Biogeochemistry (2012) 108:317–334
DOI 10.1007/s10533-011-9602-2

# Lithologic controls on biogenic silica cycling in South African savanna ecosystems

**Susan E. Melzer · Oliver A. Chadwick ·
Anthony S. Hartshorn · Lesego M. Khomo ·
Alan K. Knapp · Eugene F. Kelly**

Received: 1 December 2010 / Accepted: 28 March 2011 / Published online: 8 April 2011

**Abstract** The efficacy of higher plants at mining Si from primary and secondary minerals in terrestrial ecosystems is now recognized as an important weathering mechanism. Grassland ecosystems are a particularly large reservoir of biogenic silica and are thus likely to be a key regulator of Si mobilization. Herein, we examine the effects of parent material (basaltic and granitic rocks) on the range and variability of biogenic silica pools in grass-dominated ecosystems along two precipitation gradients of Kruger National Park, South Africa. Four soil pedons and adjacent dominant plant species were characterized for biogenic silica content. Our results indicate that although soils derived from basalt had less total Si and dissolved Si than soils derived from granite, a greater proportion of the total Si was made up of biogenically derived silica. In general, plants and soils overlying basaltic versus granitic parent material stored greater quantities of biogenic silica and had longer turnover times of the biogenic silica pool in soils. Additionally, the relative abundance of biogenic silica was greater at the drier sites along the precipitation gradient regardless of parent material. These results suggest that the biogeochemical cycling of Si is strongly influenced by parent material and the hydrologic controls parent material imparts on soils. While soils derived from both basalt and granite are strongly regulated by biologic uptake, the former is a "tighter" system with less loss of Si than the latter which, although more dependent on biogenic silica dissolution, has greater losses of total Si. Lithologic discontinuities span beyond grasslands and are predicted to also influence biogenic silica cycling in other ecosystems.

**Keywords** Biogenic silica · Soil · Parent material · South African savannas · Terrestrial plants

**Abbreviations**

| | |
|---|---|
| ANPP | Aboveground net primary productivity |
| BSi | Biogenic silica |

---

S. E. Melzer (✉) · E. F. Kelly
Department of Soil and Crop Sciences, Colorado State University, Fort Collins, CO 80523-1170, USA
e-mail: Susan.Melzer@colostate.edu

O. A. Chadwick
Geography Department and Environmental Studies Program, University of California, Santa Barbara, Santa Barbara, CA 93106-4060, USA

A. S. Hartshorn
Department of Geology and Environmental Science, James Madison University, Harrisonburg, VA 22807, USA

L. M. Khomo
School of Animal, Plant and Environmental Studies, University of the Witwatersrand, Johannesburg, Wits 2050, South Africa

A. K. Knapp
Department of Biology and Graduate Degree Program in Ecology, Colorado State University, Fort Collins, CO 80523, USA

| | |
|---|---|
| DSi | Dissolved silica |
| SOC | Soil organic carbon |
| TSi | Total silica |
| WRB | World Reference Base |

## Introduction

Growing evidence suggests a major role of biologically mediated silica cycling in regulating silica storage and mobility in terrestrial ecosystems (Conley 2002; Blecker et al. 2006; Melzer et al. 2010). In some ecosystems, this biogenic silica (BSi) can comprise up to 80% of the soluble silica pool (Derry et al. 2005) that is readily mobilized 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 2002).

Grassland ecosystems support a particularly large reservoir of BSi due to dominance by grasses which have relatively high silica content. Grassland BSi 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. 2010). In general, increased chemical weathering and biological activity in grassland ecosystems associated with increasing precipitation, for example result in increased BSi availability for plant uptake.

Although previous studies have focused on the influence of parent material on weathering rates, soil nutrients (e.g. Hamdan and Burnham 1996), and the physical properties that influence soil hydrology (e.g. Osher and Buol 1998), little is known about how parent material influences the biological cycling of silica. Identifying how geologic factors like mineral type and crystal size control the production, mobilization, and storage 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 and Sherwood 1971). In general, basalts contain less Si than granites; however, basalts are more easily weathered (Maybeck 1986; Amiotte-Suchet and Probst 1993) because they are mafic in composition and contain most of their Si in the minerals feldspar and olivine. Conversely, granites have higher amounts of Si and are more stable at the Earth’s surface because they are felsic in composition and contain most of their Si in the minerals quartz and feldspar. Although granites weather at a slower rate than basalts, they contain more silica and can provide a longer-term supply to the biota.

The geochemical weathering of silicate minerals is a slow process (Lerman 1988) that is accelerated by the effects of plant growth (Richter and Markewitz 1995; Blecker et al. 2006). Meunier (2003) demonstrated that the inclusion of plants increased estimates of geochemical weathering by a factor of up to eight. Several key biological mechanisms are identified as directly influencing weathering, namely, production of $CO_2$ and organic acids (Berner 1992), and biocycling of metals (Drever 1994) and silica (Kelly et al. 1998). The 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 ($Si(OH)_4$) and transform it into BSi, (e.g. phytoliths or more soluble forms of $SiO_4{\cdot}nH_2O$) (Raven 1983; Piperno 1988; Datnoff et al. 2001). Plants can 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 plant tissues decompose, BSi enters the soil system where it may be distributed throughout the profile by physical translocation and chemical dissolution (Bartoli 1981, 1983). Grassland soil BSi typically makes up ~3 to 5 wt% on a total (<2 mm) soil basis (Drees et al. 1989; Kelly 1989), but may range from <0.5 to 5, and in some cases up to 20 wt% (Hart 1992; Alexandre et al. 1997; Clarke 2003). Dissolution rates of BSi can be 5 orders of magnitude faster than those of mineral silicates 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 rates (Kelly et al. 1991; Meunier 2003; Blecker et al. 2006); however, this is dependent on the suite of silicate minerals present and their solubility potential, and the saturation state of the solution.

Weathering processes and soil formation are impacted strongly but variably by plant cycling of Si (Kelly et al. 1998). As much as 80% of the total Si inputs to oceans is from rivers (e.g. Treguer et al. 1995), and as much as 16% of the total Si is biogenically derived (Conley 1997). In tropical ecosystems, 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 capacitor role of rocks, with different primary mineral assemblages, on BSi dissolution is not completely understood and is necessary information to determine the fate and mobility of Si in soils. Based on isolated mineral Si and plant and soil BSi pools, we (1) evaluated the variability of BSi concentrations in aboveground biomass and soils with parent materials that compositionally fall within the range of basalts and granites, (2) determined whether a precipitation gradient affects Si dynamics in soils of granitic and basaltic composition.

## 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 (Fig. 1). The north–south trending park extends ~400 km and covers two climatic zones: the lowveld bushveld zone near Skukuza in the south (rainfall of 500–700 mm $\text{year}^{-1}$) and the arid bushveld zone near Shingwedzi in the north (rainfall of 300–500 mm $\text{year}^{-1}$) (Venter et al. 2003). Both climatic zones are classified as dry, low-latitude steppe (BSh) by the Koppen climate classification (Peel et al. 2007). For the purposes of this paper we assume that past rainfall has not shifted dramatically at least over the past two or three hundred thousand years. The best available analysis of recent climate shifts come from reconstructions of summer (wet season) rainfall for Pretoria over the past 200 ka (Partridge et al. 2004), which fixes the range in insolation-driven variation of rainfall at 540 and 90 mm $\text{year}^{-1}$ with a present-day value of 780 mm $\text{year}^{-1}$. Full glacial rainfall was likely lower than the present value.

The rocks in KNP display a long geologic history that has been described in detail by Schutte (1974), Bristow (1980), Bristow and 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 (<5% slopes), 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 and 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 and 3) and granites (pedons 2 and 4) in both climatic regions (Fig. 1). We infer similar residence times for basaltic and granitic soils within each climatic zone based on their geomorphological juxtapositioning (i.e. general processes of denundation, weathering, and mass wasting that shape geomorphic environments are expected to operate similarly in terrains with comparable tectonic histories and topographic highs and lows or superpositioning) upstream of the rhyolite ridge which sets base level for the entire KNP. The average catchment erosion rates in the granites that make up the western portion of the park is 3.5 m $\text{Ma}^{-1}$ ($\pm 0.5$; $n = 16$) based on $^{10}$Be measurements in quartz sand collected from 1st through 4th order streams in four river catchments throughout the park (Chadwick et al. 2009). Soil thickness on the granite crests range from about 60 cm in the northern, drier region to about 100 cm in the southern, wetter region. Based on the catchment erosion rates and the average soil thickness it can be estimated that soil residence times range from about 200 ka in the north to about 500 ka in the south (Chadwick et al. 2010). 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

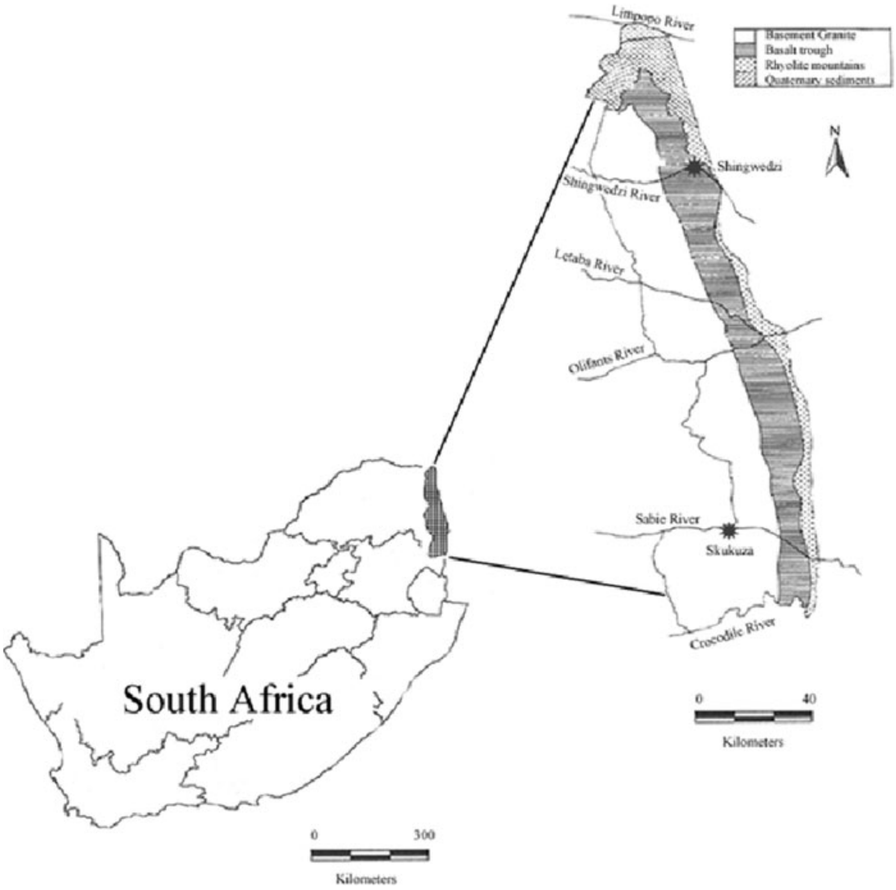

**Fig. 1** The site locations in Kruger National Park in South Africa at Shingwedzi and Skukuza (adapted from Van Riet and Cooks 1990)

referred to as basalts and granites and their overlying soils are referred to as basaltic and granitic soils respectively. Khomo (2008) recognized a distinction between the Skukuza and Shingwedzi granitic lithologies in which the latter exhibited migmatization and migmatite fractionation during weathering. Migmatite was less prevalent at Skukuza as was shown by their average Ti and Zr concentrations. The climatic and lithologic differences among the four sites provided an opportunity to quantify the relative importance of the effects of soil parent material on BSi cycling (Table 1).

## Field sampling

Soil pit locations were selected based on their topographic positioning (e.g. level uplands), 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. Four pedons, representing each lithologic-climatic pair, were described and sampled based on genetic horizons (Schoeneberger et al. 1998). The drier granitic and basaltic soils are classified as Typic Haplocambids and Typic Haplocalcids, respectively. The wetter granitic and basaltic soils are classified as Typic Dystrustepts and Vertic Eutrudepts (Khomo 2008; Khomo et al. 2011). 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, except for the Skukuza basalt site. 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 at the study site (Vorster 1979; Khomo 2008). 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 1) and combined into a bulk sample for analyses.

**Table 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)[a] | 454 | 599 |
| MAT (°C)[b] | 23 | 22 |
| ANPP (g $m^{-2}$)[c] | | |
| Granite | 445 | 329 |
| Basalt | 473 | 417 |
| Climate[d] | BSh | BSh |
| Biome | Savanna | Savanna |
| Grass species | | |
| Granite | *Cedrus ciliaris* | *Eragrostis rigidior, Cymbopogon plurinodis* |
| Basalt | *Bothriochloa radicans* | *Themeda triandra, Heteropogon contortus* |

[a] MAP = Mean annual precipitation (Codron et al. 2005)

[b] MAT = Mean annual temperature (Venter 1990)

[c] ANPP = Aboveground annual net primary productivity

[d] BSh = Dry low latitude steppe (Peel et al. 2007)

## 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 was analyzed on a LECO-TruSpec CN analyzer at the Natural Resource Ecology Laboratory at Colorado State University.

Soil texture on <2-mm unground soil was determined using the hydrometer method (Gee and Bauder 1986). Bulk density was determined by the clod method (Blake and Hartge 1986). Pedon 3 clods were fragile and could not be used upon receipt at the laboratory, so we estimated bulk density for these samples using an empirical equation relating bulk density to organic carbon (Adams 1973; Rawls 1983). Parent material bulk densities were 2.9 and 2.8 g $cm^{-3}$ for basalts and granites, respectively (Mussett and 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, Ba, Ca, Cr, Fe, K, Mg, Mn, Na, Nb, P, Si, Sr, Ti, Y, Zn, and Zr after Li-metaborate fusion.

Mineralogy was determined on a Scintag PADV from 2° to 65° $2\theta$ at 2° per min with Cu-radiation (University of Colorado, Boulder). Clay samples were additionally exposed to ethylene glycol and scanned at 2–20° $2\theta$ at 2° per min to distinguish the 2:1 expandable clays from the 1:1 clays. Rock thin-section analysis was also conducted for mineralogical composition. Si concentration in soil solution (dissolved silica, DSi) was determined on saturation paste extracts (Lajtha et al. 1999).

## 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 1:1:8 ratios, respectively. Samples were then thoroughly rinsed with DI, treated with 80°C, 70% ethanol to strip the 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 desiccator and weighed. The resultant ash was then treated at a temperature of 65°C with 10% HCl, filtered through pre-weighed 0.2 µm polycarbonate membranes, treated at a temperature of 65°C with 30% $H_2O_2$ 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 kg $ha^{-1}$ by incorporating aboveground net primary productivity (ANPP). Only standing crop biomass data was available for the study sites; ANPP data were 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 $Na_2CO_3$. Although the $Na_2CO_3$ 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 (Saccone et al. 2006, 2007; Sauer et al. 2006). Approximately 30 (±0.05) mg of hand-ground freeze-dried soil was measured into 60 mL polypropylene round flat-bottom bottles with 40.0 mL of 1% $Na_2CO_3$. 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 (DSi) was conducted using the molybdate blue spectrophotometric method where the spectrophotometer was set at 812 nm (Mortlock and Froelich 1989), a modification from the reduced molybdosilicic acid spectrophotometric method (Strickland and Parsons 1968; Fanning and Pilson 1973). Disodium hexaflourosilicate, 99+% $Na_2SiF_6$ 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 $Na_2CO_3$) 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 areal units (e.g. kg $ha^{-1}$) by incorporating depth and bulk density data. The total volumetric Si value for a pedon is found from the sum of its horizons.

## Mass balance

Constituent mass balance is used to quantify fluxes by focusing on element losses on the basis of volume change and parent material composition. Specifically, it uses the amounts of immobile constituents to quantify the gains and losses of less mobile material during pedogenesis. The processes of primary mineral weathering can be partitioned into three major groups: (1) the release of ions or molecules into solution, (2) the production of new secondary minerals, and (3) the residual accumulation of insoluble material (Bland and 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 quantify the extent of weathering by calculating the volume changes associated with the mass fluxes (gains and losses) within soil horizons and among soils.

Strain, $\varepsilon_{i,w}$, 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 and 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 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 element flux. Mass transfer was computed from density, chemical composition data, and volume change (Brimhall and 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 versus 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. The last horizon of each pedon was either lengthened or shortened to normalize soils to equivalent depths (i.e. 100 cm) for conducting mass balance calculation.

We calculated mass fluxes of Si by summing the product of horizon-specific mass transfer coefficients and rock density ($\sim$3 g cm$^{-3}$). For example, a 1-m deep soil profile with a depth-weighted average $\tau_{Zr,Si}$ of $-0.5$ would produce a long-term flux of $-1.5$ g Si cm$^{-2}$ or $-1.5$E7 kg Si ha$^{-1}$.

## Results

### Physical, chemical and mineralogical composition of the soils

Regardless of parent material and precipitation regimes, soils possess similar morphological features (Table 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, which is likely due to the greater organic carbon and clay content. 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 2). The pH values were generally more acidic in granitic soils and in soils obtained in the higher precipitation zone (Skukuza) (Table 2).

The granites are primarily composed of quartz and plagioclase with some microcline and minor amounts of ferromagnesian minerals. Kaolinite and mica make up a majority of the clay fraction. Textural evidence from petrographic analysis suggests a metamorphic overprint on the granitic rocks. 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.

The chemical composition of the granites and basalts used for our mass balance determinations are presented in Table 3. Granites at Shingwedzi and Skukuza were uniform in their elemental concentration with a <3% difference in the major (Si and Al) and less than 4% difference in the intermediately abundant (Ca, Na, K, and Fe) elements (Table 3). The minor granitic constituents Mg and P were less than 0.3% different and the trace constituents Zr and Ti were less than 0.02% different from Shingwedzi to Skukuza. Basalt was not exposed at Skukuza so data used were derived from Shingwedzi basalt samples.

### 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 (Fig. 2). Both granitic soils exhibited uniform strain with depth. Although the granitic Shingwedzi soils do not show significant collapse, these soils have net elemental loss in each horizon. Silicon and Al show uniform losses with depth and the greatest losses are in surface horizons (Table 4). Base cations (e.g. Ca, K, and Na) do not show a clear trend in losses or gains with depth. In general, the granitic Skukuza soils show greatest loss of cations and exhibit a uniform distribution for Si, Al, and Mg. All soils experienced more intense weathering in the surface. The base cations that are likely more susceptible to biocycling, such as K, do not show this depth distribution as greater losses of these elements, relative to other

**Table 2** Abbreviated morphological descriptions for each of the four pedons within Kruger National Park

| Site location/ lithology | Pedon | Diagnostic horizon | Depth (cm) | Bulk density (g cm$^{-3}$) | Texture class | Clay (%) | pH | Organic carbon (%) | Color moist/dry | Structure |
|---|---|---|---|---|---|---|---|---|---|---|
| Shingwedzi/ basalt | 1 | A | 0–5 | 1.4 | c | 53 | 7.1 | 2.4 | 10YR 2/1<br>10YR 3/1 | 1 f sbk |
| | | BA | 5–31 | 1.7 | c | 61 | 6.6 | 2.0 | 10YR 2/1<br>10YR 3/1 | 3 f sbk |
| | | Bw1 | 31–75 | 1.4 | c | 67 | 7.3 | 1.9 | 10YR 2/1<br>10YR 3/1 | 2 f sbk |
| | | Bw2 | 75–100 | 1.6 | c | 61 | 7.6 | 1.4 | 10YR 2/1<br>10YR 3/1 | 1 f sbk |
| Shingwedzi/ granite | 2 | A | 0–1 | 1.4 | sl | 11 | 6.7 | 1.1 | 10YR 3/3<br>10YR 4/4 | 0 sg |
| | | Bw1 | 1–13 | 1.5 | sl | 14 | 6.6 | 0.6 | 10YR 2/2<br>10YR 4/3 | 1 vf sbk |
| | | Bw2 | 13–22 | 1.7 | sl | 15 | 6.8 | 0.4 | 10YR 3/3<br>10YR 4/4 | 2 m sbk |
| | | Bw3 | 22–45 | 1.7 | sl | 14 | 6.6 | 0.4 | 7.5YR 3/3<br>7.5YR 4/4 | 2 f sbk |
| Skukuza/ basalt | 3 | A | 0–8 | 1.5 | cl | 30 | 5.9 | 2.2 | 5YR 2.5/2<br>5YR 3/3 | 2 m gr/2 m sbk |
| | | Bw1 | 8–19 | 1.3 | cl | 39 | 6.0 | 1.9 | 5YR 2.5/2<br>5YR 3/3 | 1 m f gr/1 f sbk |
| | | Bw2 | 19–32 | 1.6 | cl | 39 | 6.3 | 1.0 | 2.5YR 2.5/3<br>2.5YR 2.5/4 | 1 m sbk |
| | | C1 | 32–46 | 1.7 | scl | 28 | 6.6 | 0.5 | 7.5YR 3/4<br>7.5YR 4/4 | 0 m |
| | | C2 | 46+ | 1.7 | scl | 33 | 6.4 | 0.4 | 7.5YR 3/4<br>7.5YR 4/4 | 0 m |
| Skukuza/ granite | 4 | A | 0–15 | 1.7 | sl | 14 | 5.0 | 0.5 | 7.5YR 2.5/3<br>7.5YR 5/4 | 1 f-m sbk |
| | | Bw1 | 15–41 | 1.8 | sl | 14 | 4.7 | 0.3 | 7.5YR 3/4<br>7.5YR 4/4 | 1 f-m-co sbk |
| | | Bw2 | 41–62 | 1.8 | sl | 17 | 4.7 | 0.3 | 5YR 4/4<br>7.5YR 5/4 | 1 f sbk/ 1 f-m gr |
| | | Bw3 | 62–95 | 1.9 | sl | 14 | 5.0 | 0.2 | 7.5YR 4/4<br>7.5YR 6/4 | 1 vff gr/sg |
| | | C | 95–105 | 1.9 | sl | 11 | 4.7 | 0.2 | 10YR 4/3<br>10YR 6/4 | 0 m |

Abbreviations are according to USDA Soil Survey Staff (1975)

elements, are partially due to active mining by plant roots deeper in the profile (Jobbagy and Jackson 2004).

Basaltic soils exhibited dilation which varied with depth at both sites. Dilation increased with depth in the Skukuza soils to nearly three times its original

**Table 3** Chemical composition of rock parent material for each of the four pedons within Kruger National Park

| | Shingwedzi | | Skukuza | |
|---|---|---|---|---|
| | Basalt (%) | Granite (%) | Basalt (%)[a] | Granite (%) |
| $SiO_2$ | 53.05 | 70.59 | 53.05 | 68.45 |
| $Al_2O_3$ | 13.23 | 15.68 | 13.23 | 14.74 |
| $Fe_2O_3$ | 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 |
| $Na_2O$ | 2.29 | 5.53 | 2.29 | 2.43 |
| $K_2O$ | 4.46 | 1.93 | 4.46 | 5.06 |
| $TiO_2$ | 3.84 | 0.28 | 3.84 | 0.30 |
| $P_2O_5$ | 0.69 | 0.14 | 0.69 | 0.05 |
| Zr | 0.06 | 0.01 | 0.06 | 0.01 |

[a] Data derived from Shingwedzi basalt samples

volume and increased in the A and Bw1 horizons in the Shingwedzi soils to nearly double its original volume (Fig. 2). Similar to the granitic soils, the base cations from basaltic Shingwedzi soils showed a net loss throughout their depth. Silicon and Al showed net gains and their increase with depth at Skukuza may indicate their incorporation into secondary minerals. Skukuza soils exhibit a net cation loss at the surface with cation gains at depth from Al, Ca, Mg, Na, and Si. In all soils, mass balance calculations suggest that strain is primarily attributed to base cation transfers downward within the pedons (Table 4). The incorporation of organic carbon and clay illuviation may also contribute to dilation, especially in the basaltic soils.

Soil elemental fluxes 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 5). Aluminum contributed to volume change following in a similar pattern to that of Si. Calcium, K, Mg, and Na were primarily lost from the Shingwedzi basaltic and both granitic soils (Table 5).

## Si transformations, transfers and losses

The elemental losses and gains from soils are the result of multiple processes and the compositional difference among parent materials. These processes regulate the intensity of transformations, transfers, and net loss of Si from soils. Shingwedzi and

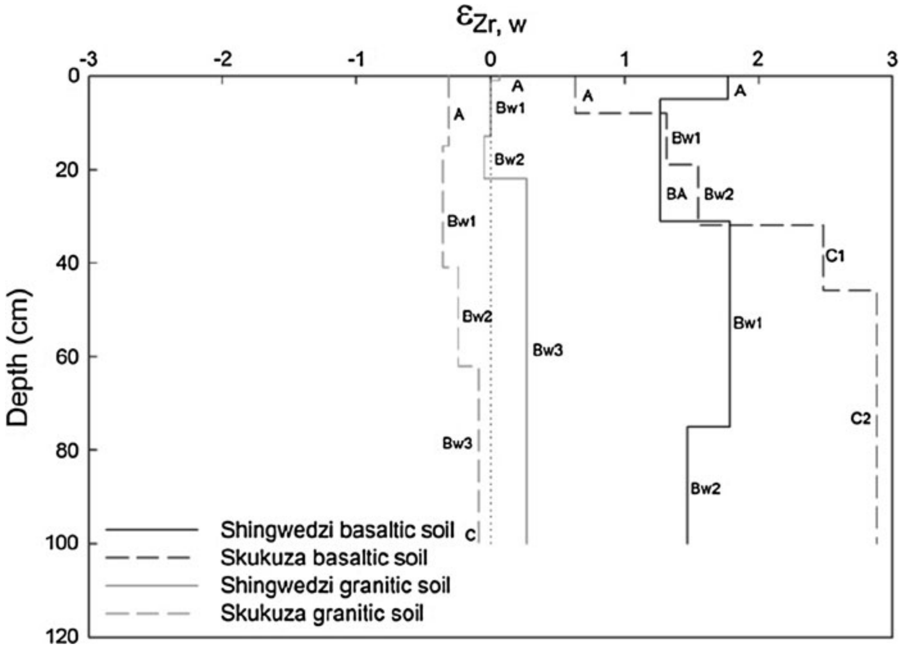

**Fig. 2** Strain ($\varepsilon_{Zr,w}$) as a function of a depth to 100 cm for soils derived from basalt and granite at Shingwedzi and Skukuza. *Dotted vertical line* represents zero strain or zero volume change. Positive strain denotes dilation or volume gain and negative strain denotes collapse or volume loss. Strain calculations used Zr as the immobile element

**Table 4** Select elemental constituents and their mass transfers within and among pedons in Kruger National Park

| Site: lithology | Pedon: horizon | % | | | | | | $\tau_{j,w}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Si | Al | K | Ca | Na | Mg | Si | Al | K | Ca | Na | Mg |
| Shingwedzi: 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 | −0.2 |
| | 1: Bw1 | 23.9 | 6.1 | 2.4 | 1.2 | 0.8 | 1.6 | 0.3 | 0.2 | −0.1 | −0.6 | −0.4 | −0.1 |
| | 1: Bw2 | 24.4 | 6.2 | 2.3 | 1.1 | 0.8 | 1.7 | 0.3 | 0.2 | −0.2 | −0.6 | −0.4 | 0.0 |
| Shingwedzi: 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 | −0.6 |
| | 2: Bw1 | 33.7 | 7.2 | 1.7 | 1.0 | 2.3 | 0.3 | −0.4 | −0.5 | −0.4 | −0.6 | −0.7 | −0.5 |
| | 2: Bw2 | 33.7 | 7.3 | 1.7 | 0.9 | 2.3 | 0.2 | −0.4 | −0.5 | −0.4 | −0.7 | −0.7 | −0.6 |
| | 2: Bw3 | 34.4 | 7.2 | 1.7 | 0.8 | 2.4 | 0.2 | −0.2 | −0.3 | −0.2 | −0.6 | −0.5 | −0.5 |
| Skukuza: 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 | −0.8 |
| | 3: Bw1 | 20.1 | 7.2 | 1.3 | 1.0 | 0.8 | 0.6 | −0.2 | 0.1 | −0.6 | −0.7 | −0.5 | −0.7 |
| | 3: Bw2 | 19.7 | 8.5 | 1.0 | 2.0 | 0.9 | 1.1 | 0.1 | 0.7 | −0.6 | −0.2 | −0.3 | −0.3 |
| | 3: C1 | 19.3 | 8.2 | 0.7 | 3.5 | 1.1 | 1.9 | 0.6 | 1.4 | −0.6 | 1.0 | 0.4 | 0.7 |
| | 3: C2 | 20.8 | 7.7 | 0.6 | 4.8 | 1.4 | 2.5 | 0.9 | 1.5 | −0.6 | 2.0 | 0.8 | 1.4 |
| Skukuza: granitic soils | 4: A | 36.0 | 6.3 | 3.0 | 0.6 | 1.7 | 0.0 | −0.5 | −0.7 | −0.7 | −0.9 | −0.6 | −1.0 |
| | 4: Bw1 | 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: Bw2 | 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: Bw3 | 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 |

**Table 5** Select elemental constituents and their mass flux (g cm$^{-2}$) for each pedon within Kruger National Park

| | Shingwedzi | | Skukuza | |
|---|---|---|---|---|
| | Basaltic soil | Granitic soil | Basaltic soil | Granitic soil |
| Si | 8.6 | −18.8 | 9.9 | −53.0 |
| Al | 1.5 | −7.1 | 5.9 | −17.2 |
| Ca | −2.4 | −2.1 | 2.5 | −7.1 |
| Na | −0.8 | −5.5 | 0.3 | −3.6 |
| K | −0.6 | −0.9 | −2.2 | −10.1 |
| Mg | −0.3 | −0.3 | 0.9 | −2.0 |

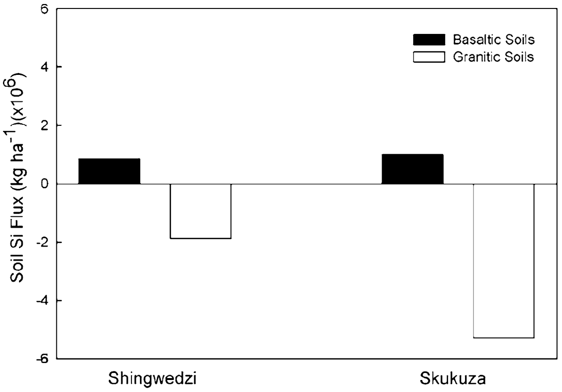

**Fig. 3** Soil Si flux (kg ha$^{-1}$) (×10$^6$) for basaltic and granitic soils at Shingwedzi and Skukuza sites. Calculations were based on soil depths of 100 cm

Skukuza basaltic soils accumulated Si relative to the parent materials while granitic soils at both locations presented net losses relative to parent material amounts (Fig. 3). There is also an important interaction between climate and rock type, where wetter granitic soils have greater Si loss than drier granitic soils. This climatic relationship is not apparent in the basaltic soils.

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 mineral formation. In general, the DSi levels were greater in the surface horizons and less at lower horizons of the basaltic versus granitic soils (Fig. 4). At greater depths, Skukuza soils had lower DSi concentrations than Shingwedzi soils which, on average, was a difference of 3% for granitic soils and 27% for basaltic soils (Fig. 4).

Biogenic Si values in plants ranged from ∼ 4 to 7% by weight (131–325 kg ha$^{-1}$) (Fig. 5a) and are generally higher than those of North American

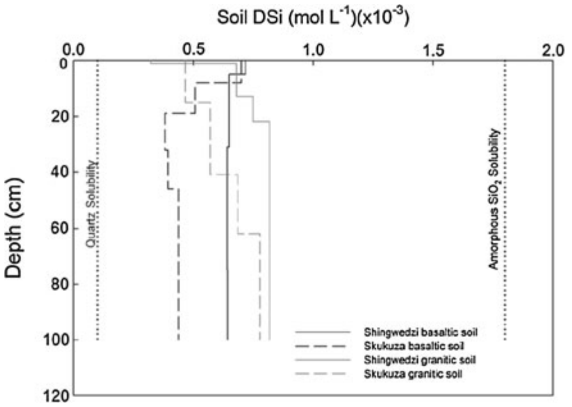

**Fig. 4** Soil dissolved Si (DSi) concentrations (mol $L^{-1}$) ($\times 10^{-3}$) as a function of depth to 100 cm for basaltic and granitic soils at Shingwedzi and Skukuza sites

grasslands (Raven 1983; Sangster and Hodson 1986; Piperno 1988; Epstein 1999; Datnoff et al. 2001; Blecker et al. 2006; Melzer et al. 2010). Although plant species differences (Table 1) 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; at Skukuza, plants overlying basaltic soils had 46% more BSi than those overlying granitic soils (Fig. 5a). Plants overlying basaltic soils at Shingwedzi had 26% greater BSi than those at Skukuza. Plants overlying granitic soils at Shingwedi had 28% greater BSi than those at Skukuza (Fig. 5a).

Soil BSi values ranged from 1 to 7% by weight and pedon totals ranged from ~317,000 to 793,000 kg $ha^{-1}$ (Fig. 5b). On average, soil BSi was 45% higher in basaltic soils than granitic soils, comparing within climatic zones (Fig. 5b). The drier Shingwedzi basaltic and granitic soils had 13 and 39% greater BSi, respectively, than their wetter Skukuza counterparts (Fig. 5b). The proportion of total soil Si derived from soil BSi is greatest in the upper portions of the soil profile in basaltic soils (Fig. 6a, 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 contrast to the basaltic soils, the granitic soils did not exhibit a well defined depth distribution; however, slightly greater quantities of BSi were found deeper in the soil profile (Fig. 6b, d).

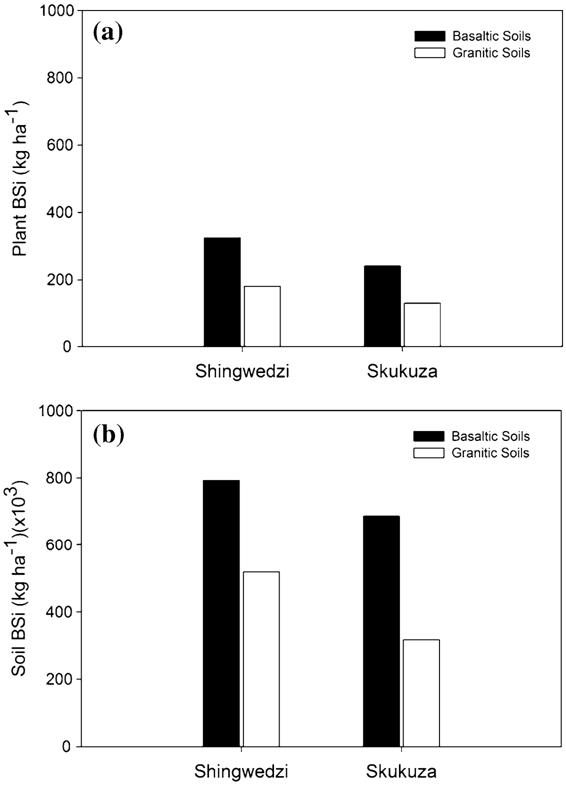

**Fig. 5** **a** Plant biogenic silica (BSi) (kg $ha^{-1}$) for the dominant grass species overlying basaltic and granitic soils at Shingwedzi and Skukuza sites. **b** Soil biogenic silica (BSi) (kg $ha^{-1}$) ($\times 10^{3}$) for basaltic and granitic soils at Shingwedzi and Skukuza sites. Calculations were based on soil depths of 100 cm

## Discussion

Figure 7 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:

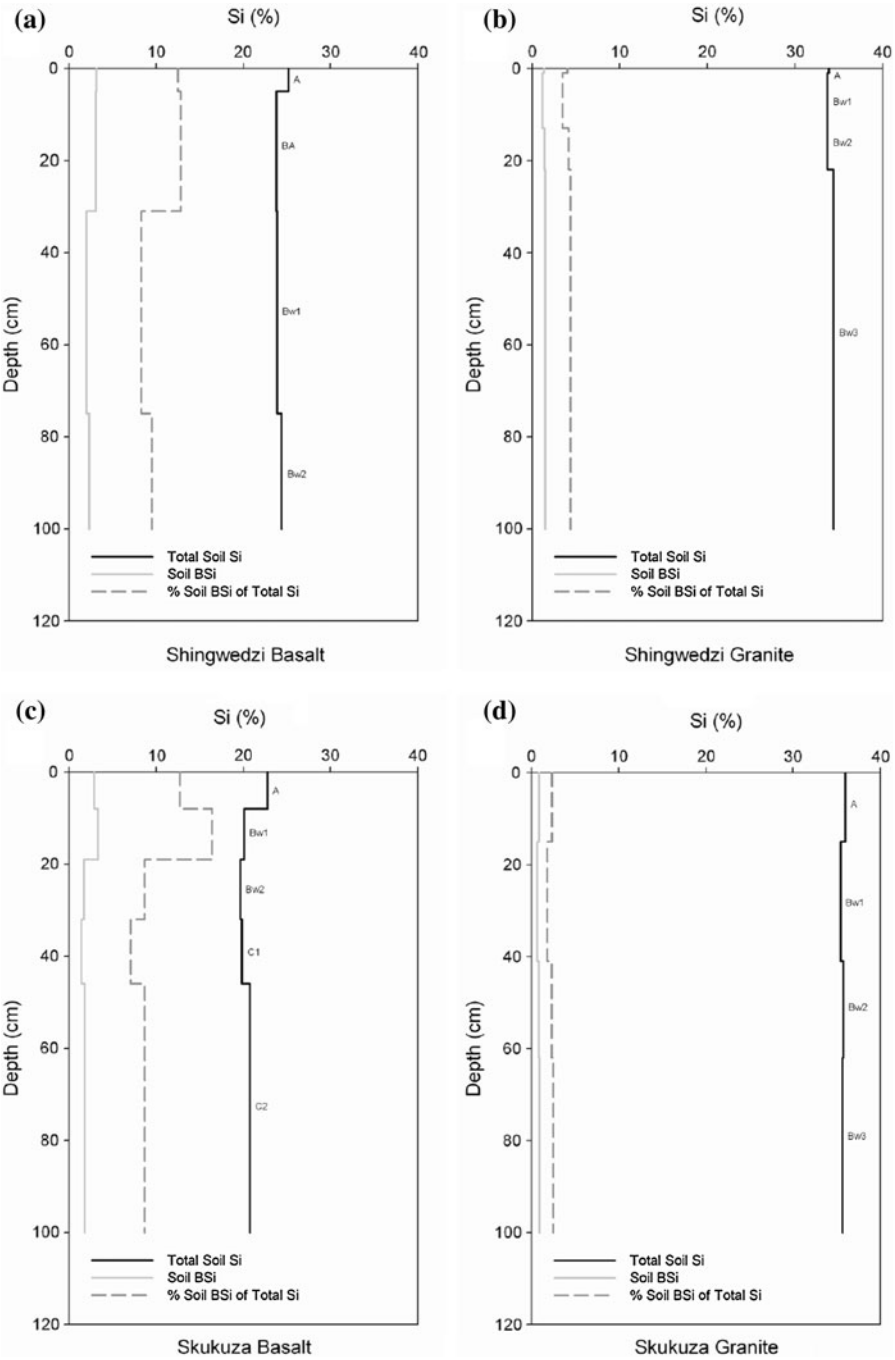

**Fig. 6** Total soil Si, soil biogenic silica (BSi), and %BSi of total Si as a function of a depth to 100 cm for **a** Shingwedzi basalt, **b** Shingwedzi granite, **c** Skukuza basalt and **d** Skukuza granite

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

where $F$ is the flux.

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 higher surface area, lower Al

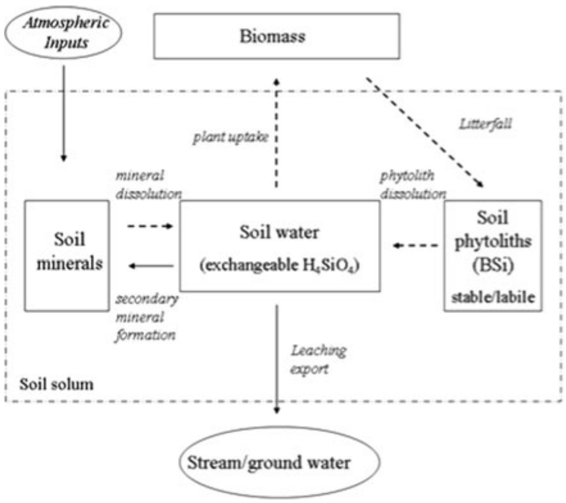

**Fig. 7** Conceptual model of the terrestrial silica cycle. *Boxes* represent pools and *arrows* represent fluxes. *Dashed arrows* emphasize the area of the cycle that was of particular interest for measurements in this study (adapted from Blecker et al. 2006)

concentration, and greater water content (Bartoli and 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 appears to be complexly influenced by parent material (and associated textural and mineralogical differences) and by climate: for basaltic soils, increasing precipitation does not alter overall Si gains relative to parent material, but for granitic soils, increasing precipitation (e.g. Skukuza site) magnifies Si losses.

Based on the inherent weatherability differences 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 (i.e. Na end-member of plagioclase), specifically, could be an important source of Si while anorthite (i.e. Ca end-member of plagioclase) dissolution does not release Si as readily as it more commonly weathers to kaolinite. The basaltic soils are high enough in Al and Mg so that the formation of kaolinite and smectite is possible which, upon dissolution, may be an additional Si source to solutions. 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 (Fig. 8), but have greater concentrations of DSi in the surface horizons (i.e. uppermost horizon for each respective soil pedon) (Fig. 4), which reflects the importance of soil texture and hydrology. In general, basaltic soils retained more Si (positive mass transfer coefficients), while granitic soils exhibited net losses 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, mass balance calculations suggest there have been smaller losses of Si from basaltic soils; this likely reflects long-term pedological and hydrological dynamics. For example, the finer textures in the basaltic soils should lead to much lower hydraulic conductivities, which should reduce losses of soluble Si from the soil profile over the long term. The more porous and quartz-rich granitic soils, by contrast, have coarser textures and these higher hydraulic conductivities should lead to more rapid loss of Si 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; on average, 11% of basaltic soil Si was BSi and 3% of granitic soil Si was BSi. The greater plant BSi production and finer textures, which slows down the translocation process, associated with the basaltic soils may account for their greater amounts of BSi storage and retention. The depth distribution of BSi suggests that the soils of the South African savanna show a high degree of

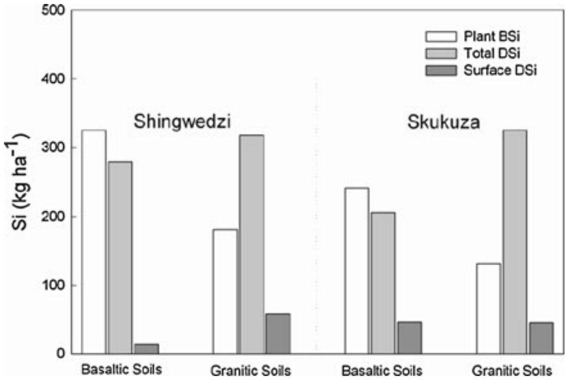

**Fig. 8** Plant biogenic silica (BSi) and soil total and surface (to 20 cm depth) dissolved silica (DSi) (kg ha$^{-1}$) for each basaltic and granitic soil at Shingwedzi and Skukuza

bioturbation. Undisturbed soils (not highly bioturbated) should have highest BSi values at the soil surface (Gol'eva 1996, 1999, 2001; Oehler 1979) while highly bioturbated soils or soils exposed to percolating soil water would have a more uniform or irregular depth distribution of BSi where downward movement may result in accumulation in the B-horizon (Hart and Humphreys 1997; Boettinger 1994; Piperno 1988). Bioturbation by termite mound building, in particular, is a key contributor to the vegetative distribution in this savanna landscape and a useful indicator of hydrogeomorphic conditions (Levick et al. 2010). Levick et al. (2010) conducted their study on termite mound distribution across the granitic semi-arid portions of the park and found that these bioturbators prefer well drained crest hillslope positions. In the soils of semi-arid systems where leaching is generally low, the presence of BSi at greater depths (such as in the granitic soils) suggests 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 (kg Si ha$^{-1}$)/annual litterfall Si input (kg Si ha$^{-1}$ year$^{-1}$) and found turnover times ranging from 250 to 1300 years across a bioclimosequence from tallgrass prairie (MAP: >800 mm) to shortgrass steppe (MAP: <500), respectively. The same calculation was utilized in this study and resulted in average turnover times of BSi in surface horizons (the biologically active zone) of ~460 years for granitic soils and ~700 years 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 but much cooler annual temperatures have shorter 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 years 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 6). 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 turn over time of BSi in granitic systems is likely due to the availability of Si from BSi because, compared to quartz, it has a higher solubility. Relative to basaltic soils, surface horizons of granitic soil solutions 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 major sources of Si to the soil solution. Because there are two major sources of Si and because little Si is being lost, surface horizons of basaltic soil solutions are closer to saturation with respect to Si which allows greater potential storage of Si (as BSi) in these soils with longer turnover times. The DSi concentrations (μmol L$^{-1}$) are higher in the surfaces of basaltic soils which, along with their

**Table 6** Relative differences in key properties between basaltic and granitic soils within Kruger National Park

| BSi cycle properties | Basaltic soils | Granitic soils |
|---|---|---|
| Total Si-profile (kg ha$^{-1}$) | – | + |
| Dissolved Si-surface (mol L$^{-1}$) | + | – |
| Plant biogenic Si (kg ha$^{-1}$) | + | – |
| Soil biogenic Si (kg ha$^{-1}$) | + | – |
| Total Si loss-profile (kg ha$^{-1}$) | – | + |
| Turnover time-surface (kg ha$^{-1}$ year$^{-1}$) | + | – |

+ represents greater quantities; – represents lower quantities

slightly higher ANPP, contribute to the higher abundances of BSi in their overlying plants. Dissolved Si concentrations of the soil subsurface (i.e. soil horizons stratigraphically below the uppermost horizon) are similar in both soil types but are greater in the surface (relative to the subsurface) in basaltic soils. Furthermore, Fig. 8 demonstrates that DSi totals (kg ha$^{-1}$) 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 suggesting Si storage in less labile forms and hence its longer term preservation. 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, supporting the idea that Si is mobilized by plants and regulated by BSi dissolution.

## Conclusions

The cycling of BSi in terrestrial ecosystems has been shown to greatly impact the global biogeochemical cycle of Si (Conley 2002; Blecker et al. 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 to assess the role that the global expansion of grasslands played during the late Neogene, and continue to play in the future, on both marine and terrestrial Si cycles, and thus the global C cycle.

In this study, we have found that the quantities, fate, and mobility of BSi in the soils of South African 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 total initial amount of Si in rocks may not be important except for the longer-term supply of Si. Although previous studies have shown that ANPP drives Si uptake by plants, these studies were conducted on soils that have similar parent materials. Our results suggest that while ANPP is an important mechanism driving Si mobilization, parent material strongly influences Si cycling through differences in soil textures and hydrology.

**Acknowledgments** Support was provided by the Shortgrass Steppe Long Term Ecological Research Group, a partnership between Colorado State University, U.S. Department of Agriculture, Agricultural Research Service, and U.S. Forest Service Pawnee National Grasslands, through a grant from the National Science Foundation Long Term Ecological Research Program and NSF award DEB-074386. The authors extend thanks to Dan Reuss at the Natural Resources Ecology Laboratory and Dr. Thomas Borch in the Soil and Crop Sciences Department at Colorado State University for their analytical expertise and Richard Fynn in the School of Biological and Conservation Sciences at the University of KwaZulu-Natal for identifying the plant species.

## References

Adams WA (1973) The effect of organic matter on the bulk and true densities of some uncultivated podzolic soils. J Soil Sci 24:10–17

Alexandre A, Meunier J, Colin F, Koud J (1997) Plant impact on the biogeochemical cycle of silicon and related weathering processes. Geochim Cosmochim Acta 61: 677–682

Amiotte-Suchet P, Probst JL (1993) Modelling of atmospheric $CO_2$ consumption by chemical weathering of rocks: application to the Garonne, Congo and Amazon basins. Chem Geol 107:205–210

Bartoli F (1981) Le cycle biogeochimique du silicium sur roche acide: application a deux systemes forestiers temperes (Vosges). PhD thesis, Univ Nancy (in French)

Bartoli F (1983) The biogeochemical cycle of silicon in two temperate forest ecosystems. Environ Biogeochem Ecol Bull 35:469–476

Bartoli F, Wilding LP (1980) Dissolution of biogenic opal as a function of its physical and chemical properties. Soil Sci Soc Am J 44:873–878

Barton JM, Bistrow JW, Venter FJ (1986) A summary of the Precambrian granitoid rocks of the Kruger National Park. Koedoe 29:39–44

Berner RA (1992) Weathering, plants, and the long term carbon cycle. Geochim Cosmochim Acta 56:3225–3231

Blake GR, Hartge KH (1986) Bulk density. In: Klute A (ed) Methods of soil analysis. Part I. Physical and mineralogical methods: agronomy monograph no 9, 2nd edn. Am Soc Agron, Madison, WI, pp 363–375

Bland W, Rolls D (1998) Weathering: an introduction to the scientific principles. Edward Arnold, London

Blecker SW, McCulley RL, Chadwick OA, Kelly EF (2006) Biologic cycling of silica across a grassland bioclimosequence. Global Biogeochem Cycles 20:1–11

Boettinger JL (1994) Biogenic opal as an indicator of mixing in an alfisol/vertisol landscape. In: Proceedings of the 9th international working meeting on soil micromorphology, pp 17–26

Bormann BT, Wang D, Bormann FH, Benoit G, April R, Snyder MC (1998) Rapid plant induced weathering in an aggrading experimental ecosystem. Biogeochemistry 43:129–155

Brimhall GH, Dietrich WE (1987) Constructive mass balance relations between chemical composition, volume, density, porosity, and strain in metasomatic hydrochemical systems: results on weathering and pedogenesis. Geochim Cosmochim Acta 51:567–587

Brimhall GH, Chadwick OA, Lewis CJ, Compston W, Williams IS, Danti KH, Dietrich WE, Power ME, Hendricks DM, Bratt J (1992) Deformational mass transport and invasive processes in soil evolution. Science 255:695–702

Bristow JW (1980) The geochronology and geochemistry of Karoo volcanics in the Lebombo and adjacent areas. PhD thesis, University of Cape Town

Bristow JW, Venter FJ (1986) Notes on the Permian to recent geology of the Kruger National Park. Koedoe 29:117–124

Chadwick OA, Brimhall GH, Hendricks DM (1990) From a black box to a gray box: a mass balance interruption of pedogenesis. Geomorphology 3:369–390

Chadwick O, Levick SR, Khomo L, Hartshorn AS, Heimsath AM, Bern C (2009) Soil collapse and dilation as a modiifer of hillslope morphology, Fall Meeting 2009, abstract #EP44A-06. American Geophysical Union

Chadwick OA, Heimsath AM, Roering J, Levick S, Hartshorn AS, Khomo L (2010) Climate-driven soil dilation and collapse controls hillslope morphology in tectonically quiescent regions. Geological Society of America Abstracts with Programs, vol 42, No 5, p 364

Clarke J (2003) The occurrence and significance of biogenic opal in regolith. Earth-Sci Rev 60:175–194

Codron J, Codron D, Lee-Thorp JA, Sponheimer M, Bond WJ, de Ruiter D, Grant R (2005) Taxonomic, anatomical, and spatio-temporal variations in the stable carbon and nitrogen isotopic composition of plants from an African savanna. J Archaeol Sci 32:1757–1772

Conley DJ (1997) Riverine contribution of biogenic silica to the oceanic silica budget. Limnol Oceanogr 42:774–777

Conley DJ (1998) An interlaboratory comparison for the measurement of biogenic silica in sediments. Mar Chem 63:39–48

Conley DJ (2002) Terrestrial ecosystems and the global biogeochemical silica cycle. Global Biogeochem Cycles 16:1121

Conley DJ, Sommer M, Meunier JD, Kaczorek D, Saccone L (2006) Silicon in the terrestrial biogeosphere. In: Ittekkot V, Unger D, Humborg C, An NT (eds) The silicon cycle: human perturbation and impacts on aquatic systems. Island Press, WA, pp 12–28

Datnoff LE, Snyder GH, Korndofer GH (eds) (2001) Silicon in agriculture: studies in plant science. Elsevier, Amsterdam

DeMaster DJ (1981) The supply and accumulation of silica in the marine environment. Geochim Cosmochim Acta 45:1715–1732

Derry LA, Kurtz AC, Ziegler K, Chadwick OA (2005) Biological control of terrestrial silica cycling and export fluxes to watersheds. Nature 433:728–731

Drees LR, Wilding LP, Smeck NE, Senkayi AL (1989) Silica in soils: quartz and disordered silica polymorphs. In: Dixon JB (ed) Weed SB Minerals in Soils Environments. Soil Sci Soc Am, Madison, pp 913–974

Drever JI (1994) Effects of plants of chemical weathering rates. Geochim Cosmochim Acta 58:2325–2332

Epstein E (1994) The anomaly of silicon in plant biology. Proc Natl Acad Sci USA 91:11–17

Epstein E (1999) Silicon. Annu Rev Plant Physiol Plant Mol Biol 50:641–664

Fanning KA, Pilson MEQ (1973) The diffusion of dissolved silica out of deep-sea sediments. J Geophys Res 79:1293–1297

Farmer VC, Delbos E, Miller JD (2005) The role of phytolith formation and dissolution on controlling concentrations of silica in soil solutions and streams. Geoderma 127:71–79

Gee GW, Bauder JW (1986) Paticle-size analysis. In: Klute A (ed) Methods of soil anlaysis. Part I. Agron Monogr 9. Am Soc Agron, Madison, pp 383–411

Gol'eva AA (1996) Experience in using phytolith analysis in soil science. Eurasian Soil Sci 28:248–256

Gol'eva AA (1999) The application of phytolith analysis for solving problems of soil genesis and evolution. Eurasian Soil Sci 32:884–891

Gol'eva AA (2001) Biomorphic analysis as a part of soil morphological investigations. Catena 43:217–230

Hamdan J, Burnham CP (1996) The contribution from parent material in three deeply weathered soils of Peninsular Malaysia. Geoderma 74:219–233

Hart DM (1992) A field appraisal of the role of plant opal in the Australian environment. PhD thesis, University of Australia (unpublished)

Hart DM, Humphreys GS (1997) The mobility of phytoliths in soils: pedological considerations. In: Pinilla A, Juan-Tresserras J, Machado MA (eds) First European meeting on phytolith research. Centro de Ciencias Medioambientales del Con sejo Superior de Investigaciones Cientificas Serrano, Madrid, pp 93–100

Hurd DC (1983) Physical and chemical properties of siliceous skeletons. In: Aston SR (ed) Silicon geochemistry and biogeochemistry. Academic, pp 187–244

Jobbagy EG, Jackson RB (2004) The uplift of soil nutrients by plants: biogeochemical consequences across scales. Ecology 85:2380–2389

Kelly EF (1989) A study of the influence of climate and vegetation on the stable isotope chemistry of soils in grassland ecosystems of the Great Plains. PhD thesis, Colorado State University, Fort Collins

Kelly EF (1990) Methods for extracting opal phytoliths from soil and plant material, report. Department of Agron, Colorado State University, Fort Collins

Kelly EF, Amundson RG, Marino BD, DeNiro MJ (1991) Stable isotope ratios of carbon in phytoliths as a quantitative method of monitoring vegetation and climate change. Quatern Res 35:222–233

Kelly EF, Chadwick OA, Hilinski TE (1998) The effects of plants on mineral weathering. Biogeochemistry 42:21–53

Khomo L (2008) Weathering and soil properties on old granitic catenas along climo-topographic gradients in Kruger National Park. PhD thesis, University of Witwatersrand, Johannesburg

Khomo L, Hartshorn AS, Rogers KH, Chadwick OA (2011) Impact of topography and rainfall on the clays and major cations in granitic catenas in southern Africa. Catena (in revision)

Koning E, Epping E, Raaphorst WV (2002) Determining biogenic silica in marine samples by tracking silicate and aluminum concentrations in alkaline leaching solutions. Aquat Geochem 8:37–67

Lajtha K, Jarrell WM, Johnson DW, Sollins P (1999) Collection of soil solution. In: Robertson GP, Coleman DC, Bledsoe CS, Sollins P (eds) Standard soil methods for long-term ecological research. Oxford Univ Press, New York, pp 166–182

Lerman A (1988) Weathering rates and major transport processes: an introduction. In: Lerman A, Meybeck M (eds) Physical and Chemical Weathering in Geochemical Cycles. Kluwer, pp 1–10

Levick SR, Asner GP, Chadwick OA, Khomo LM, Rogers KH, Hartshorn AS, Kennedy-Bodoin T, Knapp DE (2010) Regional insight into savanna hydrogeomorphology from termite mounds. doi:10.1038/ncomms1066

Lindsay WL (1979) Chemical equilibria in soils. Wiley, New York

Lovering TS (1959) Significance of accumulator plants in rock weathering. Bull Geol Soc Am 70:781–800

Maybeck M (1986) Composition chimique des ruisseaux non pollues de France. Sci Geol, Strasbourg, 3–77 (in French)

Melzer SE, Knapp AK, Kirkman KP, Smith MD, Blair JM, Kelly EF (2010) Fire and grazing impacts on silica production and storage in grass dominated ecosystems. Biogeochemistry 97:263–278

Meunier JD (2003) The role of plants in the transfer of silicon at the surface of the continents. Geoscience 335:1199–1206

Mortlock RA, Froelich PN (1989) A simple method for the rapid determination of biogenic opal in pelagic marine sediments. Deep-Sea Res 36:1415–1426

Moulton KL, West J, Berner RA (2000) Solute flux and mineral mass balance approaches to the quantification of plant effects on silicate weathering. Am J Sci 300:539–570

Mussett AE, Khan MS (2000) Looking into the earth: an introduction to geological geophysics. Cambridge University Press, Cambridge

Oehler JH (1979) Deposition and diagenesis of biogenic silica. In: Trudinger PA, Swain DJ (eds) The Biogeochemical Cycling of Mineral-Forming Elements. Elsevier, Amsterdam, pp 467–479

Osher LJ, Buol SW (1998) Relationship of soil properties to parent material and landscape position in eastern Madre de Diós, Perú. Geoderma 83:143–166

Parr JF, Lentfer CJ, Boyd WE (2001) A comparative analysis of wet and dry ashing techniques for the extraction of phytoliths from plant material. J Archaeol Sci 28:875–886

Partridge TC, Scott L, Schneider RR (2004) Between Agulhas and Benguela: responses of Southern African climates of the late Pleistocene to current fluxes, obital precession and the extent of the circum-Antarctic vortex. In: Battarsbee RW, Gasse F, Stickley CE (eds) Past climate variability through Europe and Africa. Developments in paleoenvironmental research. Springer, Dordrecht, pp 45–68

Peel MC, Finlayson BL, McMahon TA (2007) Updated world map of the Koppen-Geiger climate classification. Hydrol Earth Syst Sci 11:1633–1644

Piperno DR (1988) Phytolith analysis: an archaeological and geological perspective. Elsevier, New York

Plaster RW, Sherwood WC (1971) Bedrock weathering and residual soil formation in central Virginia. Geol Soc Am Bull 82:2813–2826

Raven JA (1983) The transport and function of silicon in plants. Biol Rev 58:179–207

Rawls WJ (1983) Estimating soil bulk density from particle-size analysis and organic-matter content. Soil Sci 135:123–125

Richter DD, Markewitz D (1995) How deep is soil? Bioscience 45:600–609

Robb LJ (1977) The geology and geochemistry of the archean granite-greenstone terrane between Nelspruit and Bushbuckridge, Eastern Transvaal. MS thesis, University of Witwatersrand, Johannesburg

Saccone L, Conley DJ, Sauer D (2006) Methodologies for amorphous silica analysis. J Geochem Explor 88:235–238

Saccone L, Conley DJ, Koning E, Sauer D, Sommer M, Kaczorek D, Blecker SW, Kelly EF (2007) Assessing the extraction and quantification of amorphous silica in soils of forests and grassland ecosystems. Eur J Soil Sci 58:1446–1459

Sangster AG, Hodson MJ (1986) Silica in higher plants. In: Ciba foundation symposium, vol 121. Wiley, Chichester, pp 90–111

Sauer D, Saccone L, Conley DJ, Herrmann L, Sommer M (2006) Review of methodologies for extracting plant-available and amorphous Si from soils and aquatic sediments. Biogeochemistry 80:89–108

Schoeneberger PJ, Wysocki DA, Benham EC, Broderson WD (1998) Field book for describing and sampling soils. Natural Resources Conservation Services, USDA, National Soil Survey Center, Lincoln

Schutte IC (1974) 'n Nuwe voorkoms van die Formasie Malvernia, suid van Pafuri, Nasionale Krugerwildtuin. Ann Geol Surv S Afr 9:83–84

Soil Survey Staff (1975) Soil taxonomy. A basic system of soil classification for making and interpreting soil surveys. In: USDA—soil conservation service agricultural handbook #436. US Gov Print. Office, Washington

Stephen I (1952) A study of rock weathering with reference to the soils of the Malvern Hills: weathering of biotite and granite. J Soil Sci 3:20–33

Strickland JDH, Parsons TR (1968) A handbook of seawater analysis bulletin 167. Fish Res Board, Canada (Ottowa)

Treguer P, Nelson DM, Van Bennekom AJ, DeMaster DJ, Leynaert A, Queguiner B (1995) The silica balance in the world ocean: a reestimate. Science 268:375–379

Van Riet WF, Cooks J (1990) Ecological planning proposal for Kruger National Park. Environ Manage 14:349–358

Venter FJ (1990) A classification of land management planning in the Kruger National Park. PhD thesis, University of South Africa

Venter FJ, Scholes RJ, Eckhardt HC (2003) The abiotic template and its associated vegetation pattern. In: DuToit JK, Rogers K, Biggs H (eds) The Kruger Experience. Island Press, Washington D.C., pp 83–129

Vorster CJ (1979) Die geologie van die Klein-Letabagebeid, noord-oos Tranvaal met speciale verwysing na die granitiese gesteentes. MS thesis, Rand Afrikaans University