents zero strain or zero volume change. Positive strain denotes dilation or volume gain and negative strain denotes collapse or volume loss. Strain calculations used zirconium as the immobile element.

Table 3.5. Select elemental constituents and their mass transfers for each horizon for each pedon within Kruger National Park

| Site:<br>Lithology            | Pedon:<br>Horizon   | Si          | Al  | K   | Ca  | Na  | Mg  | Si   | Al                          | K    | Ca   | Na   | Mg    |
|-------------------------------|---------------------|-------------|-----|-----|-----|-----|-----|------|-----------------------------|------|------|------|-------|
|                               |                     | -----%----- |     |     |     |     |     |      | -----T <sub>j,w</sub> ----- |      |      |      |       |
| Shingwedzi:<br>basaltic soils | 1: A                | 25.2        | 6.1 | 2.5 | 1.1 | 0.8 | 1.2 | 0.4  | 0.2                         | -0.1 | -0.6 | -0.4 | -0.3  |
|                               | 1: BA               | 23.8        | 6.2 | 2.4 | 1.1 | 0.7 | 1.4 | 0.3  | 0.2                         | -0.1 | -0.6 | -0.5 | -0.19 |
|                               | 1: B <sub>w</sub> 1 | 23.9        | 6.1 | 2.4 | 1.2 | 0.8 | 1.6 | 0.3  | 0.2                         | -0.1 | -0.6 | -0.4 | -0.07 |
|                               | 1: B <sub>w</sub> 2 | 24.4        | 6.2 | 2.3 | 1.1 | 0.8 | 1.7 | 0.3  | 0.2                         | -0.2 | -0.6 | -0.4 | 0.01  |
| Shingwedzi:<br>granitic soils | 2: A                | 33.9        | 6.9 | 1.6 | 1.0 | 2.4 | 0.2 | -0.4 | -0.6                        | -0.5 | -0.6 | -0.7 | -0.64 |
|                               | 2: B <sub>w</sub> 1 | 33.7        | 7.2 | 1.7 | 1.0 | 2.3 | 0.3 | -0.4 | -0.5                        | -0.4 | -0.6 | -0.7 | -0.45 |
|                               | 2: B <sub>w</sub> 2 | 33.7        | 7.3 | 1.7 | 0.9 | 2.3 | 0.2 | -0.4 | -0.5                        | -0.4 | -0.7 | -0.7 | -0.61 |
|                               | 2: B <sub>w</sub> 3 | 34.4        | 7.2 | 1.7 | 0.8 | 2.4 | 0.2 | -0.2 | -0.3                        | -0.2 | -0.6 | -0.5 | -0.48 |
| Skukuza:<br>basaltic soils    | 3: A                | 22.8        | 6.5 | 1.6 | 1.1 | 0.7 | 0.6 | -0.2 | -0.2                        | -0.6 | -0.8 | -0.6 | -0.78 |
|                               | 3: B <sub>w</sub> 1 | 20.1        | 7.2 | 1.3 | 1.0 | 0.8 | 0.6 | -0.2 | 0.1                         | -0.6 | -0.7 | -0.5 | -0.74 |
|                               | 3: B <sub>w</sub> 2 | 19.7        | 8.5 | 1.0 | 2.0 | 0.9 | 1.1 | 0.1  | 0.7                         | -0.6 | -0.2 | -0.3 | -0.31 |
|                               | 3: C1               | 19.3        | 8.2 | 0.7 | 3.5 | 1.1 | 1.9 | 0.6  | 1.4                         | -0.6 | 1.0  | 0.4  | 0.65  |
|                               | 3: C2               | 20.8        | 7.7 | 0.6 | 4.8 | 1.4 | 2.5 | 0.9  | 1.5                         | -0.6 | 2.0  | 0.8  | 1.43  |
| Skukuza:<br>granitic soils    | 4: A                | 36          | 6.3 | 3.0 | 0.6 | 1.7 | 0.0 | -0.5 | -0.7                        | -0.7 | -0.9 | -0.6 | -1.0  |
|                               | 4: B <sub>w</sub> 1 | 35.5        | 6.4 | 3.1 | 0.6 | 1.7 | 0.1 | -0.5 | -0.7                        | -0.7 | -0.9 | -0.6 | -0.9  |
|                               | 4: B <sub>w</sub> 2 | 35.8        | 6.4 | 3.1 | 0.5 | 1.6 | 0.1 | -0.5 | -0.6                        | -0.6 | -0.9 | -0.6 | -0.9  |
|                               | 4: B <sub>w</sub> 3 | 35.7        | 6.3 | 2.8 | 0.5 | 1.7 | 0.1 | -0.3 | -0.5                        | -0.6 | -0.9 | -0.4 | -0.9  |
|                               | 4: C                | 34.8        | 6.7 | 2.9 | 0.5 | 1.8 | 0.1 | -0.5 | -0.6                        | -0.7 | -0.9 | -0.6 | -0.9  |

Soil elemental flux for each pedon are consistent with the volume changes represented by the strain calculations and elemental transfer data. Silicon losses in granitic soils were high relative to other elements while basaltic soils had net gains (Table 3.6). Aluminum contributed to volume change following in a similar pattern to that of Si. Potassium (K), Ca, Mg and Na were primarily lost in all pedons (Table 3.6).

Table 3.6. Select elemental constituents and their mass flux for each pedon within Kruger National Park

|    | Shingwedzi     |                | Skukuza        |                |
|----|----------------|----------------|----------------|----------------|
|    | Basaltic soils | Granitic soils | Basaltic soils | Granitic soils |
|    | -----Flux----- |                |                |                |
| Si | 8.56           | -18.76         | 9.94           | -52.95         |
| Al | 1.44           | -7.08          | 5.90           | -17.15         |
| Ca | -2.35          | -2.07          | 2.51           | -7.13          |
| Na | -0.76          | -5.47          | 0.27           | -3.63          |
| K  | -0.57          | -0.85          | -2.20          | -10.06         |
| Mg | -0.26          | -0.33          | 0.9            | -1.57          |

### *Si Transformations, Transfers and Losses*

The elemental losses and gains from soils are the result of multiple processes and of course the compositional difference among parent materials. These processes regulate the intensity of transformations, transfers and net loss of Si from soils. Shingwedzi and Skukuza basaltic soils accumulated Si relative to the parent materials while granitic soils at both locations presented net losses relative to parent material amounts (Figure 3.4).

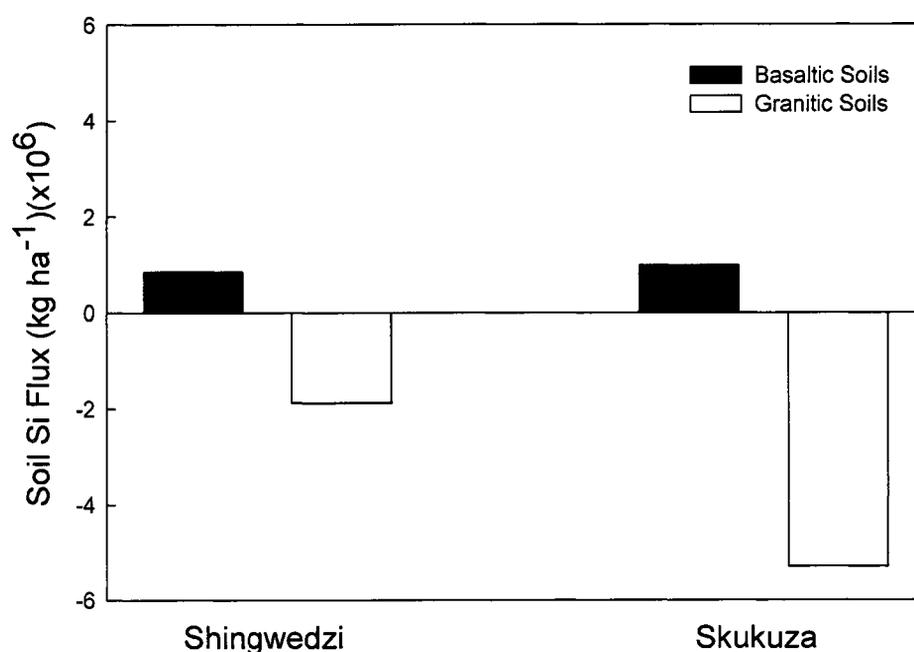


Figure 3.4. Soil Si flux (kg ha<sup>-1</sup>)(x10<sup>6</sup>) for basaltic and granitic soils at Shingwedzi and Skukuza sites. Calculations were based on soil depths of 100 cm.

Dissolved Si (DSi) concentrations from the soil solution reflect the degree to which the soil mineral pool provides labile Si for either plant uptake, leaching or secondary processes. In general, the solution Si levels were greater in the surface horizons of the basaltic versus granitic soils and lower with depth (Figure 3.5). Granitic soils at both Shingwedzi and Skukuza had similar dissolved Si concentrations and depth

distributions. Basaltic soils at Shingwedzi had 26% greater DSi concentrations than at Skukuza (Figure 3.5).

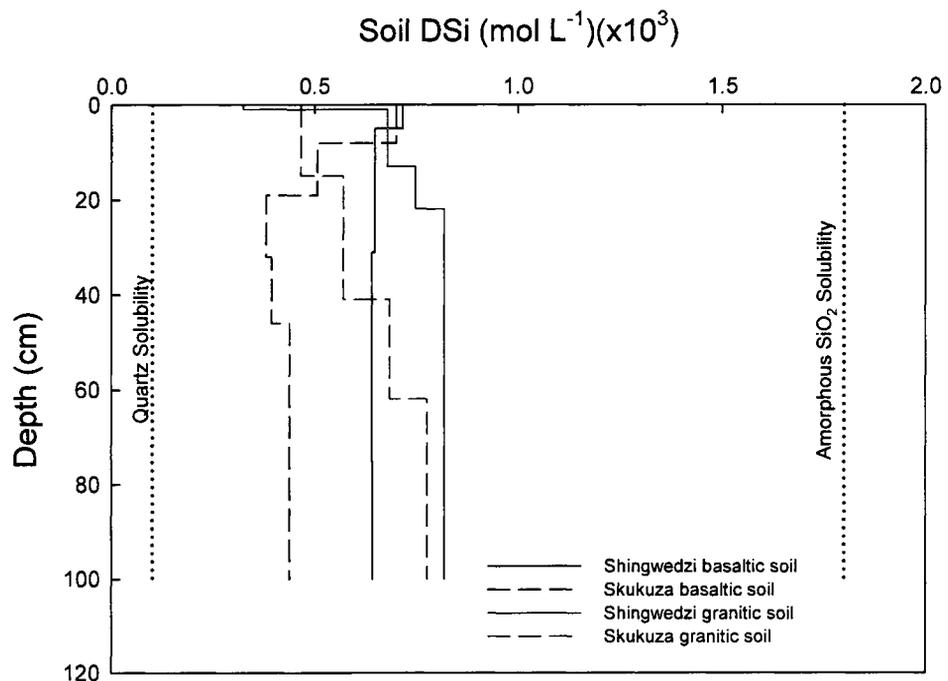


Figure 3.5. Dissolved SiO<sub>2</sub> (mol L<sup>-1</sup>)(x10<sup>3</sup>) as a function of depth to 100 cm for basaltic and granitic soils at Shingwedzi and Skukuza sites.

In general, BSi values in plants ranged from ~ 4 to 7% by weight (131-325 kg/ha) (Figure 3.6) and are generally higher than those of North American grasslands (Raven 1983; Sangster & Hodson 1986; Piperno 1988; Epstein 1999; Datnoff 2001; Blecker et al. 2006; Melzer et al. in review). Although plant species differences can account for some of the BSi variability, precipitation and soil Si availability seem to predominate (Blecker et al. 2006). Regardless of site, plants overlying basaltic soils had greater BSi than plants overlying granitic soils. At Shingwedzi, plants overlying basaltic soils had 44% more BSi than those overlying granitic soils while at Skukuza, plants overlying basaltic soils had 46% more BSi than those overlying granitic soils (Figure 3.6). Plants overlying

basaltic soils at Shingwedzi had 26% greater BSi than those at Skukuza. Plants overlying granitic soils at Shingwedzi had 28% greater BSi than those at Skukuza (Figure 3.6).

Soil BSi values ranged from 1 to 7% by weight and pedon totals ranged from ~146,000 to 372,000 kg/ha (Figure 3.7). Soil BSi was higher in basaltic soils, regardless of site. The greater quantities of soil BSi were found in Shingwedzi and Skukuza basaltic soils and were 35% and 54% greater than granitic counterparts respectively (Figure 3.7). Basaltic and granitic Shingwedzi soils had 13% and 39% greater BSi, respectively, than their Skukuza counterparts (Figure 3.7). The proportion of total soil Si derived from soil BSi is greatest in the upper portions of the soil profile in basaltic soils (Figure 3.8 a, c). The Bw1 horizon of the basaltic Skukuza soil was made up of ~16% BSi and the BA horizon of the basaltic Shingwedzi soil was made up of ~13% BSi. In stark contrast to the basaltic soils, the greatest quantities of BSi in the granitic soils were found deeper in the soil profile (Figure 3.8 b, d).

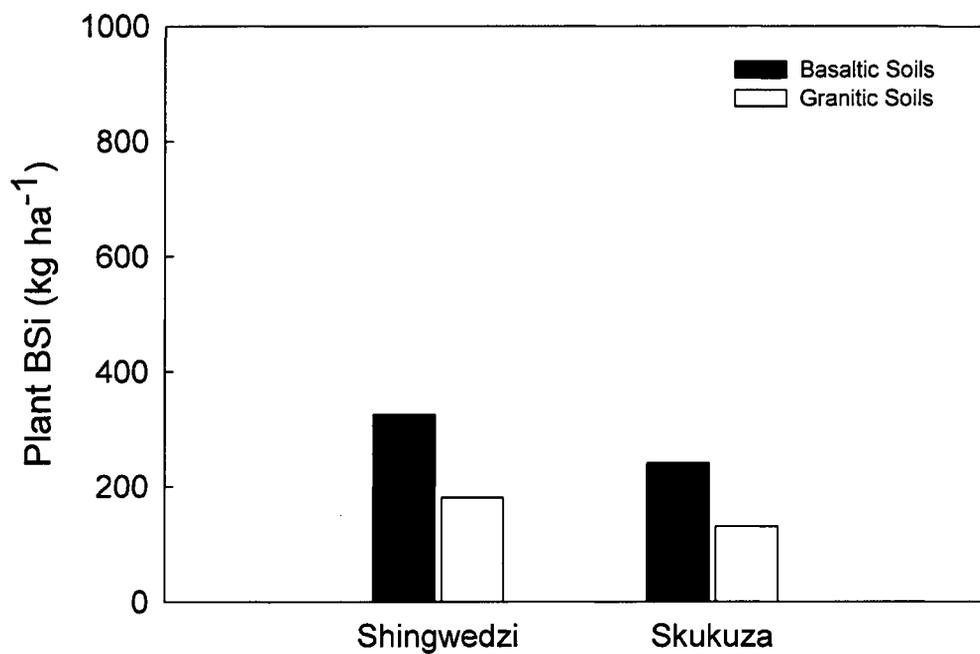


Figure 3.6. Plant biogenic silica (BSi) (kg ha<sup>-1</sup>) for the dominant grass species overlying basaltic and granitic soils at Shingwedzi and Skukuza sites.

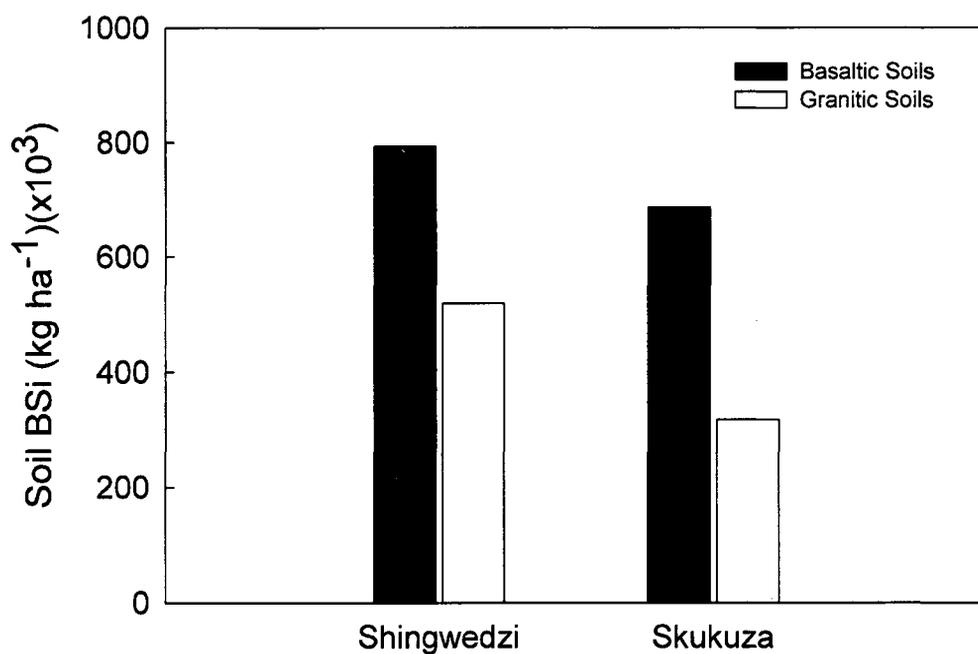


Figure 3.7. Soil biogenic silica (BSi) (kg ha<sup>-1</sup>)(x10<sup>3</sup>) for basaltic and granitic soils at Shingwedzi and Skukuza sites. Calculations were based on soil depths of 100 cm.

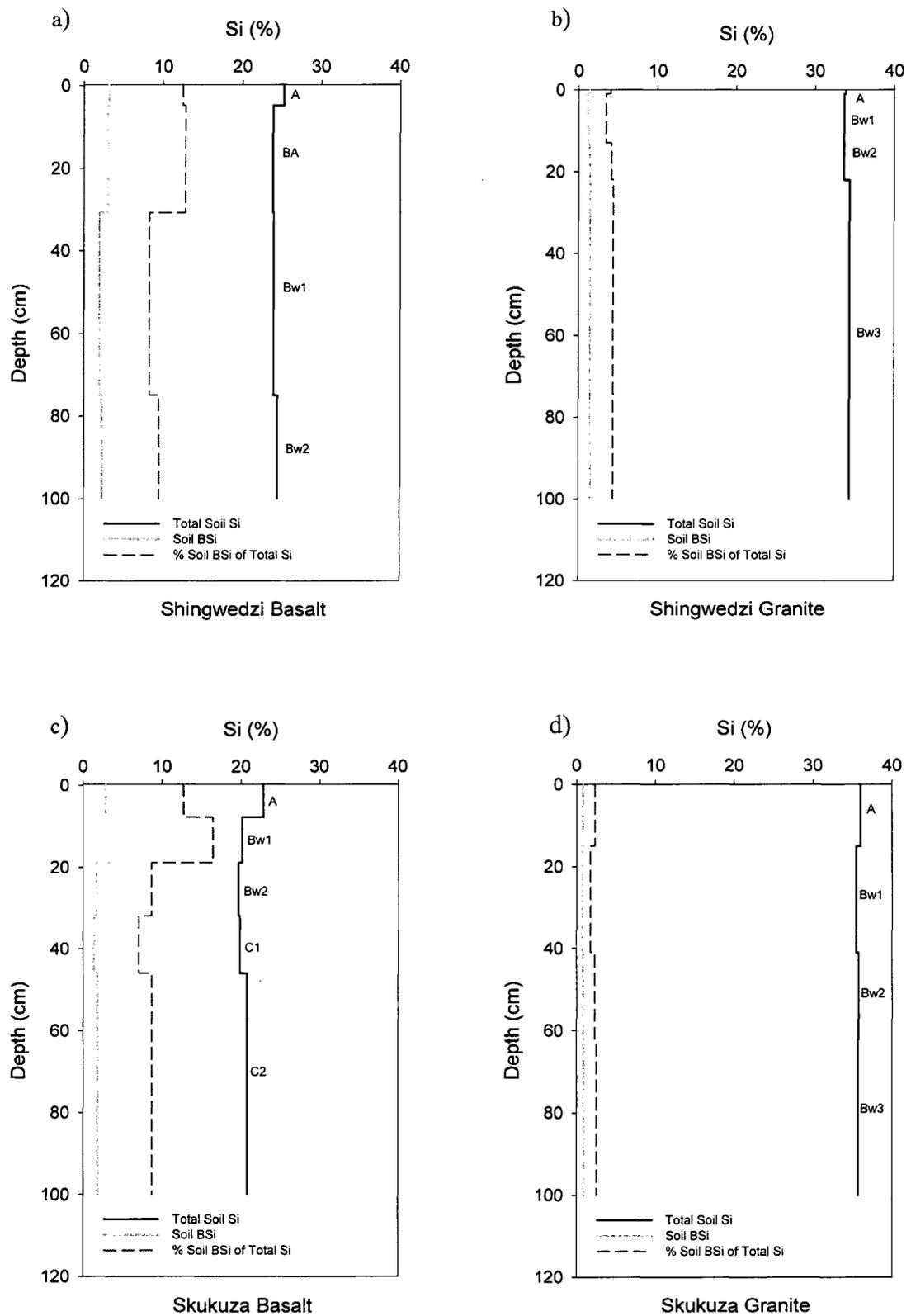


Figure 3.8. Total soil Si, soil biogenic silica (BSi), and %BSi of total Si as a function of a depth to 100 cm for a) Shingwedzi basalt, b) Shingwedzi granite, c) Skukuza basalt and d) Skukuza granite.

## Discussion

Figure 3.9 illustrates the important processes and components of the biogeochemical cycling of Si used to guide this research. For this study the central focus of the Si cycle takes place at the soil-plant interface where chemical and biological processes interact to form mineral and biogenic pools. Additionally, the Si pools are parameterized by fluxes, mainly, mineral and soil BSi dissolution, plant uptake, litterfall, secondary mineral formation and atmospheric inputs and leaching outputs that define the Si biogeochemical mass balance (Bormann et al. 1998; Moulton et al. 2000) as:

$$F_{\text{atmospheric}} + F_{\text{weathering}} + F_{\text{litterfall}} = F_{\text{vegetationuptake}} + F_{\text{soilstorage}} + F_{\text{drainage}}$$

where F is the flux.

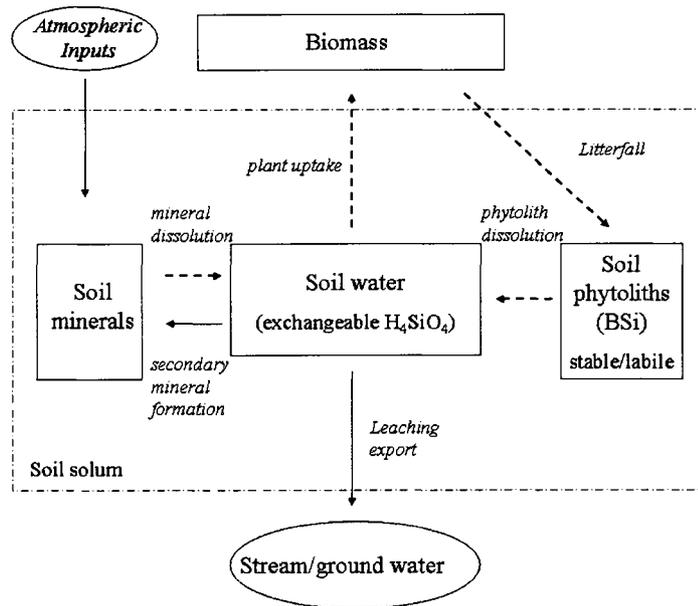


Figure 3.9. Conceptual model of the terrestrial silica cycle. Boxes represent pools and arrows represent fluxes. Dashed arrows emphasize the area of the cycle that was of particular interest for measurements in this study. (Adapted from Blecker et al. 2006)

Simple modeling of Si biogeochemistry at the ecosystem scale (by estimating pools and fluxes) requires consideration of parent material (the primary source of Si), stage of soil development (Conley et al. 2006) and the consequent mineralogical composition in the soil. The mineralogical form of silica regulates solubility and its availability for plant uptake; however, in the case of soil BSi, the relative solubility is accelerated by lower surface area, lower Al concentration and greater water content (Bartoli & Wilding 1980). We use a model that separates BSi deposited into the soil by differences in relative solubility. These fractions include, (1) soil BSi particles that have lower solubilities and are vertically translocated and stored in the soil (stable BSi) and (2) soil BSi particles that have higher solubilities (labile BSi) and are more likely to be dissolved into solution and either taken up by plants or leached out of the soil. The compartmentalization and cycling of soil BSi may be influenced by parent material (and associated textural and mineralogical differences) and by climate.

Based on the inherent weatherability of the parent materials we expected basaltic soils to have lower total soil Si but greater total soil DSi than granitic soils due to the congruent dissolution associated with basalt weathering. Our mineralogical analyses also suggest that basalts will release more Si to solution than granites as it is almost entirely made up of plagioclase. The dissolution of albite, specifically, could be an important source of Si while anorthite dissolution does not release Si as readily as it more commonly weathers to kaolinite. The basaltic soils are high enough in Al so that the formation of kaolinite is possible; however, Mg concentrations result in smectite formation. Granitic rocks are more unpredictable in their weathering as they are made up of a greater assemblage of minerals although quartz and feldspars make up the largest

percentage of all the constituents in the granitic rocks. Although quartz would require less water to dissociate and release Si to solution it is not an important source of silicic acid in the soil solutions.

We found that basaltic soils have lower total DSi (on a mass profile basis) relative to granitic soils (Figure 3.10), but have greater concentrations of DSi in the surface horizons (Figure 3.5) which, reflects the importance of soil texture and hydrology. In general, they appear to have greater retention of Si (a reported net gain based on total Si values) while granitic soils exhibited a net loss relative to the parent material. The additions of eolian materials to these systems are largely unknown but it is apparent that inputs of Si to these ecosystems could offset losses due to leaching and erosional processes. Although basaltic soils have less total Si than granitic soils it is apparent that the export of Si out of these systems has been dampened and could be related directly to long term pedological and hydrological dynamics. For example, the finer textures in the basaltic soils could slow the export of soluble Si out of the soil profile over the long term while the more porous granitic soils are likely to lose more Si to leaching over time under similar climatic regimes.

The retention of BSi in these basaltic and granitic soil systems is likely due to the degree and rates of biocycling that are responsible for the production (by plant uptake) and perhaps the degree of redistribution (by fauna). A greater proportion of the total Si is composed of BSi in basaltic soils. The greater plant BSi production and finer textures associated with the basaltic soils may account for their greater amounts of BSi storage and Si retention. The depth distribution of BSi suggest that the soils of the South African Savanna show a high degree of bioturbation. Undisturbed soils (not highly bioturbated)

should have highest BSi values at the soil surface (Gol'eva 1996, 1999, 2001) while highly bioturbated soils would have a more uniform or irregular depth distribution of BSi. In the soils of semi arid systems where leaching is generally low, the transport of BSi to greater depths (such as in the granitic soils) suggest a greater degree of bioturbation. This bioturbation may act to preserve BSi in soils by physically removing the biogenically derived minerals deeper into the profile away from weathering agents that may accelerate dissolution (e.g. organic acids).

The dissolution rate of BSi into the soil solution is calculated from mean residence time of soil BSi. Blecker et al. (2006) determined soil BSi turnover for North American grasslands by the ratio of the soil BSi pool ( $\text{kg Si ha}^{-1}$ )/annual litterfall Si input ( $\text{kg Si ha}^{-1}\text{y}^{-1}$ ) and found turnover times ranging from 250 to 1300 y. The same calculation was utilized in this study and resulted in average turnover times of BSi in surface horizons of  $\sim 458$  y for granitic soils and  $\sim 707$  y for basaltic soils. Relative turnover times of BSi between these parent materials may be driven by the site specific hydrological differences. Sites located in North America with similar precipitation have lower turnover times (Blecker et al, 2006). When turnover time is presented on a total soil profile basis bioturbation appears to contribute to overall longer turnover times, especially in granitic systems, by transporting BSi out of or into the biologically inactive zone, thus preserving it or enhancing dissolution respectively. The same calculation for BSi in the entire soil profile was approximately 2,650 y regardless of parent material suggesting that the greater bioturbation in soils derived from granite contributed to stabilization (increasing the turnover times) deep within the profile.

Distinctions are made between the Si cycling in basaltic versus granitic soils based on their relative pool sizes and turnover time (Table 3.7). We suggest that the biocycling of Si is 'tighter' in the basaltic soil system and 'leakier' in the granitic soil system. Although plants overlying both basaltic and granitic soils rely on BSi dissolution as their primary Si source, the granitic soils turnover BSi at a faster rate. The shorter turnover time of BSi in granitic systems is likely due to the availability of Si from BSi and from other less soluble sources, namely, quartz. Relative to basaltic soils, solutions of granitic soils are farther from saturation with respect to Si due to limited Si sources, greater leaching potential and greater translocation due to bioturbation; soil BSi is thus, more readily dissolved in these systems in the biologically active surface horizons. In contrast, BSi in basaltic soils have a longer turnover time because BSi and plagioclase dissolution are probably major sources of Si to the soil solution. Because there are two major sources of Si and because little Si is being lost, we believe that the soil solution is closer to saturation with respect to Si in basaltic soils which, allows greater potential storage of Si (as BSi) in these soils with longer turnover times. The DSi concentrations are higher in the surfaces of basaltic soils which, along with their slightly higher ANPP, contribute to the higher abundances of BSi in their overlying plants. Dissolved Si concentrations of the soil subsurface are similar in both soil types but are greater in the surface (relative to the subsurface) in basaltic soils. Furthermore, figure 3.10 demonstrates that DSi totals in granitic soils are far greater than plant BSi totals and can result in Si loss from the system while DSi totals from basaltic soils are slightly less than plant BSi totals and can result in less potential loss of soil DSi. We suggest that plants deriving Si from granitic soils relative to basaltic soils must mine deeper within the soil

to get the same supply of Si which, confirms the idea that Si is mobilized by plants and regulated by BSi dissolution.

Table 3.7. Relative differences in key properties between basaltic and granitic soils within Kruger National Park (+ represents greater quantities; - represents lower quantities)

| BSi Cycle Properties  | Basaltic Soils | Granitic Soils |
|---|----------------|----------------|
| Total Si- profile ( $\text{kg ha}^{-1}$ )                   | -              | +              |
| Dissolved Si –surface ( $\text{mol L}^{-1}$ )               | +              | -              |
| Plant Biogenic Si ( $\text{kg ha}^{-1}$ )                   | +              | -              |
| Soil Biogenic Si ( $\text{kg ha}^{-1}$ )                    | +              | -              |
| Total Si loss- profile ( $\text{kg ha}^{-1}$ )              | -              | +              |
| Turnover time- surface ( $\text{kg ha}^{-1}\text{y}^{-1}$ ) | +              | -              |

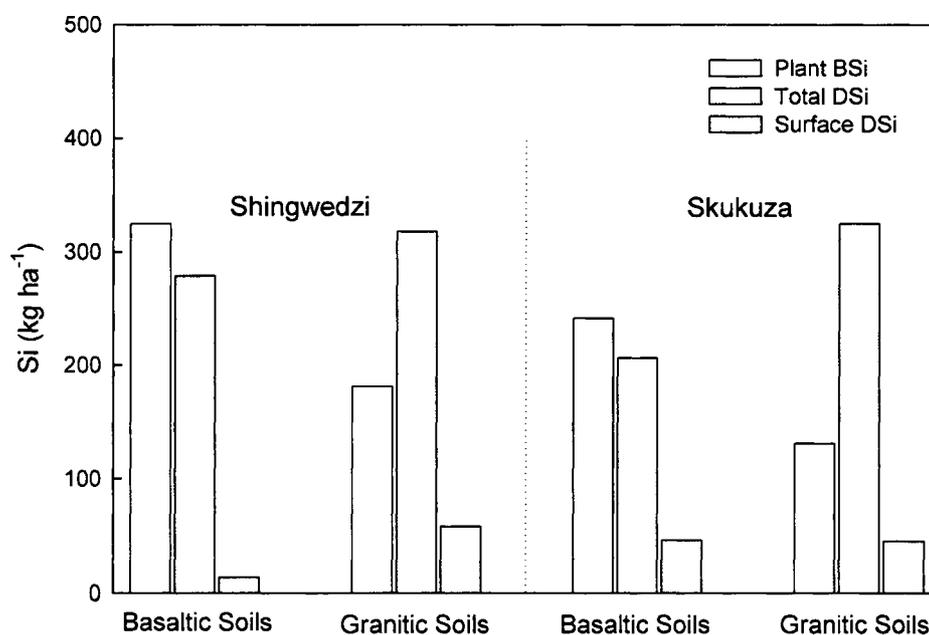


Figure 3.10. Plant biogenic silica (BSi) and soil total and surface (to 20 cm depth) dissolved silica (DSi) ( $\text{kg ha}^{-1}$ ) for each basaltic and granitic soil in Shingwedzi and Skukuza.

## Conclusions

The cycling of BSi in terrestrial ecosystems has been shown to greatly impact the global biogeochemical cycle of Si (Conley 2002; Blecker 2006). Recent studies have focused on quantifying BSi pools and fluxes in various ecosystems to understand the mechanisms driving Si transport among inorganic and organic pools. Ultimately, a better understanding of how plants mobilize Si transport from terrestrial to oceanic systems is necessary.

In this study, we have found that the quantities, fate and mobility of BSi in the soils of grassland ecosystems is strongly influenced by the chemical and physical nature of the soil parent material. A comparison of finer basaltic soils with coarser granitic soils showed a distinction between Si cycling driven by biologic uptake and by mineral dissolution respectively. The total initial amount of Si in rocks may not be important except for the longer-term supply of Si. Previous studies show that ANPP drives Si uptake by plants however, these studies were conducted on soils that have similar parent materials.

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# C HAPTER FOUR

Global Estimates of Silica in the Terrestrial Environment:  
Fundamental Importance of Grass Dominated Ecosystems on the  
Global Silica Cycle

## **Introduction**

The biogeochemistry of Si plays a critical role in soil development (Kelly et al. 1998), buffering capacity against acidic deposition (Drever 1994) and long-term regulation of atmospheric carbon dioxide through weathering reactions in soils (Berner 1992; Chadwick et al. 1994). Global silica and carbon cycles are closely linked in the oceans (Treguer et al. 1995); however, a primary source of marine silica is terrestrial. Fluxes of silica from the terrestrial environment to the oceans may have played an important role in the ancient global carbon (C) cycle (Dugdale et al. 1995) as the productivity of important diatom-dominated regions, such as those found in southern hemisphere oceans, is silica-limited (Dugdale & Wilkerson 1998). Most previous assessments of the controls on silica export from the terrestrial environment have largely ignored the biogenic silica (BSi) pool stored in soils and vegetation, assuming that mineral weathering reactions alone control silica fluxes into the riverine systems (e.g. Berner & Berner 1996). However, recent evidence that BSi is of fundamental importance in controlling silica storage in the terrestrial environment is growing (Clarke 2003; Meunier 2003; Derry et al. 2005; Blecker 2006; Perrot & Barker 2008). Biogenic silica is more labile than mineral silica (Hurd 1983), and in some ecosystems BSi can comprise up to 80% of the soluble silica pool (Derry et al. 2005) that is readily mobile (through leaching or erosional loss). It is this form of silica that is likely the most important source of silica export from land to sea. Grassland ecosystems are a particularly large reservoir of BSi (due to dominance by grasses with relatively high silica content) and these ecosystems are very efficient in the mobilization of Si in terrestrial environments (Blecker et al. 2006; Melzer et al. in review).

We attempt to make a first order estimate of BSi storage in the vegetation and underlying soils of grass dominated ecosystems worldwide based on both intensive studies in North American and South African grasslands (Kelly et al. 1991; Blecker et al. 2006; Melzer et al. in review) and compilations of productivity and soils data at continental scales. These data are further utilized in conjunction with paleoenvironmental studies and ocean records to assess how major periods of grassland expansion and contraction may have influenced the terrestrial storage, mobilization and delivery of BSi to the oceans. The global Si cycle is depicted in figure 4.1 with major pools (boxes) and fluxes (arrows) identified.

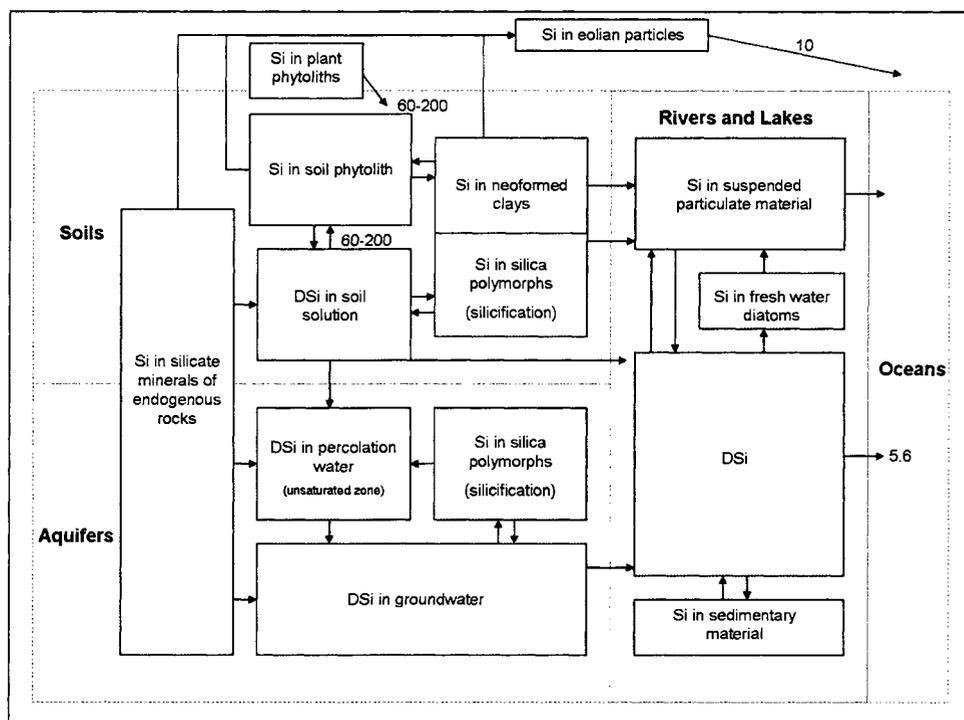


Figure 4.1. Conceptual model of the global silica cycle. Boxes represent pools and arrows represent fluxes (Tmol Si<sup>-1</sup> yr<sup>-1</sup>). (Adapted from Basile-Doelch et al. 2005)

## *Contemporary Records of the Terrestrial Si Cycle*

The original source of silica available to plants is derived from mineral weathering (Kelly et al. 1998). The importance of primary mineral dissolution and formation of secondary minerals has been recognized as a primary control on silica concentrations in soil water (soil solution) and stream water and is generally linked to climate and weathering intensity (White & Blum 1995; Gaillardet et al. 1999). The silica export from more mesic terrestrial ecosystems is the result of a positive water balance that drives water below the rooting zone and out of the soil profile (soil solum). Stream waters draining these ecosystems may export silica from groundwater inputs or surficial runoff and erosion. In more arid environments such as grasslands and savannas, groundwater loss is much less important (Shaetzel & Anderson 2005) and quantities of silica lost to streams are low (Blecker 2006); thus, silica and other soluble constituents precipitate in the soil profile. Accumulated soil BSi may only be lost from the system episodically during droughts (aeolian erosion), fires and floods; extreme climatic events that characterize grasslands and that are expected to increase in the future (IPCC 2001).

Silicon budgets have been constructed at the pedon scale using a biogeochemical mass balance approach for various forest ecosystems including coniferous (Bartoli 1983; Markewitz & Richter 1998), mixed hardwood (Garvin 2006), temperate deciduous (Bartoli 1983) and bamboo forests (Meunier et al. 1999), and Amazon (Lucas et al. 1993) and Congo (Alexandre et al. 1997) rainforests. The biogeochemical cycling of BSi documented in these studies exemplify the important control of plants and soils in mobilizing Si from mineral reserves. Furthermore, Conley (2002) stressed the importance of quantifying the production and storage of BSi in grassland systems as this

would compliment BSi data available from other biomes for a more complete estimate of BSi in terrestrial ecosystems. Other BSi productive biomes with Si-accumulator plants include savannas and wetlands (Clarke 2003). In a study across a bioclimatic gradient in the Great Plains grasslands of North America, Blecker et al. (2006) found that the biocycling of Si in grasslands is comparable to that of forests. In their grassland study, they suggest that the geochemical behavior as well as the variability of BSi within grassland ecosystems was linked closely to climate and ANPP. They identified a positive relationship between Si uptake and ANPP.

Conley (2002) provided a global average BSi content of 60-200 Tmol Si yr<sup>-1</sup> for terrestrial aboveground biomass (by scaling DSi uptake to global primary productivity), which is comparable to Treguer et al. (1995) oceanic production of BSi of 240 Tmol Si yr<sup>-1</sup> and orders of magnitude larger than their 5 Tmol Si yr<sup>-1</sup> estimation of DSi inputs into oceans. More recently, Blecker et al. (2006) provided the first systematic assessment of BSi in grasslands and pointed to these ecosystems as globally important reservoirs of BSi. They estimated Si abundance in North American nonwoody grasslands by scaling up their ANPP and plant Si data and found that approximately 0.3 Tmol Si for above ground biomass and 130 Tmol Si for soil in these North American grasslands alone. These preliminary studies suggest that the Si stores of temperate grassland soils (alone) rivals the estimated global storage in biomass (Blecker 2006). Although terrestrial plants are shown to play a critical role in global Si mass balance and biogeochemistry, further quantification of grassland ecosystems are needed (Conley 2002) to refine global estimations of terrestrial BSi reservoirs. Estimates of grassland Si storage is of particular interest as they are regarded as large and active BSi reservoirs whose global expansion

during the Late Neogene (Axelrod 1985; Stromberg 2004) may have had and continues to influence the global carbon cycle (Conley 2002).

### *Riverine and Oceanic Records of Si Cycling*

Terrestrial silicate weathering is considered the primary source of dissolved silica (DSi) in rivers (Subramanian et al. 2006), which, contribute about 80% of the annual DSi input into oceans (Treguer et al. 1995). The major factors that regulate weathering processes and determine DSi inputs into rivers are climate, geology (lithology) and tectonics; however, global change and other anthropogenic factors such as river regulation, waste disposal and land use changes have also been identified as important in DSi delivery on global scales (Jennerjahn et al. 2006).

In terms of chemical denudation, Stallard (1995) distinguished two end-member terrains, 1) weathering limited terrain and 2) transport limited terrain. Weathering limited terrains are steep and are dominated by rapid physical erosion. Although chemical weathering is not severe in weathering limited terrains, the continuous removal of sediment promotes silicate weathering and CO<sub>2</sub> consumption. Transport limited terrains are flat and are dominated by sediment storage due to low rates of bedrock weathering and physical erosion. Transport limited terrains are likely to form thicker weathering profiles with an abundance of secondary minerals and low rates of CO<sub>2</sub> consumption. Jennerjahn et al. (2006) conducted a thorough analysis of the factors that control DSi in tropical rivers and showed Asian and Oceanic rivers (over other tropical rivers) to have the highest DSi yields. They attribute these high yields to young geology, active

tectonism and high precipitation, runoff and runoff temperatures, which represent ideal physical and chemical weathering conditions lying between Stallards (1995) two end member terrains. Unlike tropical rivers draining areas characterized by young geology and high tectonic activity, the DSi concentrations in rivers draining from the weathering limited boreal and arctic terrains are lower than the 150  $\mu\text{M}$  global average (Treguer et al. 1995) which ranges from 100 in arctic regions to 700 in the tropics (Humborg et al. 2006).

Few studies have investigated the role of BSi as a possible source of DSi. Although, some studies have evaluated the impact of higher plants on silicate weathering (Cawley et al. 1969; Drever & Zobrist 1992; Kelly et al. 1998; Moulton et al. 2000), few have quantified the biocycling of Si in plants and soils (Bartoli 1983; Alexandre et al. 1997; Lucas 2001; Meunier 2003; Blecker 2006). Jennerjahn et al. (2006) explain how the grasslands associated with floodplains that are typical of large tropical rivers act as filters to reduce the DSi river load as DSi is extracted by grasses and stored as phytolith in soil. The same effect was not observed for weathering limited terrains or for tropical transport-limited, but less tectonically active regions like Africa and South America. In these regions, vegetation and soils act more as chemical weathering agent than as storage pools.

Germanium (Ge) and Si are considered “psuedoisotopes” (Azam & Volcani 1981) and have similar geochemical cycles (Wittman & Horman 1976; Bernstein 1985). Germanium is a trace element that is in the same group of the periodic table as silicon and often substitutes for Si in the lattices of aluminosilicates (Kurtz et al. 2002). In terrestrial systems, the original source of Ge and Si is from the weathering of primary

minerals. Germanium/Si ratios in most continental rocks range from 1 to 3  $\mu\text{mol/mol}$  (Mortlock & Froelich 1987) while ratios in stream waters are lower and reflect weathering intensity as Ge is retained in soils as it is preferentially incorporated into the lattices of secondary clay minerals during chemical weathering (Murname & Stallard 1990). Oceanic opaline sediment cores record fluctuations in Ge/Si ratios over time. Marine diatoms do not fractionate against Ge or Si from seawater during silicification (Shemesh et al. 1989) and are therefore valuable recorders of temporal changes in continental weathering (Shemesh et al. 1989; Murname & Stallard 1990; Mortlock et al. 1991) that have been used to study temporal variations in global silica cycling and oceanic productivity.

A record of oceanic Ge/Si from 0 – 35 Ma shows a general decline during the Neogene (Shemesh et al. 1989). Higher resolution Quaternary records show significant glacial-interglacial variation, with lowest values occurring during glacial maxima (Froelich et al. 1992). Germanium/Si of the oceans is primarily influenced by changes in river fluxes (Froelich et al. 1985; 1992), and therefore Ge/Si ratios can be an important tool to study the evolution of silica fluxes to the oceans. Moreover, Froelich et al. (1992) used Ge/Si to determine that the greater riverine DSi flux during glacial times resulted from greater weathering of primary minerals. A number of paleoceanographic indicators show interesting behavior around the time of the apparent Mio-Pliocene grassland expansion. Filippelli, (1997) and Derry and France-Lanord (1997) noted that the shift in Ge/Si at that time correlates with increased weathering intensity in the Himalayan foreland, an event closely correlated with the expansion of  $C_4$  grasslands in that region (Quade & Cerling 1990; France-Lanord & Derry 1994). This is one example of

intriguing suggestions that the Mio-Pliocene expansion of grasslands influenced chemical fluxes to the oceans; however, the interpretation of these signals has been a matter of debate for some time.

### *Grassland Distribution and Evolution*

Grasslands are widespread ecosystems that are found on five of the seven major continents and make up 40.5% or 52.5 million square kilometers of the terrestrial land area (World Resource Institute 2000, based on ICBP data) (Figure 4.2). This estimate is partitioned into woody savanna and savanna (13.8%), open and closed shrub (12.7%), non-woody grassland (8.3%), and open tundra (5.7%) which merge with one another depending on precipitation amount (FAO 2005). Savannas are typical of tropical and subtropical grass dominated landscapes, but like temperate grasslands, their species composition and overall complexity are dependent on climate, soil and disturbances (Pratt et al. 1966; Cole 1986; Morell 1997). Grasslands occur across a wide range of climatic conditions in areas that receive anywhere from 200 mm to 1300 mm of precipitation annually and that have mean annual temperatures from 0°C to 30°C (Sauer 1950; Risser et al. 1981; Oesterheld et al. 1999). They have adapted to, and are reliant on, periodic drought, fire and grazing (Axelrod 1985; McNaughton 1985; Stebbins 1981).



Figure 4.2. Potential native vegetation classified by grassland biome.

The evolution of grasslands ultimately reflects a record of environmental and climatic change. Proxies recovered from soils and sediments such as the  $\delta^{13}\text{C}$  of fossil mammal tooth enamel (Cerling et al. 1997) and paleosol carbonates (Quade et al. 1989; Latorre et al. 1997) has been used to infer an abrupt increase in grasslands and particularly in  $\text{C}_4$  grasses across low latitudes between 8 and 4 million years ago (Cerling et al. 1997). Because of the physiological advantage of  $\text{C}_4$  grasses under low  $p\text{CO}_2$  conditions, Cerling et al. (1997) suggested that a large decline in atmospheric carbon dioxide triggered this ecological transition. Although a shift in grassland ecosystems most likely occurred, it is not certain that this event represented a rapid evolution of  $\text{C}_4$  grasses, or that it was caused by a decrease in atmospheric  $\text{CO}_2$  (Pagani et al. 1999; Pearson & Palmer 2000).

Evolutionary trends in mammals (and other fauna) and flora from the middle to late Miocene suggest a pattern of increasing seasonality and aridity of climates worldwide (Wolfe 1985; Flynn & Jacobs 1982). Soil carbonate  $\delta^{18}\text{O}$  values from many locations (Quade et al. 1989; Quade & Cerling 1990; Latorre et al. 1997), as well as tooth enamel  $\delta^{18}\text{O}$  values from Argentina and North America (Latorre et al. 1997) also increased during this time, suggesting increasing evaporation and aridity preceding and

accompanying the expansion of grassland flora. Dust fluxes, likely driven by the development of aridity in Asia and South America, increase in the North Pacific at about 8 Ma and again near 3 Ma at the opening of the Pleistocene (Rea 1994). Additionally, a more recent explanation for the onset of the grassland expansion was made by Keeley and Rundel (2005) who suggest that a seasonal climate emerged that produced high biomass during a warm and moist season which was followed by a dry season favoring fire, produced by lightning strikes. The climatic environment described by Keeley and Rundel is similar to today, and the presence of a changing and variable climate may further the expansion of grasslands.

## **Methods**

An important component in understanding the role of soils in the global Si cycle is developing reliable estimates of the amounts of BSi stored in the terrestrial Si pools. The first estimates of BSi storage in terrestrial environments at the global scale were made by Conley (2002). These estimates relied heavily on global plant production data and published research on ratios of BSi stored above ground and how that related to what was found in soils of terrestrial ecosystems. For example, BSi in plants were determined on the basis of an average and global annual C production and soil BSi was estimated to contain at least 500 to 1,000 times more BSi than stored in plant biomass.

Many other studies involving the extrapolation of plant and soils data (mostly for C assessments) have done so at many different scales, namely, continental (Amichev & Galbraith 2004; Tan et al. 2004), regional (Homann et al. 1998; Galbraith et al. 2003), and landscape (Bell et al. 2000; Arrouays et al. 1995, 1998; Chaplot et al. 2001; Terra et

al. 2004) scales. These studies have used a range of techniques by which point measurements of a soil property (e.g. SOC) are extrapolated to larger scale predictions of storage of a given element. These various techniques can be divided into two general methods of spatial extrapolation, namely, “*measure and multiply*” and “*paint by numbers*” (Schimel & Potter 1995).

The *measure and multiply method* is the most prominent method of producing coarse predictions of elemental storage at regional to global scales. Soils information is collected within a fixed unit of measurement and data are stratified to extrapolate to larger areas. Measurements within each of these strata are then aggregated and multiplied by the area of each stratum (Schimel & Potter 1995). Soil survey maps and laboratory characterization data are the primary resources for estimating the amount of a given element stored in soils using this approach (e.g., Homann et al. 1998; Kern et al. 1998; Galbraith et al. 2003; Tan et al. 2004)

An alternative to the measure and multiply approach is referred to as “*paint by numbers*” (Schimel & Potter 1995). This approach incorporates information on multiple environmental factors within common geographic areas that are used as input variables to models, which then are used to make predictions that can be multiplied by the areal extent of given combinations of each of these factors. This approach is akin to soil-landscape modeling (McSweeney et al. 1994), in which the variability of soils is analyzed with respect to changes in environmental variables known to influence soil property variability, such as topography, hydrology, or geology.

Continental plant and soil BSi values were estimated using variations of these two approaches. First, we attempted a “*measure and multiply*” approach utilizing plant and

soils data collected from our intensive investigations of diverse grassland ecosystems and the ecological, pedological and geological controls on plant and soil BSi storage that are outlined in previous chapters (Figure 4.3). This approach relies on continental estimates of the distribution of three grassland types and the demarcation of coarse versus fine textured soils. Secondly, we utilized the “*paint by numbers*” approach by developing simple regression models to predict both plant and soil BSi values using collected data from our investigations along environmental gradients.  $R^2$  statistics on simple linear regressions were used to measure the significance of the slope of the regression lines. The variability within the regression models and a test of their significance was conducted using an ANOVA with  $p < 0.05$ .

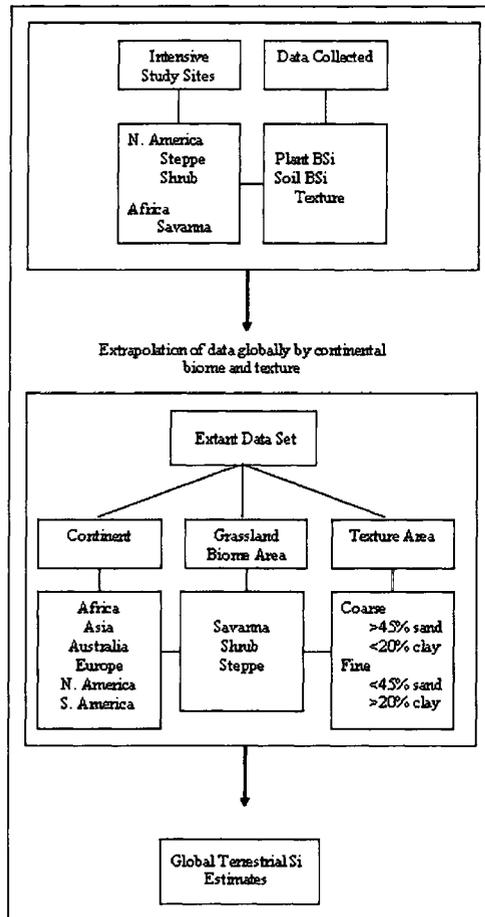


Figure 4.3. Flow chart describing systematic approach used to determine global terrestrial BSi estimates derived from data collected from intensive study sites and extant data.

### *Extant Data Sets Utilized for Estimates of BSi*

Global vegetation data was generated using the IBIS model at the University of Wisconsin (Ramankutty & Foley 1999) and converted to shape file polygons in ESRI ArcMap and joined with ESRI continental area GIS data using centroids. Total queries were performed on vegetation type data to summarize grassland area within continents. Data were calculated within a Cylindrical Equal Area projection for the mapview. Soil texture data from the Harmonized World Soils Dataset (FAO/IIASA/ISRIC/ISSCAS/JRC

2008) was intersected with the vegetation data by continent in ESRI ArcMap using the Arc toolbox, intersect function. Total queries were performed in Microsoft Access to summarize data by continent, grassland type, and textural class. Annual aboveground net primary productivity data (Grosso et al. 2008) for grassland type on each continent was calculated using the spatial analyst, zonal statistics function in ESRI ArcMap.

Plant and soil BSi data (Table 4.1) from intensive study sites in North America and South Africa were applied to grasslands worldwide by biome using extant data sets to systematically scale up by continental grassland area (Ramankutty & Foley, 1999) (Figure 4.2), soil textural variability (FAO/IIASA/ISRIC/ISSCAS/JRC 2008) (Figure 4.4) and ANPP (Grosso et al. 2008) (Figure 4.5).

Table 4.1. Grassland biomes, generalized soil texture, aboveground net primary productivity (ANPP), plant biogenic silica (BSi), and soil BSi data from intensive study sites. NA: North America; SA: South Africa; KS: Kansas; CO: Colorado; NM: New Mexico; gr: granite; bs: basalt.

| Site  | Biome   | Soil texture | ANPP<br>(g/m <sup>2</sup> /y) | Plant BSi<br>(kg/ha) | Soil BSi<br>(x10 <sup>3</sup> ) (kg/ha) |
|-------|---------|--------------|-------------------------------|----------------------|---|
| NA-KS | steppe  | fine         | 406                           | 140 (±1)             | 163 (±21)                               |
| NA-CO | steppe  | coarse       | 125                           | 35 (±1)              | 113 (±5)                                |
| NA-NM | shrub   | coarse       | 185                           | 36 (±3)              | 106 (±2)                                |
| SA-gr | savanna | coarse       | 329                           | 61 (±1)              | 89 (±27)                                |
| SA-gr | savanna | coarse       | 445                           | 85 (±9)              |   |
| SA-bs | savanna | fine         | 417                           | 113 (±1)             | 189(±24)                                |
| SA-bs | savanna | fine         | 473                           | 152 (±6)             |   |

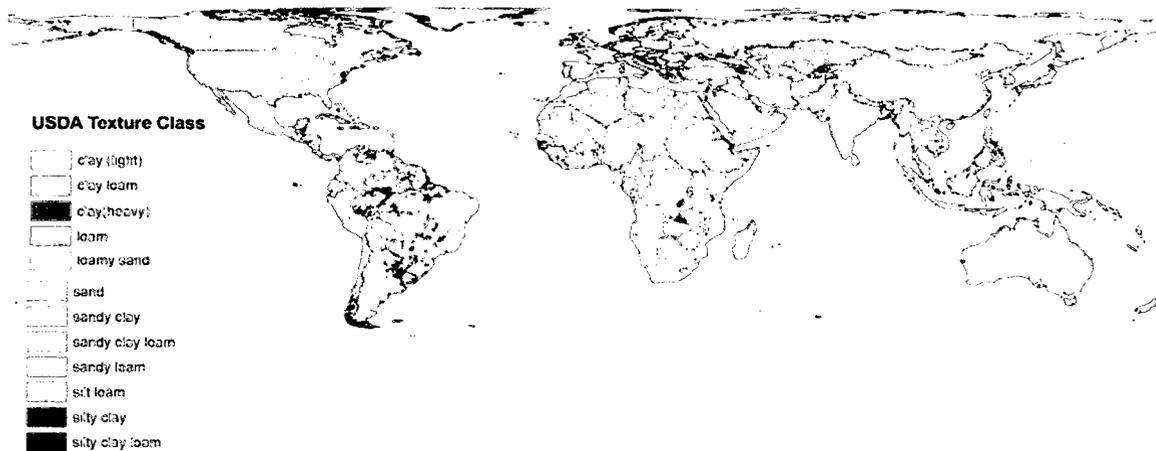


Figure 4.4. Global USDA soil textural classification.

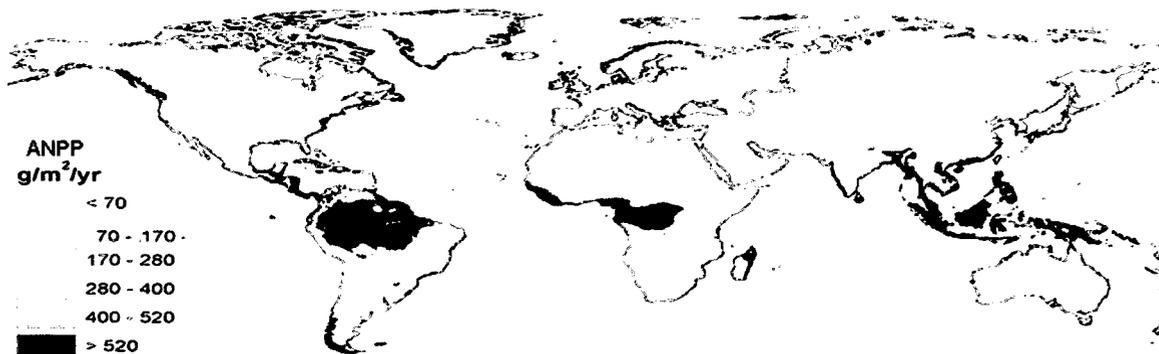


Figure 4.5. Aboveground net primary productivity (ANPP) for potential native vegetation predicted by the NCEAS model.

## Results and Discussion

### *Global Estimates of BSi*

Our estimates indicate that the global average BSi content for grassland aboveground biomass is  $\sim 8 \text{ Tmol Si yr}^{-1}$  (Figure 4.6) which, makes up approximately 5 to 16 % of Conley's (2002) estimate of 60 to 200  $\text{Tmol Si yr}^{-1}$  for all terrestrial aboveground biomass. At a larger scale, our aboveground biomass BSi estimates for non-woody

grasslands in North America alone reveal the same value of  $0.315 (\pm 0.002) \text{ Tmol Si yr}^{-1}$  as Blecker et al.'s (2006) estimate. The remaining 84 to 95 % of BSi not stored in the vegetation of grasslands is likely found in forest and wetland ecosystems where ANPP and active (vs. passive) Si transport dominate Si uptake respectively. Continental differences in BSi concentrations reflect the differences in BSi production as it is influenced by ANPP and biome area.

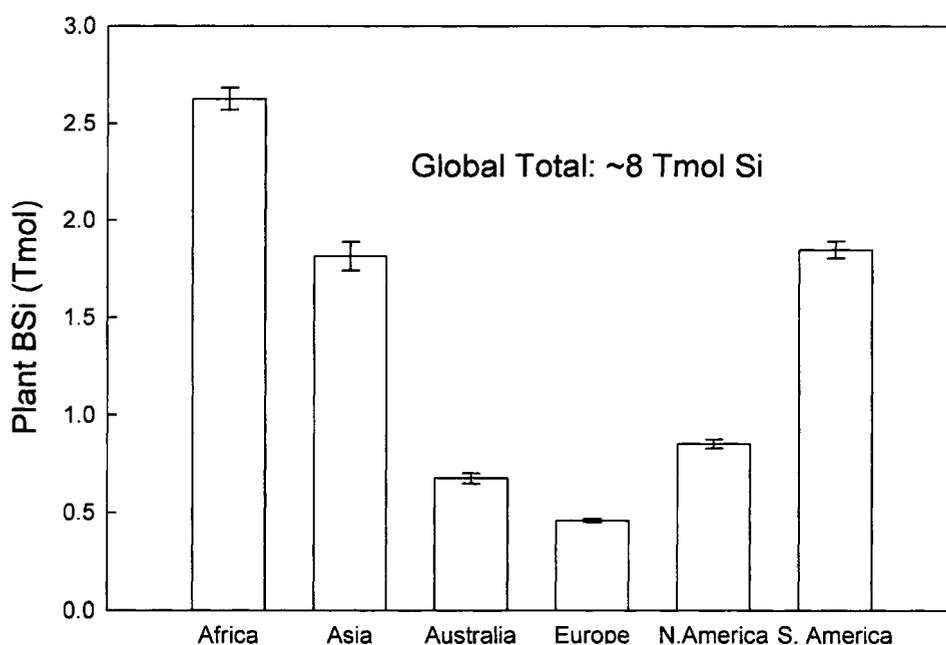


Figure 4.6. Mean plant biogenic silica (BSi) concentrations (Tmol) ( $\pm 1$  standard error of the mean) for grass dominated ecosystems per continent summed to determine the global total.

We estimated global average BSi content for grassland soils to be  $\sim 23,000 \text{ Tmol Si yr}^{-1}$  (Figure 4.7) which, is approximately 100 to 400 times greater than BSi in all terrestrial aboveground biomass and approximately 3,000 times greater than global estimates for grasslands alone. Non-woody North American grasslands had a BSi content of  $\sim 1,476 (\pm 164) \text{ Tmol Si yr}^{-1}$ ; however, 87% of this total resides within the fine

size fraction and only 13% in the coarse size fraction. The  $\sim 185 (\pm 9)$  Tmol Si  $\text{yr}^{-1}$  in the coarse fraction of nonwoody North American soils is similar to Blecker et al's (2006) estimate of these grasslands. The relationship of ANPP to BSi is important as previous studies suggest that plant BSi distribution in North American grasslands is largely driven by ANPP (Blecker et al. 2006). Blecker et al. (2006) found that plant BSi increases with increasing ANPP along a bioclimate sequence.

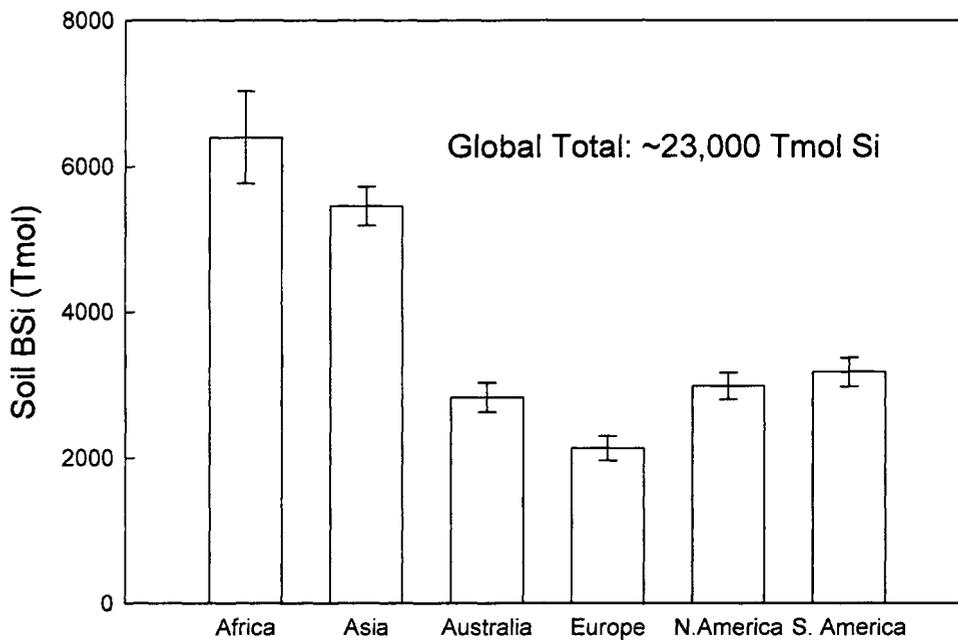


Figure 4.7. Mean soil biogenic silica (BSi) concentrations (Tmol) ( $\pm 1$  standard error of the mean) per continent summed to determine the global total.

We also utilized simple regression models to predict plant BSi values using ANPP data (Figure 4.8) and found that 76% of the variance in plant BSi is explained by ANPP ( $plantBSi(kg/ha) = 0.3088(ANPP) + 15.674$ ). Similar to chapter 2, a separate regression model was used for determining soil BSi quantities by regressing plant BSi against soil BSi (Figure 4.9). However, in this chapter, the regression was based on soil

BSi to depths of 100 cm (vs 20 cm) and results are reported on a mass basis (vs wt. % basis). Results show that most of the variance in soil BSi is explained by plant BSi ( $soilBSi(kg/ha) = 0.8296(plantBSi) + 63.087$ ). Continental ANPP data were applied to equation 1 (Figure 4.10) and these predicted plant BSi data were input into equation 2 (Figure 4.11). In either case, similar plant and soil global average results were obtained using this approach; global plant BSi averaged  $\sim 8.3 \text{ Tmol Si yr}^{-1}$  and soil BSi averaged  $\sim 18,096 \text{ Tmol Si yr}^{-1}$ . Africa and Asia had the greatest stores of BSi in both plant and soil which, is related to the larger grassland area; grassland biome type was not a determining factor. Europe had the lowest stores of plant and soil BSi.

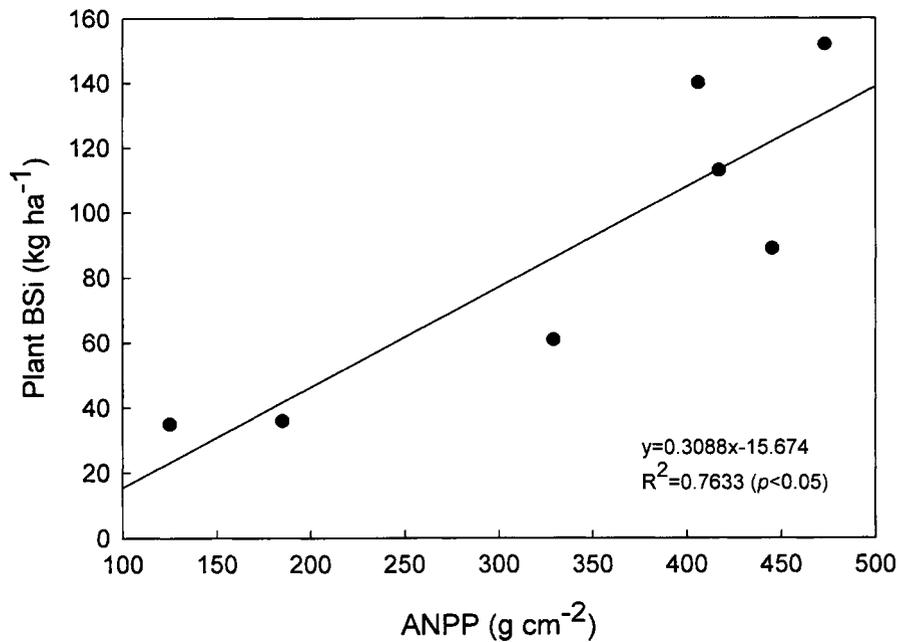


Figure 4.8. Relationship between aboveground net primary productivity (ANPP) and plant biogenic silica (BSi) quantities for North American and South African sites. Regression significance determined at  $P < 0.05$ .

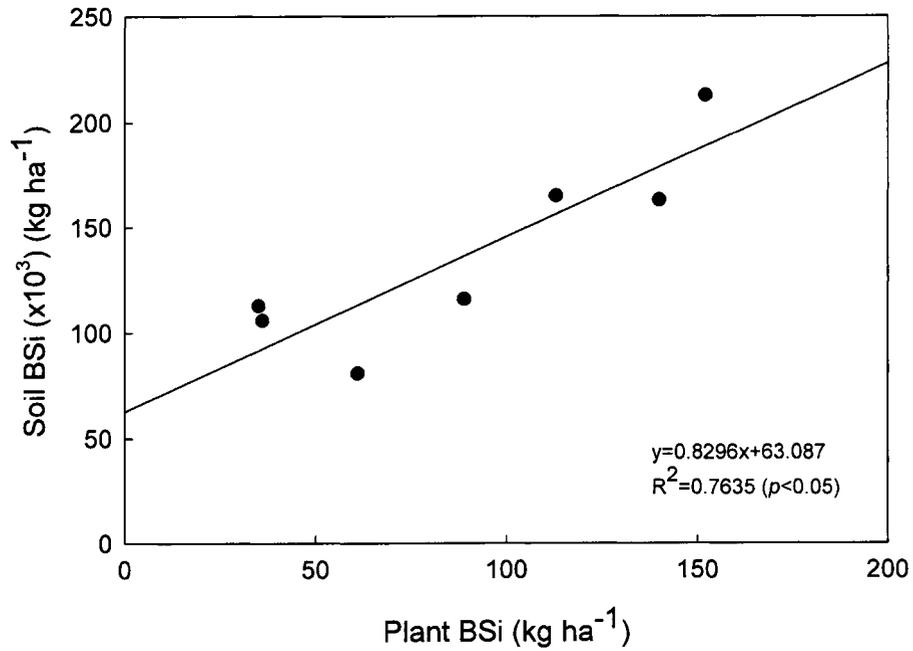


Figure 4.9. Relationship between plant and soil biogenic silica (BSi) quantities for North American and South African sites. Regression significance determined at  $P < 0.05$ .

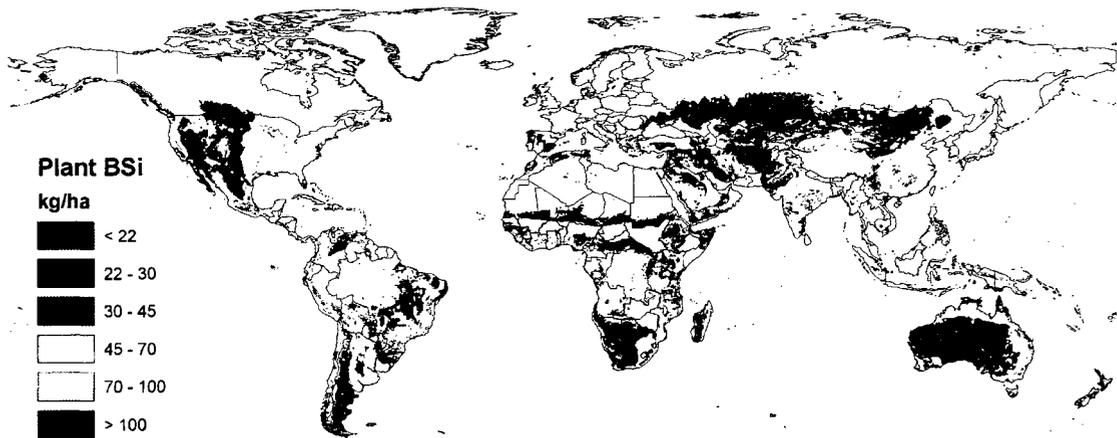


Figure 4.10. Plant biogenic silica (BSi) for grasslands predicted by the aboveground net primary productivity (ANPP) model.

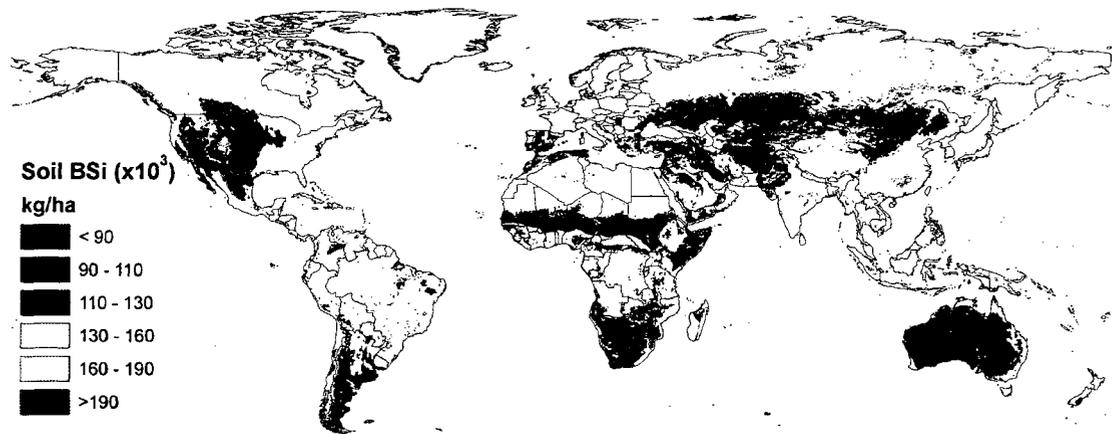


Figure 4.11. Soil biogenic silica (BSi) for grasslands predicted by the plant BSi model.

### *Grassland Evolution and Si Mobilization*

Evidence provided by this research supports a major role for BSi in controlling silica storage in and potential export from the terrestrial environment. We and others (e.g. Conley, 2002) hypothesized early on that there is a critical link in global biogeochemistry between the biogeochemical silica in terrestrial systems and its export to the better documented marine biogeochemical cycle of Si. Based on our results, the size of the terrestrial Si reservoir in grassland systems is indeed a large and active reservoir of BSi, and we argue that global expansion of grasslands might have had a profound influence on Si mobilization and storage globally. In the following section we attempt to link grassland expansion and contraction to marine records of terrestrial Si mobilization.

During the Cenozoic, the world's climate changed to include the glacial-interglacial cycles which have shaped much of the Earth's surface to what we see it as today. The three major causes of these cycles are the quality of radiation received from the sun, the composition of the atmosphere, and the distribution of land and sea (Bennett

& Glasser 1996). These changes in climate are most notably recognized by changes in the flora and fauna and are well recorded in oceanic sediments. Although a cooling climate affected the southern hemisphere at the onset of the Cenozoic due to the Antarctic Circumpolar Current, the northern hemisphere was not affected until the late Pliocene (three million years ago) when glaciers were able to form due to the strengthening of the North Atlantic currents after the closure of the seaway between North and South America (Bennett & Glasser 1996). Atmospheric circulations were also strongly influenced by the Late Cenozoic uplifts of the Tibetan Plateau and the Himalayan mountains of Asia and the Cordilleras of North America. These uplifts likely promoted the growth of mid-latitude ice sheets by the movement of polar air into these regions (Bennett & Glasser 1996). The glacial-interglacial cycles of mid-latitude regions were primarily driven by the amount of radiation received by the Earth which is dependent on its orbital cycles around the sun (Bennett & Glasser 1996).

Glacio-eustasy is one mechanism that explains global sea level changes. During periods of glaciation, global sea level falls resulted in regressions or basinward shifts in facies. The new base level created by the fall in sea level also caused rivers to incise and increased erosion (Nichols 1999). Additionally, drier climates prevailed (Street-Perrott et al. 2008) which promoted increased erosion and eolian transport of sediment from land to sea. The Last Glacial Maximum (LGM) is one example of increased aridity and aeolian flux of BSi (Pokras & Mix 1985).

From the paleoenvironmental record it is clear that the change to a cooler, drier climate triggered a shift in vegetation during the Miocene in which grass dominated ecosystems prevailed and may have had sufficient draw down of atmospheric CO<sub>2</sub> to

continue global cooling (Retallack 2001). Although grass dominated ecosystems are thought to have expanded during the mid to late Miocene, their temporal correlative contribution as a silica source for diatomaceous productivity remains uncertain.

The model outlined by Kidder and Gierlowski-Kordesch (2005) that Si flux and diatom accumulation are a direct response to Si mobilization by grass dominated systems and furthermore, that sea level regressions during glacial advances promoted erosion and the release of BSi from the soil. The lower Ge/Si ratios of diatom sediments retrieved from oceanic regressive facies intervals is proposed to be due to the contribution of phytolith Si with low Ge/Si ratios (Derry et al. 2005) which is a 3<sup>rd</sup> component added to the Murname-Stallard-Froelich (MSF) two-component model of primary and secondary mineral weathering. Because diatoms do not fractionate against Ge and represent the chemistry of their surrounding water (Barielle et al. 1998; Filippelli et al. 2000) diatomaceous Ge/Si ratio records are linked to glacial-interglacial cycles and furthermore, draws importance to terrestrial weathering (Shemesh et al. 1989; Froelich et al. 1992; Filippelli 1997) which controls eolian and riverine nutrients to the oceans (Barielle et al. 1998). Interglacial periods are marked by an increase in chemical weathering when grasses are productive and actively taking up and cycling Si which results in a more labile pool of stored BSi in soil with low Ge/Si ratios. During these interglacial times, Ge is also preferentially incorporated into secondary minerals (Murname & Stallard 1990) and released to oceanic basins if chemical weathering becomes intense.

Quaternary glacial-interglacial periods (determined from opaline Ge/Si ratios reported in Street-Perrott & Parker (2008)) influenced grassland area (Adams et al. 1990)

and thus Si biologic uptake and storage in soils. Based on grassland area (Adams et al. 1990) and our use of the definition of grasslands we calculated a 57% reduction in plant and soil BSi values today in comparison to the LGM, ~18 kyr ago (Figure 4.12). Lucustrine sediments also record a significant spike in total phytolith abundance during the LGM (Street-Perrott & Barker 2008) relative to today. Although grasses are likely mining and cycling greater amounts of Si today, the greater grassland area of the LGM is more important in determining global terrestrial Si storage in plants and soils. Additionally, the greater phytolith abundance in lucustrine deposits is accounted for by the physical erosion and transport prevalent during the LGM which is perhaps considered a weathering limited environment compared to today's transport limited environment.

An assessment of terrestrial Si storage and outflux during the Miocene is complicated as many processes are working in concert to determine the weathering regime which changes from the early to late Miocene. Germanium/Si ratios from the early Miocene sediments onward suggest that a grass-dominated ecosystem arose and prevailed (Figure 4.12). Prior to this time (Oligocene) grasses were rising, but were primarily in the form of dry, bunch grasslands (Retallack 2004). During the early and middle Miocene, the dominant grasses were dry climate short sod grasslands (Retallack 2004) whereas the late Miocene was a moister climate with tall grass production and likely widespread grasslands. Grassland type, spatial coverage, climate and tectonic activity (which determines physical and chemical weathering potential) together create a different environment in the early Miocene as compared to the late Miocene. Physical weathering is expected to dominate in the dry, tectonically active early Miocene whereas the physical weathering was coupled with a strong chemical weathering component

(Delaney & Filippelli 1994) and monsoonal conditions (Filippelli 1997) during the moist late Miocene. In previous studies (and in this work) we and others (Blecker et al. 2006; Melzer et al. in review) suggest that BSi uptake in plants increases with increasing ANPP. Melzer et al. (in review) suggest that this greater BSi in aboveground biomass results in greater BSi in the soil. The expansion of grasslands and their increased diversity (Kidder & Gierlowski-Kordesch 2005) from early to late Miocene under the climatic and tectonic conditions described above would indicate a peaked uptake and storage of BSi during the late Miocene. Phytolith influence on diatom production and their Ge/Si ratios was increasingly becoming important throughout the late Miocene and Pliocene especially during sea level regressions.

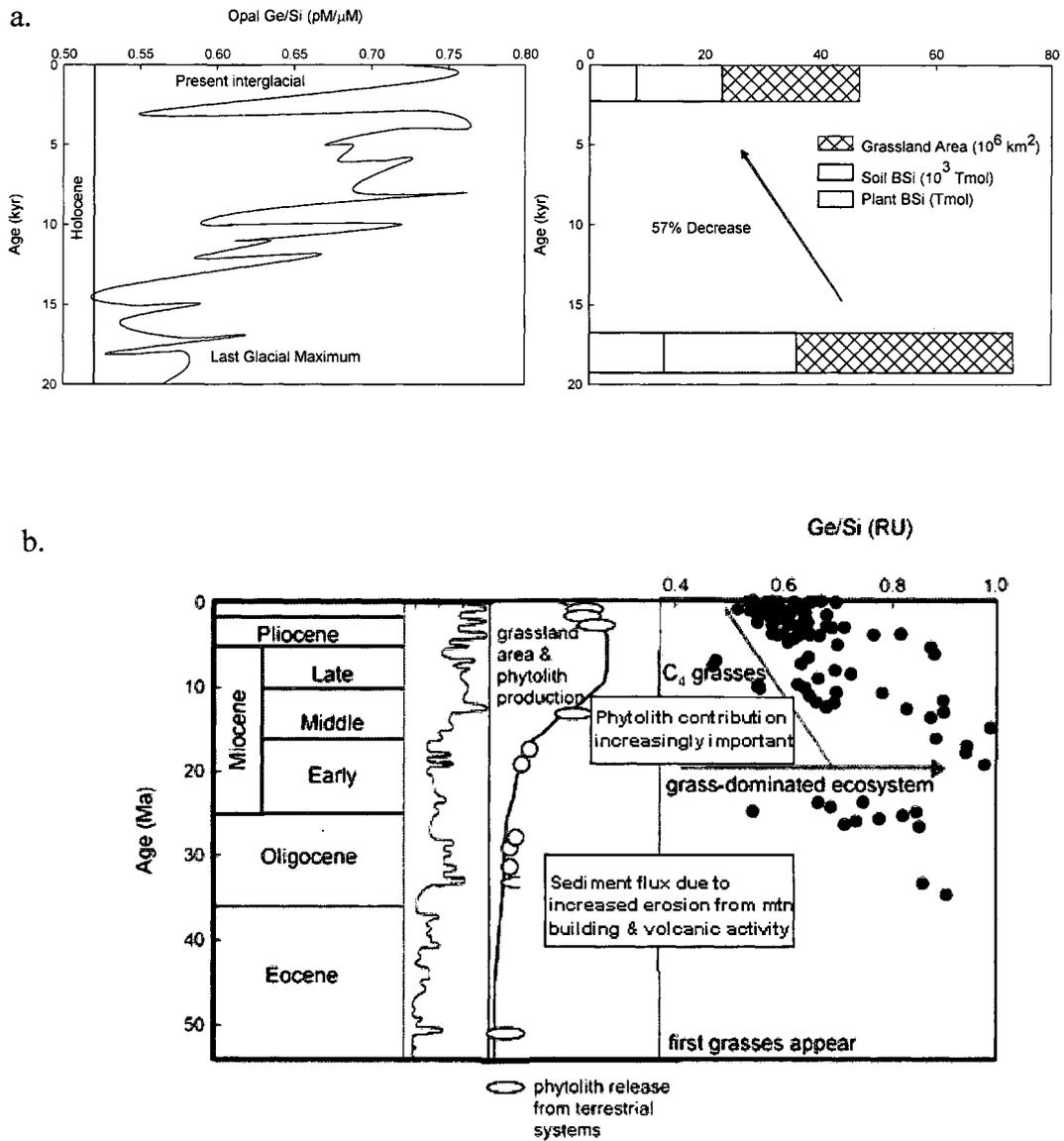


Figure 4.12. a) Grassland area (*adapted from Adams et al. 1990*) and plant and soil phytolith abundance today relative to 18kyr ago during the Last Glacial Maximum and compared to oceanic Ge/Si<sub>opal</sub> from the Holocene (Street-Perrott & Parker 2008), b) (*Modified from Kidder & Gierlowski-Kordesch 2005*) Timing of grassland expansion and expected grassland area and plant phytolith production and soil storage during the Neogene based on sea-level regressions (Haq et al. 1987), oceanic Ge/Si<sub>opal</sub> (Shemesh et al. 1989) and Ge/Si ratios of phytolith, unweathered rock and solute and secondary minerals and solute (Filippelli et al. 2000; Kurtz et al. 2002).

## Conclusion

The results of our continental and global estimates of BSi production and storage support the contention that grassland ecosystems are globally important reservoirs of labile Si whose production and storage is dependent on ANPP and geologic conditions. We suggest that soil BSi can be predicted by plant BSi using a simple linear regression whose basis relies on the idea that the quantities of BSi in the aboveground biomass is reflected in the BSi stores of the soil. Soil textural differences will inherently affect soil hydrology and thus, BSi cycling in both plants and soils.

The rise of grass dominated ecosystems globally during the Miocene was a potentially important biogeochemical stimulus for sharply increased abundance of diatomaceous sediment in the Miocene. Grasslands typically take up several times more silica per unit of carbon than other terrestrial ecosystems (Jones & Handreck 1967; Raven 1983; Epstein 1999). In doing so, they create a reservoir of soluble opal phytoliths, some of which are released quickly, such as during fires (e.g., Laclau et al. 2002; Pisaric 2002), whereas others are stored in soil for later release (Meunier et al. 1999). Germanium/Si ratios provide a proxy for the composition of seawater during diatom formation and may indicate a strong phytolith influence beginning in the late Miocene. During this time and onward, phytoliths contribute regularly to seawater chemistry, particularly during sea level falls as they are more labile sources of Si than mineral quartz.

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# C HAPTER FIVE

## Summary and Conclusions

## Summary and Conclusions

The primary objective of this work was to quantify variability in biogenic silica (BSi) pools by evaluating the ecological and pedological controls that regulate the sizes of these pools. Specifically, this primary objective allowed me to:

- (1) evaluate the range and variability of BSi production in plant biomass and storage in grassland and savanna soils as a function of fire frequency and grazing,
- (2) evaluate the importance of parent material in establishing the range and variability of BSi production and storage in plants and soils overlying granitic versus basaltic rocks.

A secondary objective of this research was to contribute to global estimations of BSi production and storage in grasslands worldwide. This secondary objective allowed me to:

- (3) evaluate climatic controls on annual net primary production and BSi levels in three grass types to help constrain global estimates of BSi mobilization and storage in grass dominated systems.

To address these objectives, I analyzed BSi pools in North American grasslands and South African savannas where controlled fire, grazing and parent material experiments were defined. The following chapter summaries address each objective as they are described above.

## *Chapter 2*

The results of this research show that BSi reservoirs are affected differently by fire and grazing in North America and South Africa which, may be linked to differences in their age and evolutionary history. South African plant and soil BSi pools were greater than in North America and, although the interaction between fire and grazing could not be assessed directly in South Africa, we did speculate on interactive factors based on their independent relationships and their comparisons to North American sites. In both North America and South Africa, fire resulted in greater amounts of soil BSi. South African soils also showed a positive response to grazing. Although North American soils did not respond to grazing in the absence of fire, they did show a response to their interactive effects.

Because plant and soil BSi *concentrations* are unresponsive to fire and grazing, we suggest that mass differences in BSi result from differences in ANPP which, is directly affected by these ecological drivers. In general, ANPP is expected to respond positively to fire (Knapp et al. 1998a) and grazing (Frank et al. 2002). Fire and grazing thus influence BSi storage indirectly because plant and soil BSi positively correlate with ANPP. Additionally, the interactive effects of fire and grazing in North America may agree with the results of Archibald et al. (2005) that fire stimulates new growth which attracts grazers. The combination of increased growth and the consumption and release of BSi rich vegetation back to soil results in greater BSi in plants and soil. The same interactive assessment could not be made for South African sites, although we speculate that grazing is more important in BSi soil storage than fire.

### *Chapter 3*

At two South African sites in Kruger National Park that are uncontrolled for fire and grazing, we evaluated the effects of parent material (soils derived from basalt vs. granite) on BSi mobilization. Our results indicate that the quantities, fate and mobility of BSi in the soils of grassland ecosystems are strongly influenced by the chemical and physical nature of the soil parent material. A comparison of finer basaltic soils with coarser granitic soils showed a distinction between Si cycling driven by biologic uptake and by mineral dissolution respectively. The basaltic soil systems had greater plant and soil BSi pools and higher surface concentrations of DSi with less total Si loss than the granitic soil systems. Although a greater proportion of the total Si is made up of BSi in basaltic soils, BSi has longer turnover times in these soils than granitic soils. We suggest tighter cycling of BSi in basaltic soil where surface processes dominate and Si is readily available. In granitic soils, the texture and inherent mineralogy results in a leakier cycling of BSi with a greater dependence on BSi dissolution. Although total DSi quantities are higher in granitic systems, their surface concentrations are lower which indicates that plants may have to mine deeper within the soil for Si uptake.

### *Chapter 4*

Data presented in chapter three from savanna sites along with additional data for North American shrub and grassland sites were analyzed to construct global BSi estimates within the context of found results that ANPP and soil texture (imparted by parent material) are important factors determining BSi mobilization. Our models indicate that the variance in plant BSi is explained by ANPP and that the variance in soil BSi is

explained by plant BSi. Using these models, our results indicate that terrestrial grassland ecosystems are indeed important reservoirs of BSi and contribute  $\sim 8 \text{ Tmol Si yr}^{-1}$  or  $\sim 15\text{-}16 \%$  to the total BSi reservoir for all terrestrial aboveground biomass determined by (Conley 2002). Soils store  $\sim 18,000 \text{ Tmol Si yr}^{-1}$ , orders of magnitude more BSi than aboveground biomass where a majority of the BSi lies within the finer soil fraction.

### *Further Considerations*

The new knowledge produced by this research increased our understanding of terrestrial Si biogeochemical cycles and will help facilitate more robust forecasts of human impacts on global-scale processes in both terrestrial and oceanic systems. The Si cycle in soils is complex and requires interdisciplinary attention for a complete understanding of the processes that drive it. The two general areas that have defined and laid the foundation of our research may be a useful context in viewing future research. These two perspective and the questions that they spawn include:

#### (1) Ecological perspective

- a. How do changes in plant species composition as a result of fire and/or grazing effect concentrations of BSi in uptake and overall storage in aboveground biomass?
- b. How do microorganisms influence Si transformations in soils by decomposition of plant litter, active mineral dissolution, and bioturbation (removing BSi from active root zone)?

#### (2) Geochemical perspective

- a. How does the depth distribution and vertical translocation of soil BSi effect possible labile and stable fractions of BSi for mobility and storage?
- b. How can we use new geochemical and isotopic tracers to quantify the paleoenvironmental biocycling of Si and how can we use these tracers to link terrestrial soil with limnological and oceanic studies as well with their BSi transport mechanisms such as by riverine and eolian transport.

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