Appendix B

Biogenic Silica Recovery from Carbonate-enriched Soils--Observations from Past Samples

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Summary:

Subsequent to processing the ULSR samples in 2012, additional soil samples from other carbonate-rich soils have been processed which also yielded low biogenic silica recoveries and poorly preserved biogenic particles from those matrices. Since those recent technical reports are not yet in print, this brief document summarizes and organizes that pending information. The USLR samples are noted, as well as samples from three previous and eight subsequent sites studied which showed evidence of carbonate/soil pH-related biogenic degradation (Table 1). These sample suites all have several traits in common: difficult biogenic silica[2] extraction and recovery from the matrix, generally poor biogenic particle preservation (i.e., often evidence of various degrees of chemical weathering, and occasionally presumed complete dissolution), low biogenic silica recoveries, and the presence of moderate to high carbonate concentration soil matrices. Relative particle dissolution (greatest solubility) appears to start with diatoms being most soluble and dissolving first, spicules being the least soluble and most resilient, and phytoliths having intermediate solubility in the soil matrix. Often, charcoal is noted to be present in many of the samples processed with preservation issues, and may accentuate dissolution. Ten sample suites with minimal to no dissolution damage were also processed (Tables 2-3).

Carbonate Background:

> "Soils in semiarid and arid regions commonly have carbonate-rich horizons at some depth below the surface, or if the climate is dry enough or the surface erosion intensive enough, these horizons may extend to the surface.... Some of these horizons are the caliche and calcrete of present and past geological literature. Pedologists call these accumulations Bk and K horizons, and because they have recognized and defined stages in the buildup of $CaCO_3$-bearing horizons..., this more precise terminology seems preferable to the general term caliche or calcrete. Both calcium and magnesium carbonates are present in these soils, with the former dominant." (Birkeland 1984:138)
>
> "...many soils of arid and semiarid regions are calcareous. Lack of rainfall has restricted the leaching and removal of $CaCO_3$ from surface soil horizons, and its presence has a profound effect on the chemistry of calcareous soils. The pH of most calcareous soils is slightly alkaline and is regulated by the interaction between calcite, soluble Ca, and the partial pressure of carbon dioxide gas ($CO_{2(g)}$)." (Doner and Grossl 2002:204-205)

Multiple models for carbonate deposition in soil have been recognized most of which require carbonate-rich soil water, movement of that carbonate-rich solution, and precipitation of the carbonates from solution (Schaetzl and Anderson 2005:403). In addition to the chemical precipitation of carbonate, bacteria, fungi, and likely algae are also actively involved in carbonate formation (Monger et al. 1991; Doner and Grossl 2002:209; Caudwell 1987; Courty et al. 1989:98).

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[1] Jschemistry@hotmail.com (http://www.JSEConsulting.com; http://www.PhytolithPress.com); 9-25-14.

[2] Biogenic silica includes phytoliths, diatoms, statospores, and sponge spicules.

To summarize soil carbonate formation, using calcium carbonate as the example:

> "the chemical reaction involved is simply
>
> $$Ca^{2+} + H_2O + CO_2 = CaCO_3 + 2H^+ \qquad (4.12)$$
>
> Alkaline conditions favor $CaCO_3$ accumulation, by consuming H^+ and driving the reaction to the right. Increasing P_{CO2} causes $CaCO_3$ to react further
>
> $$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3 \qquad (4.13)$$
>
> so that $CaCO_3$ redissolves with increasing CO_2 concentration in the gaseous phase. This is a condition of primary interest to geochemistry. In soils, the relatively high Ca^{2+} concentrations and limited water contents tend to force Reaction 4.12 to completion and to repress Reaction 4.13. The effect of P_{CO2} is therefore less important than in geochemical conditions, and $CaCO_3$ precipitates in soils despite the high P_{CO2} of soil air. In acid soils, $CaCO_3$ dissolves by reversing equation 4.12." (Bohn et al. 1979:131-132)

Soil carbonate can form from a number of inputs including soil parent material, wind deposition, groundwater, and rainfall (Doner and Grossl 2002:203) and rainfall precipitating fine aeolian dust (Goldberg and Macphail 2006:143).

Soil carbonate formation from soil weathering to release Ca^{2+} in the upper profile is unlikely due to the large amounts of calcium that would be required--an external calcium source is likely required. "Detailed study in the Las Cruces region of New Mexico indicates that the atmosphere is an important source for Ca^{2+} and $CaCO_3$. Dust-trap data ... suggest that the dust contains less than 5 percent carbonate..." but that the estimate of calcium in precipitation is enough to produce three times that amount of carbonate. (Birkeland 1984:143)

> "In many parts of the world, the climate during the early Holocene was more arid and warmer than it is now (Wright, 1983). This period, sometimes called the *altithermal*, lasted from 10ka to 7ka and caused lakes to dry up in the state of Washington and prairies to invade the state of Wisconsin. The formation of pedogenic calcite in soils would have increased during the period, with the calcic-noncalcic soil boundary (Birkeland, 1999) shifting eastward across the United States as annual precipitation dropped below 500 mm yr^{-1}. Modern soils retain little evidence of that shift because subsequent increases of effective precipitation led to dissolution the calcite. However, under the right environmental conditions, pedogenic calcite records of that period..." remain (Borchardt 2002:727-728)

Both cambic and calcic soils were encountered during the soil phytolith analyses that will be discussed. By definition, a cambic horizon is "a non-sandy, mineral soil horizon that has soil structure rather than rock structure, contains some weatherable minerals and is characterized by the alteration or removal of mineral material...." (Schaetzl and Anderson 2005:747). A calcic horizon, is "a mineral soil horizon of secondary carbonate enrichment that is more than 15 centimeters thick, has a calcium carbonate equivalent of more than 15 percent, and has at least 5 percent more calcium carbonate equivalent than the underlying C horizon" (Steila and Pond 1989:200).

The official series soil descriptions issued by the USDA and now readily available online via the Web Soil Survey often contain detailed information detailing carbonate-containing soil horizons and the carbonate content of those horizons. This data, often presented as a range, is frequently reported as calcium carbonate equivalent (i.e., all released carbonate during measurement testing is back calculated to a soil concentration assuming that all of the CO_2 released originated from calcium carbonate).

Analysis of soil carbonates can be used to help discern the source of the carbonate (pedogenic vs. environmental) via δ^{13} analysis (Schaetzl and Anderson 2005:649). Carbonates can also be used for radiocarbon dating. Winsborough (2014) recently reported diatom concentrations preserved in the carbonate formed around plant roots where they were presumably actively feeding. As the roots decayed and the diatoms fed and respired, the released CO_2 reacted to form carbonate which entombed the diatoms in the rhizosphere preserving them; diatoms were absent in the adjacent non-carbonate rich soil matrix where biogenic weathering apparently was able to continue unabated.

All silica, including biogenic silica will gradually dissolve in a basic soil environment. Iler's composite figure (1979:42, Figure 1.6) as presented in a recent discussion summarizing Iler's comments regarding the pH dependence of biogenic ("amorphous") silica solubility in an aqueous environment is shown in Figure 1 (Sudbury 2014a:38-42, Figure 33).

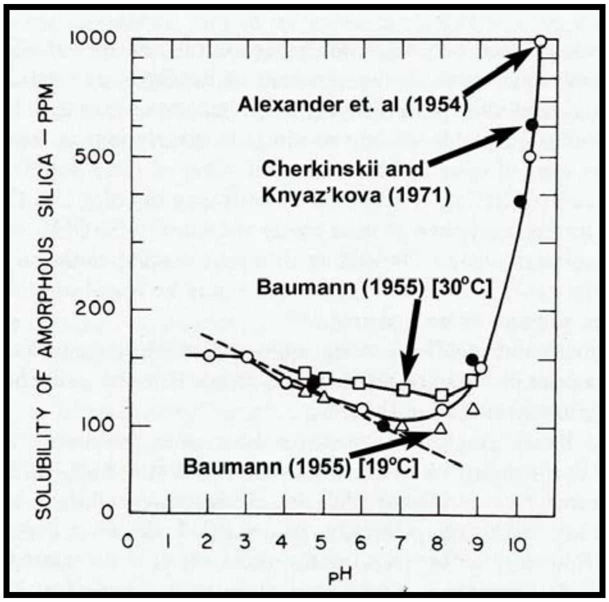

Figure 1. Relationship of amorphous silica solubility to aqueous pH.

Comments on Biogenic Recovery from Sites with pH and/or Carbonate-related Issues:

Since 2000, phytolith samples have been analyzed from 19 sets of samples (five of those sample sets contained samples from multiple sites). Samples from ten of those sites have had significant biogenic preservation issues (six of those ten problematic sample suites were processed during the last 2 years).

The sites with samples from carbonate containing soils which have shown evidence of biogenic silica preservation problems are summarized in Table 1. After the table, these samples are addressed with brief comments regarding the analytical issues and observations regarding those samples. Phytolith illustrations from those reports are also presented (Figures 2-10). Next, Table 2 summarizes sample suites from carbonate matrices where less deleterious preservation issues were noted. Finally, Table 3 summarizes the sample suites processed from sites during this fifteen year interval with excellent biogenic preservation. Then, comments and general conclusions summarizing this carbonate and basic soil pH data as it impacts biogenic silica preservation are presented.

For the most part, the soil characterization data in these tables is from the USDA Web Soil Survey site[3]. Site specific soil analysis is certainly better and provides much more specific soil characterization for a discrete location, but in general the USDA database provides a reasonably good idea of soil characteristics at any given location.

Table 1
Problematic Sites Addressed in this Carbonate/pH Issue Assessment

Site	Soil Type [Series name]	Carbonate-rich Horizons	Maximum Carbonate Equivalent	Biogenic Preservation	Reference Sudbury:
USLR	multiple sites	multiple sites	multiple sites	Variable, overall fair to very poor	(nd3)
5MT10647 & 5MT10736	Aridic Haplustalf [Wetherill]	**Calcic** Btk1-4 from 18-70"; pH 8-8.4+	up to 40%	Variable but overall fair to very poor	(nd4)
41MS69	Cumulic Haplustoll [Oakalla]	**Cambic** Ak1-2, Bk1	41-~50% [16-53"]	Variable but overall fair to very poor (2 samples = 0%)	(2014c)
41BL278	Udic Calciustoll [Venus]	**Calcic** Bk, K (14-60")	15-40%	Variable but overall fair to very poor	(2014b)
41TV2161	Udic Calciustoll [Lewisville]	**Calcic** Bk	20-40% [10-40"]	Variable but overall fair to very poor	(2014a) Big Hole
41RB112	not provided	not provided	not provided	Variable, fair to very good (some diatoms)	(2013a) Long View
41LM50 & 41LM51	Udifluventic Haplustept [Weswood]	**Cambic** Bw (4-26"), BCk (26-36"), 2Bwb (36-64), Ab (64-80); strongly effervescent	Some carbonate in Bw2, BCk3A1; slightly to moderately alkaline	Variable, but overall good to very good (relatively few diatoms)	2103b
Dempsey	Typic Haplustept [Woodward]	**Cambic** Bw or Bk, BCk	2-15% [10-28"]	Deteriorated down profile; 0% preservation below 25 cm	(2011a:109) control soil
36FA1603	not provided	not provided	not provided	Good (A-horizon) to poor (deteriorated significantly down profile)	(nd2) Sewright
34HP42	not provided	Hearth (ash) & soil samples	not provided	Hearth Ash sample-very poor; Soil samples-some preservation issues	(nd1) Waugh

General comments and observations regarding the research sites listed in Table 1 follow.

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[3] http://websoilsurvey.sc.egov.usda.gov/App/HomePage.htm

1. **USLR (Texas)** (Sudbury nd3)
   Biogenic Particle Assessment: Isolates and mounted slides returned to researcher; the few sample images taken during initial strew loading evaluation indicate variable biogenic particle preservation from good to poor. Diatoms fairly abundant in one sample, and near absent in the other nine. Phytolith preservation ranged from good to very poor. Overall very low total biogenic fraction recoveries.
   Additional Comments: Multiple sites; GPS coordinates and soil type(s) not provided. Client specifically selected the most difficult to process samples for analysis from the entire sample suite in order to obtain an independent assessment of phytolith recovery and preservation issues for their project. Prolonged processing time and repeated carbonate neutralization was required when processing these samples in order to recover biogenic silica. This was a very challenging sample set due to carbonate issues and the resulting poor biogenic preservation. Biogenic recoveries were very low.
   Overall Phytolith Status: Particle reservation ranged from good to poor, but overall generally poor, carbonate/pH-related dissolution issues (multiple site soil types unknown).

2. **5MT10647 and 5MT10736 Figure 2** (Sudbury nd4)
   Biogenic Particle Assessment: Diatoms rare other than in surface samples. Spicules in good condition. Subsurface (feature) phytolith preservation variable, but generally poor

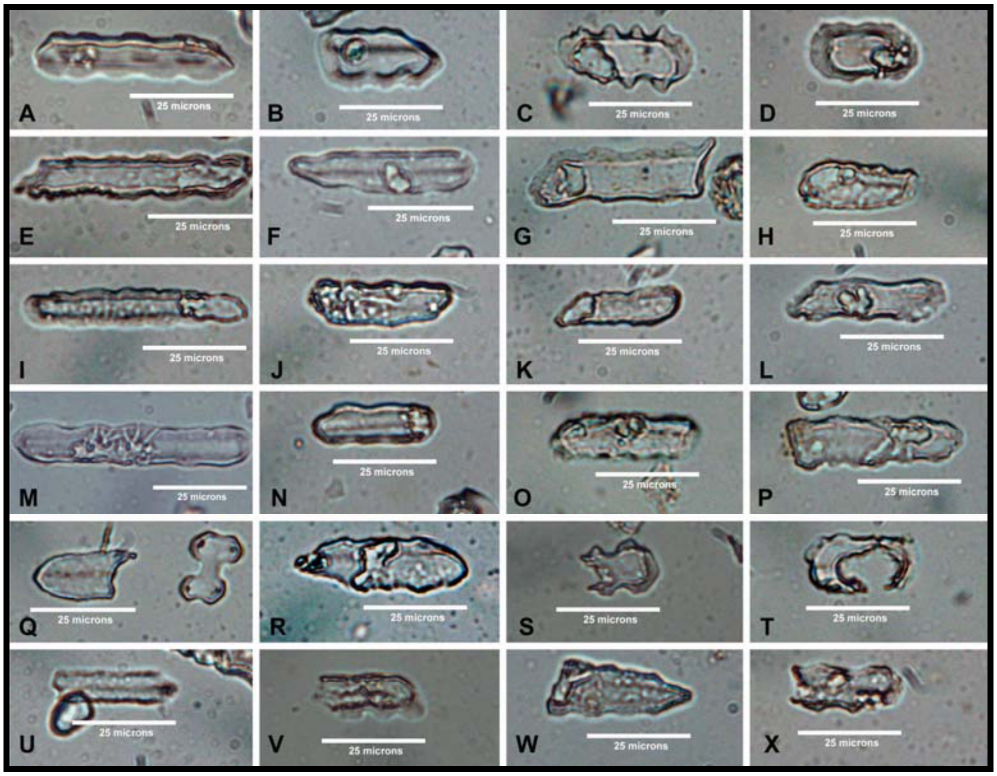

Figure 2. Pooid crenate forms from the Dillard site (5MT10647) sample 16 from showing varying degrees of surface pitting and dissolution from chemical weathering in the soil [image from Sudbury nd4:Figure 19]. Crenate short cell phytoliths recovered from the Dillard Site Sample 16. Specimens A-D are in relatively pristine condition (Specimen A is on its side). Specimens E-X are show evidence of varying degrees of chemical weathering (i.e., pH-related particle dissolution). Specimens U-X on the bottom row are scarcely recognizable as crenates.

and overall recoveries as weight % of soil very low. The crenate form was the most abundant short cell type present and preservation varied from excellent to poor; the figure used to illustrate the visible surface weathering is reproduced in Figure 2.

Additional Comments: Modern A-horizon biogenic preservation seemed to be acceptable although the two ridge top surface control samples (one from each site; same soil series) had different phytolith signatures likely due to tilling, weathering, and erosional losses. The 18 subsurface samples were feature-related samples. Soil pH not determined; visible chemical degradation (biogenic surface weathering via dissolution) was apparent and low overall particle counts obtained; biogenic isolate recoveries low.

Overall Phytolith Status: Preservation variable, overall poor, presumed carbonate-related dissolution issue (Calcic soil).

3. **41MS69, Figure 3** (Sudbury 2014c)

Biogenic Particle Assessment: In two samples, no biogenic silica was present. In the other three samples, bulliform preservation generally poor with extensive surface weathering (Figure 3). Chloridoids, the predominant short cell form observed, varied from good to poor condition; all short cell counts low. The few statospores present

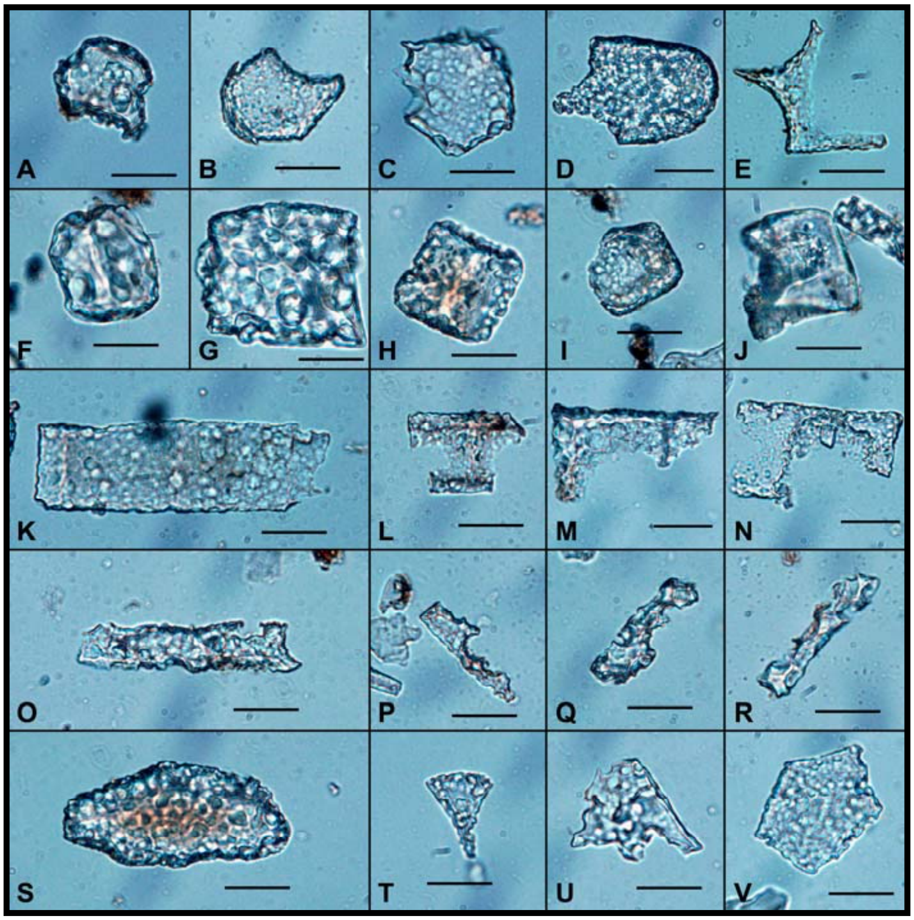

Figure 3. Large phytolith forms from 41MS69 showing varying degrees of surface pitting and dissolution from chemical weathering in the soil [image from Sudbury 2014c:Figure 13]. Bar scales are 25 microns.

appeared to be in good state of preservation. Spicules in overall good condition, several specimens show visible evidence of dissolution on an end; some long specimens present. No diatoms present in any of the five samples.

Additional Comments: Pilot testing small sample set; site setting on bank of major stream.

Overall Phytolith Status: Poor preservation, presumed pH/carbonate-related dissolution issue (Cambic soil).

4. **41BL278, Figure 4** (Sudbury 2014b)

Biogenic Particle Assessment: Short cells in limited number, some crenates showed traces of surface pitting, while some Panicoid and Chloridoid particles showed evidence of partial dissolution. Bulliform cells were much more abundant that short cells, but overall showed evidence of pitting and particle dissolution (Figure 4). Tree-related phytoliths in were better condition overall with a few specimens showing traces of small-scale surface pitting. Sponge spicules showed good surface preservation. No statospores or diatoms were present.

Additional Comments: Pilot testing small sample set; site setting near bank of a major stream.

Overall Phytolith Status: Poor preservation, presumed pH/carbonate-related dissolution issue (Calcic soil).

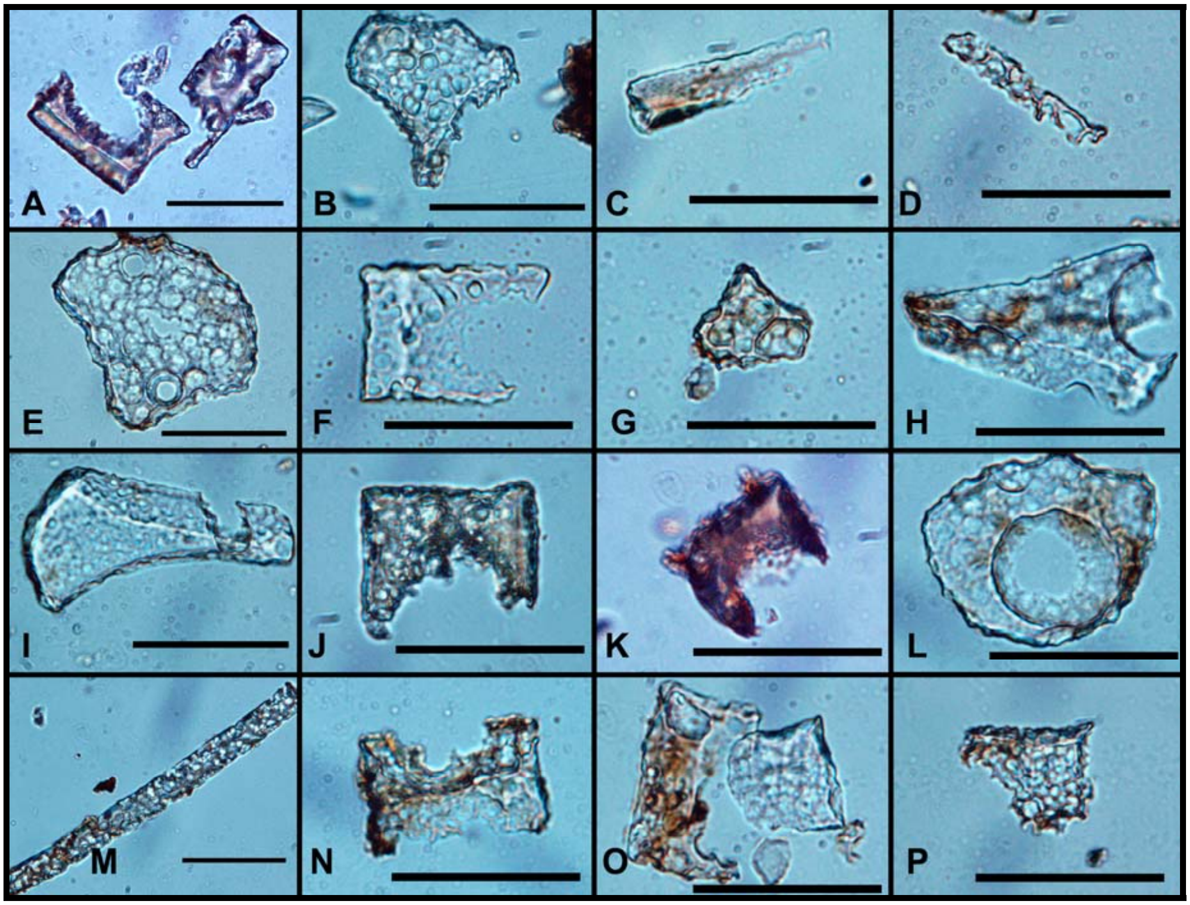

Figure 4. Large phytolith forms from 41BL278 showing varying degrees of surface pitting and dissolution from chemical weathering in the soil [image from Sudbury 2014b:Figure 10]. Bar scales 50 microns.

5. **Big Hole Site (41TV2161), Figure 5** (Sudbury 2014a)

   Biogenic Particle Assessment: A-horizon control sample had relatively good preservation status compared to the other samples. The profile samples bracketing the occupation zone and the occupation feature samples both generally had low short cell counts, and contained weathered bulliform and other larger phytolith forms. A few select samples had more bulliform cells and better short cell preservation (but still low short cell counts). Several samples produced no short cell phytoliths at all. The tree-related phytoliths tended to better preserved, but were not present in all samples. Abundant charcoal present. Bulliform cells were the predominant form present. Generally fair to very poor phytolith preservation throughout. Spicule surfaces in good condition and spicules present in very high counts in some feature samples. Diatoms were essentially absent from these samples as were Chrysophycean Cysts (except in the surface control samples).

   Additional Comments: Site set on relict paleochannel, near a small tributary of the Colorado River. Copious number of snails recovered in the sample sand fractions, oogonia of Charophytes also preserved.

   Overall Phytolith Status: Overall subsurface sample preservation poor, presumed pH/carbonate-related dissolution issue (Calcic soil).

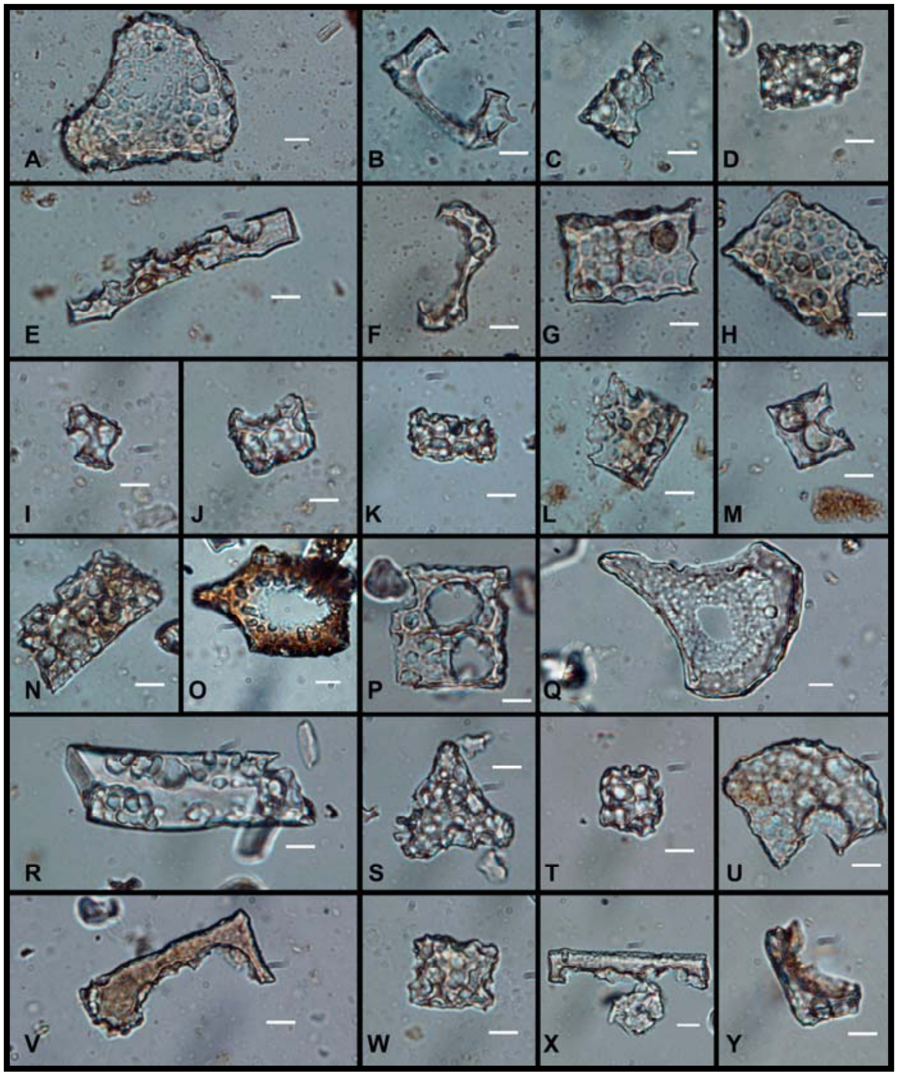

Figure 5. Bulliform cells and other large amorphous silica particles from 41TV2161 showing varying degrees of surface pitting and dissolution from chemical weathering in the soil [image from Sudbury 2014a:Figure 24]. Bar scales 10 microns.

6. **Long View Site (41RB112), Figure 6** (Sudbury 2013a)

   Biogenic Particle Assessment: A significant number of partially weathered bulliform cells were present; the examples shown (Figure 6) are all from feature samples. Bulliform preservation was variable. Abundant countable short cells present, so overall biogenic preservation issues did not draw attention at the time of analysis in 2011. Diatom count variable between samples; present but not overly abundant in these selected samples.

   Additional Comments: Site on river bank, soil very sandy which decreased the sample silt fraction and relative phytolith content. Several snail fragments. Most samples were feature-related rather samples solely for environmental assessment.

   Overall Phytolith Status: Overall preservation ranged from poor to good. Bulliform preservation issues are most noticeable due to large particle size. However, abundant short cell counts were available. Cucurbits were well-preserved, diatoms and many very large phytoliths with bordered pits were present.

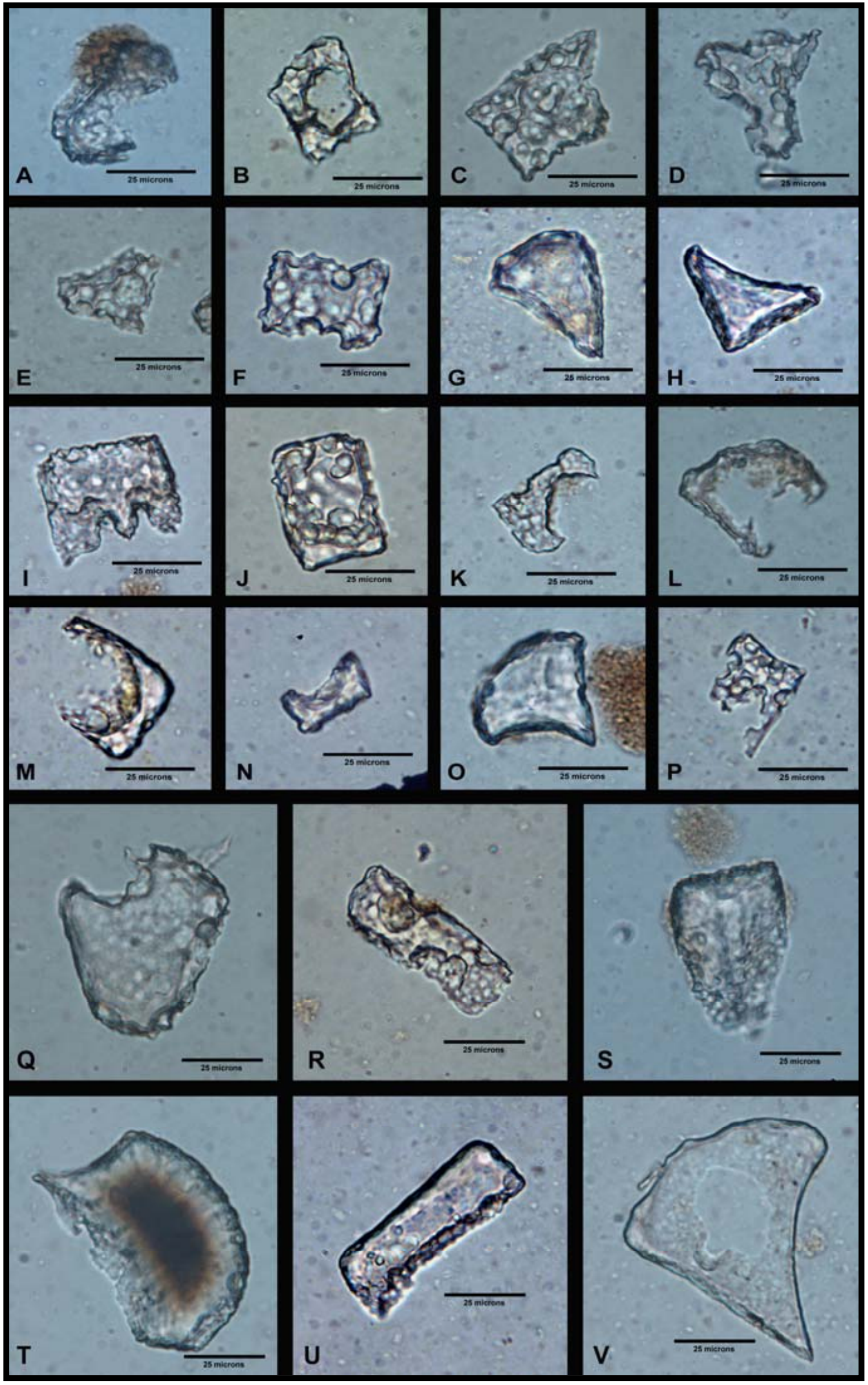

Figure 6. Long View site Bulliform cells from the pithouse floor and feature samples showing evidence of surface weather and dissolution. [image from Sudbury 2013a:Figure 13].

7. **Lampassas County Sites (41LM50 and 41LM51), Figure 7** (Sudbury 2013b)

Biogenic Particle Assessment: There were a number of pristine keystone bulliform type phytoliths that were well preserved (ibid: Figure 28) but there were also a large number of bulliforms that showed evidence of extensive chemical degradation/dissolution (Figure 7). Very few diatoms present (only one observed in the seven samples from 41LM50; 20 in one sample from 41LM51, and 0 and 1 from the other two samples). Short cell phytoliths abundant enough for statistical counts and in excellent condition. The sponge spicules very well preserved. Cucurbit phytoliths present.

Additional Comments: Site on creek bank, abundant carbonate fragments observed in sand fraction. Very good snail preservation. Abundant acicular crystals observed in the clay fractions (crystals not yet positively identified--possibly calcium oxalate raphides).

Overall Phytolith Status: Overall biogenic sample ranged from excellent to poor as demonstrated in the bulliform cell variability. Diatoms nearly absent. Countable load of well-preserved short cells present. Presumed pH/carbonate-related dissolution issue appears to affected at least a portion of the sample (bulliform cells and diatoms). Low biogenic recovery.

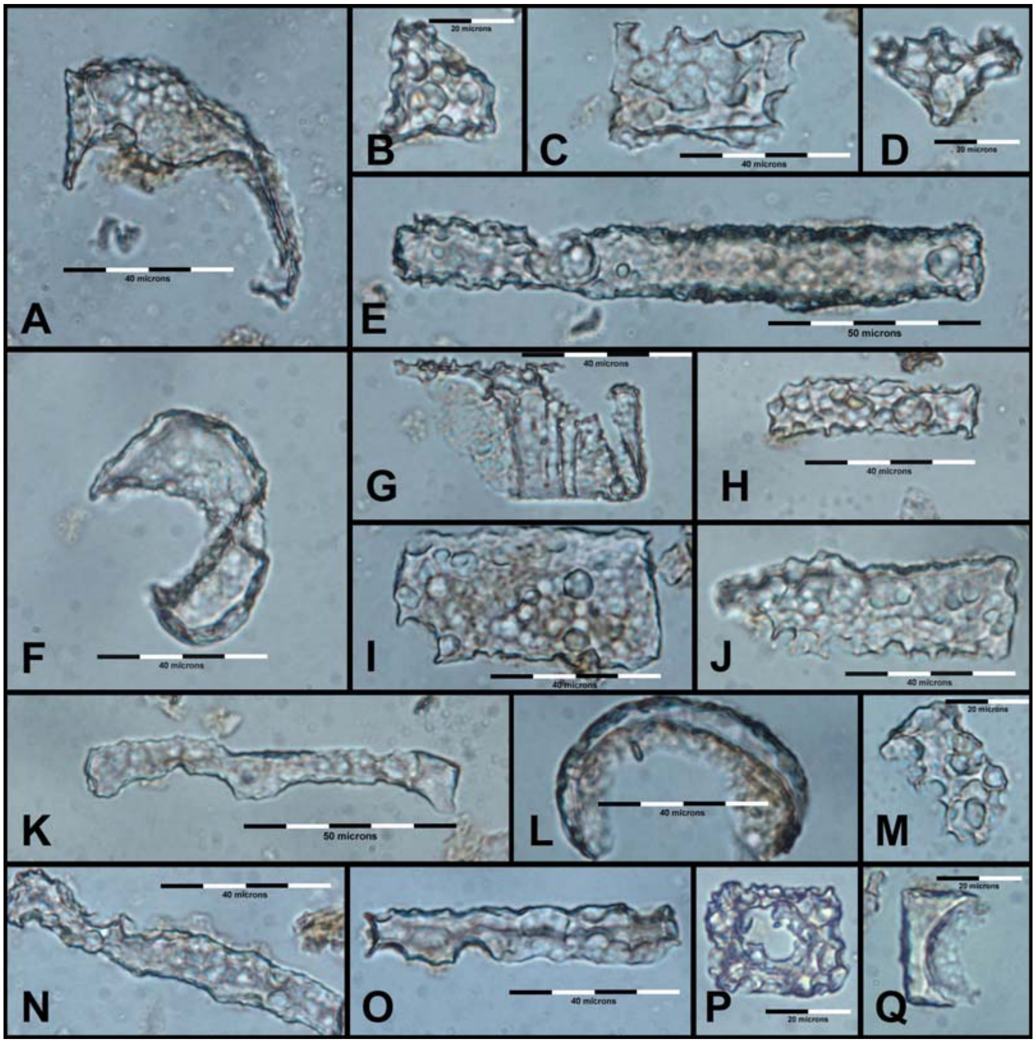

Figure 7. Representative heavily weathered bulliform and elongate phytoliths from 41LM50 and 41LM51 (Sudbury 2013b:Figure 27)..

8. **Dempsey Divide mixedgrass prairie control sample, Figure 8** (Sudbury 2011a)

Biogenic Particle Assessment: No phytoliths or other biogenic silica specimens recovered from the carbonate-rich soil below 25 cm. Bulliform preservation variable in the upper 25 cm (Figure 8). Good short cell counts available although specimens were not highly concentrated. Most basic soil pH profile measurement was 7.49. Much lower soil phytolith concentration than any other of the sites in the same report [the other sites in this report (Sudbury 2011a) are entered in Table 3 of this current document as particle preservation was much better and no soil carbonate/pH preservation-related issues were encountered at those sites.]

Additional Comments: Mixedgrass and shortgrass control prairies were on the same ranch Carbonates visible in the soil back dirt pile where the mixedgrass core study samples were collected (Sudbury 2011a:33 Figure 11). A large spike in charcoal content was noted in the biogenic strew slide from 20-25 cm.

Overall Phytolith Status: Good to poor preservation, deteriorated down profile from low soil count to zero preservation. Presumed pH/carbonate-related issue possibly exacerbated by the presence of charcoal.

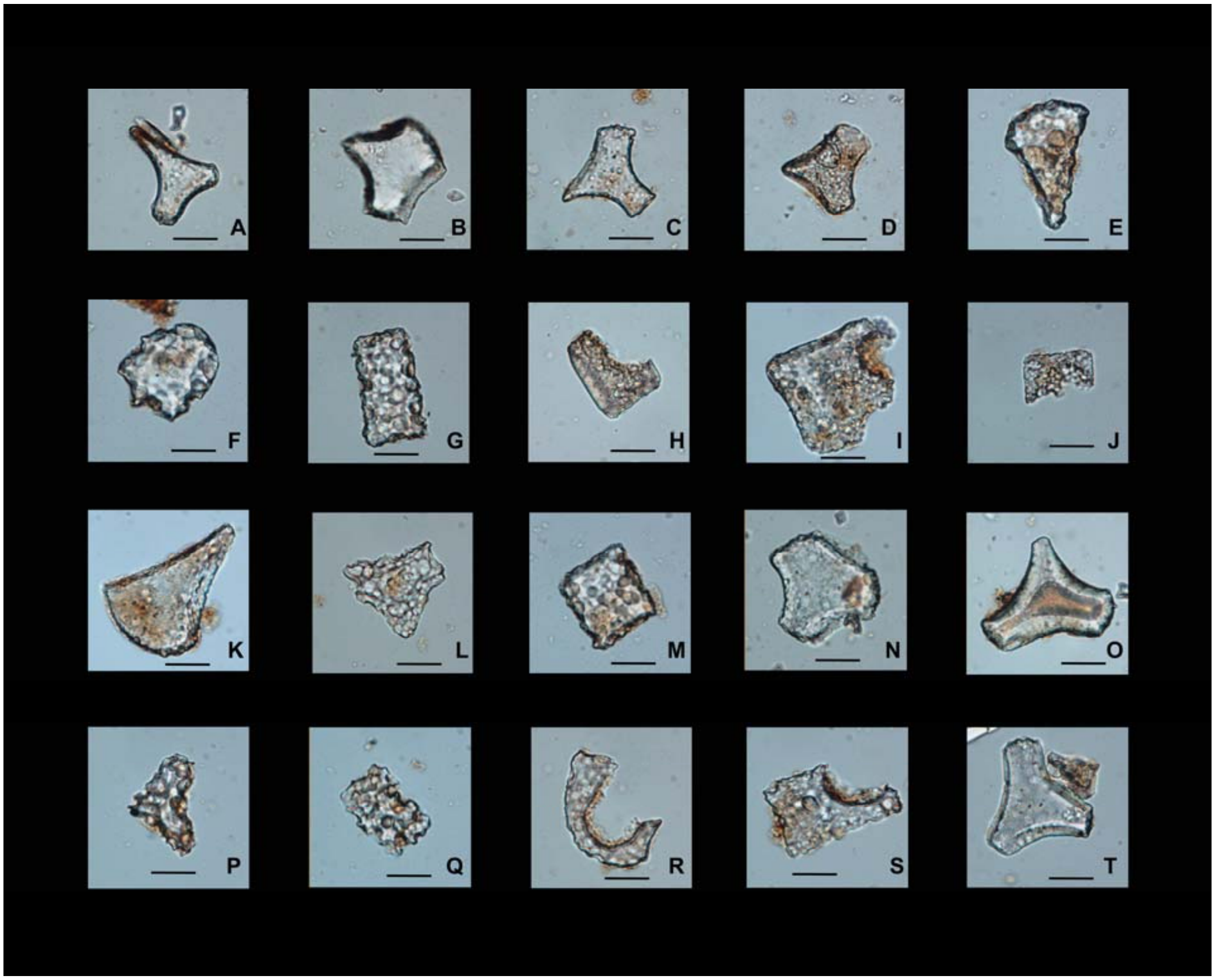

Figure 8. Bulliform phytoliths from Dempsey Divide mixedgrass profile soil samples showing variability in phytolith weathering and preservation (i.e., weathering and dissolution). A-B: 0-5 cm, C-D: 5-10 cm, E-J: 10-15 cm, K-O: 15-20 cm, and P-T: 20-25 cm. (Sudbury 2011a::111, Figure 70). (Bar scales 20 microns)

9. Sewright Site (36FA1603), Figure 9 (Sudbury nd2)

Biogenic Particle Assessment: Diatoms rare other than in the A-horizon control sample. Bulliform and large phytoliths down profile frequently show surface pitting, suggestive of surface dissolution (Figure 9). Angular tree phytoliths and spicules also show some surface disruption. Some phytolith categories were absent in many samples from the soil profile . Representative bulliform preservation illustrated in Figure 9.

Additional Comments: JSE laboratory had been actively extracting and processing soil phytolith samples full-time for three years since the Waugh Site sample [most of this intervening data was not published until dissertation completion in 2010]. Extraction methodology was constantly being re-evaluated, tweaked, and improved with progressive innovations during the interval; but good biogenic recoveries were consistently obtained during that interval. All Sewright soil fractions were examined; the "missing" biogenics were felt to be absent due to soil-related preservation issues based on surface damage noted on extant biogenics (Sudbury nd2:Figure 23 contrasts specimens from the surface sample and sample 35 [reproduced here as Figure 9]). The surface soil sample had good phytolith preservation (ibid. Figures 34-45), but phytoliths were generally sparse to absent down profile. Part may have been due to the time interval's having supported increased tree presence--but the phytoliths did exhibit definite surface damage. Numerous tree-related phytolith forms and abundant charcoal were present. Down profile, the bulliform cells showed significant surface weathering (ibid. Figure 46), and some of the tree-related phytoliths showed minor surface damage (ibid. Figures 50-52).

Overall Phytolith Status: Poor preservation, deteriorated down profile; presumed pH/carbonate-related issue possibly exacerbated by the presence of charcoal.

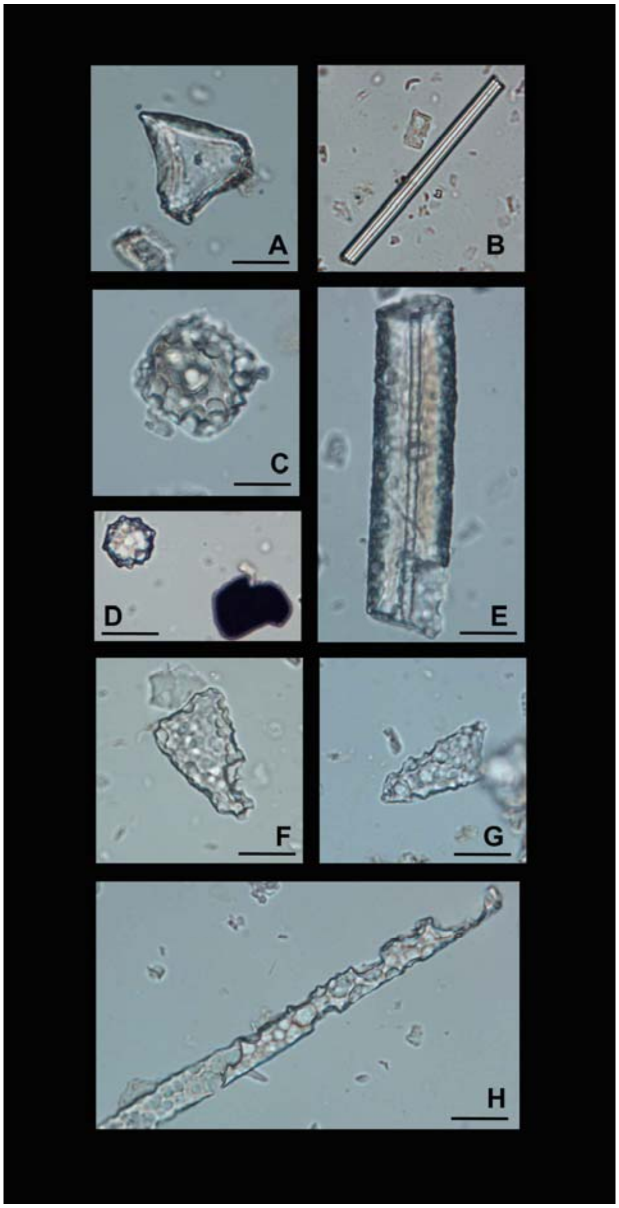

Figure 9. Image illustrating preservation issues noted when processing Sewright site soil profile samples (Sudbury nd2:17, Figure 23). A, B, from sample 1 (surface); C-H from down profile (Sample 35). Bar scales are 10 microns. Image B photographed at 200x; other specimens at 500x.

10. Waugh Site (34HP42), Figure 10 (Sudbury nd1)

Biogenic Particle Assessment: Very limited SEM time available for sample examination and photography--between competition with fellow students for time slots in the one semester class and instructor's issues with keeping the instrument operational. The sole good specimen image in the report shows an elongate cell with visible surface pitting and weathering along one edge (Figure 10). Particle distribution on the stubs was poor, so the isolates were incompletely evaluated. The botanical control specimen preps were much cleaner and resulted in better images--but do not address the soil carbonate-related issue at hand.

Additional Comments: This first phytolith sample set was processed and evaluated as a project while taking a university SEM class.. Work on the sample suite to was used to extract and examine the soil phytoliths after an initial literature review to identify an extraction methodology. Numerous learning errors occurred. Phytoliths were recovered, but not abundant. Light microscopy was not used to examine samples; only SEM gold sputter-coated specimens on stubs. The instructor called the delicate scientific instrument a "machine" and with multiple students using the SEM, the instrument was consistently out of operation as the vacuum chamber was not kept adequately clean. Work truncated in 13 weeks, so the project ended and I summarized my work--which was a good accumulation of method background information--but relatively little sample-related information. Sample retains, are available and will be reprocessed in the future now that the techniques used at JSE have been refined, and particle evaluation is being performed using mounted glass slides and polarized light microscopy.

Overall Phytolith status: Definite pH issue in the ash sample taken from the hearth; soil samples had some preservation issues (visible chemical weathering). Uncertain as sample isolates not completely evaluated.

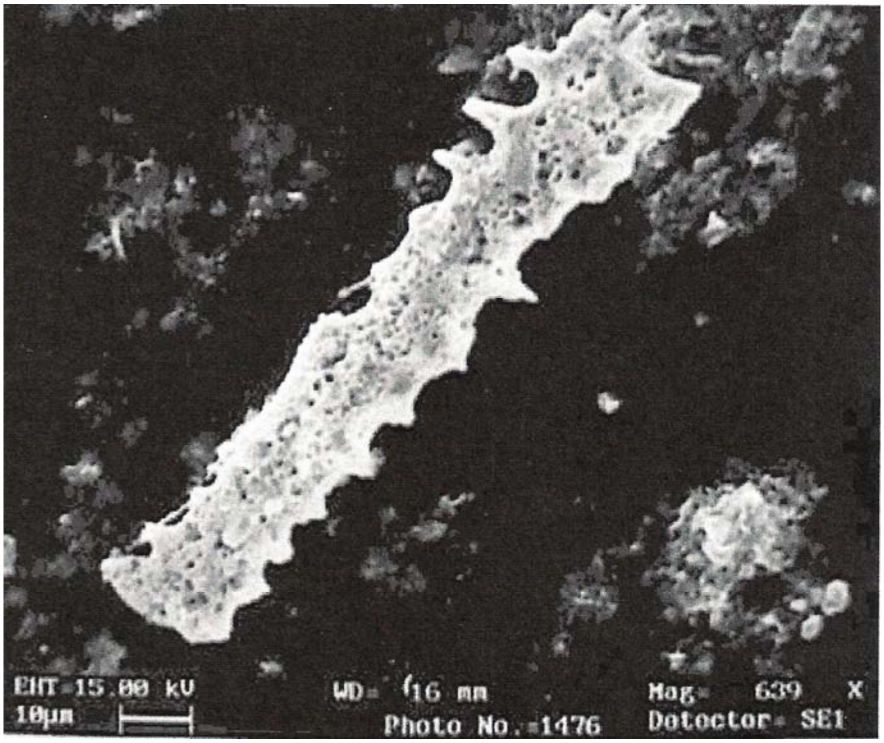

Figure 10 [above]. SEM image of Waugh site elongate phytolith showing some surface deterioration [image reproduced from printed copy of original report: (Sudbury nd1:32)].

Comments on Biogenic Recovery from Sites with Minimal to no Significant Deleterious pH and/or Carbonate-related Particle Preservation Issues--but which Contained some Carbonates:

Three sites were analyzed which are known to contain carbonates based on the USDA soil series descriptions, or which showed evidence of carbonates at the site when samples were being processed (Table 2). Overall, these sites showed very good phytolith preservation. In hindsight, the only biogenic preservation issue encountered with any of these samples was the paucity of diatoms at two sites:

- 41YN452, located on a stream-bank setting, had low diatom counts for the surface sample [1 specimen] and the six feature samples [0-1 specimens each], and
- 34BV176 had very low diatom content [several diatoms noted in two samples; nine samples contained zero diatoms in the particle counts resulting in 200+ well-preserved short cells].

The only outlier in these three sites regarding diatoms was the biogenic sample from 34WO69--preservation was very good across the board, with abundant statospores, spicules, diatoms, and phytoliths present all the way down the one meter soil profile which was sampled in 4 cm increments.

Table 2
Analyzed Sites with Minimal to No Carbonate/pH Issues Negatively Impacting Biogenic Silica Preservation

Site	Soil Type	Carbonate-related Horizons (via USDA OSD)	Comment	Biogenic Isolate (% of soil)	Reference Sudbury:...
34WO69	Pachic Argiustoll [St. Paul]	Bt1 (18-34"), Bt2 (34-45), BCk (45-56") & C (56-70"): slightly to strongly effervescent	considerable range: Bt1, Bt2, BCk, and C: some carbonate in Bt2, **BCk**, and C; **slightly to moderately alkaline**	excellent (diatoms, statospores very abundant)	2014d [written report pending in 2015]; Burnham
41YN452	Fluventic Haplustept [Wheatwood]	**Cambic** Bw Horizons (6-45") slightly to strongly effervescent	carbonate not mentioned in OSD; **moderately alkaline**	very good to excellent (relatively few diatoms)	2011c Root-be Gone
34BV176	not provided	**Akb, ABkb, & Bkb** soils in stacked buried soil series	**some carbonate present;** current upland setting	very good to excellent (relatively few diatoms)	(2011a); Bement et al. 2007; Bull Creek

These three sites (Table 2) had some visible carbonate present--or effervescence noted during processing--even though overall biogenic silica particle recoveries appeared to be good (with the exception of diatoms). Thus having soil carbonate present is not always a death knell to biogenic preservation, but it is definitely one condition that can contribute to biogenic preservation issues, and is a predictive indicator both of pH issues and possible dissolution. The sand fractions from 41LM50 and 41LM51 had a fairly high fossiliferous content which could have in part contributed to the carbonate observations for those samples; charcoal was also present. Overall, these samples appeared to have excellent biogenic preservation (with the exception of diatoms)--even with carbonate present in the soil matrix.

Comments on Biogenic Recovery from Sites without Significant Deleterious pH and/or Carbonate-related Issues:

The sites with biogenic samples recovered and described with no apparent damage (surface dissolution or particle absence) are summarized in Table 3. Additional detailed comments about these individual sites with well-preserved biogenic silica--including abundant diatoms--were not prepared due to the excellent overall preservation of the total biogenic fraction.

Most--but not all--of the sites with good preservation were acidic soil with a time range spanning the Holocene. Biogenic silica recoveries from this last set of sites was excellent (with maximums ranging from 0.6-4.6 weight percent phytolith in soil) versus the very low recoveries for the sites in Table 1 which were often as low as 0.03% [actually 0% in some samples]). The biogenic fraction recoveries for all of the sites in these three groupings as weight percent of soil are summarized in Table 4.

Table 3
Analyzed Sites with No Carbonate/pH Issues Negatively Impacting Biogenic Silica Preservation

Site	Soil Type	Carbonate-related Horizons (via USDA OSD)	Comment	Biogenic Isolate (% of soil)	Reference Sudbury:...
34NW132	Fluventic Hapludoll [Radley]	none	moderately acidic	excellent	(2011b) Opossum Creek
34WN107	Cumulic Haplludoll [Verdigris]	none	medium acidic to neutral (when present Bt is more acidic)	excellent	(2011a); Carter et al. 2009; Lizard
34CD76	Udic Haplustept [Noble]	none	"slightly acid" for entire profile	excellent	(2011a); Carter et al. 2009; Carnegie Canyon
Manning	Udic Argiustoll [Coyle]	none	slightly acidic to neutral	excellent	(2011a) prairie control soil
5GN2404 & 5GN2262	not provided		primarily processed feature samples	excellent	(2009)
34CN176	not provided		promontory	excellent	(2006) Farris Buser

Discussion:

The soil weight percent of the biogenic isolate fraction for all of the soil samples discussed in the preceding pages are summarized in Table 4; the sites are in the same order as in Tables 1-3.

In the first section (data for sites listed in Table 1) the lowest concentration in each set of samples was always $\leq$ 0.05 weight %. In some cases (Dempsey Divide, 4TV2161, 41MS69) the actual biogenic weight percent was zero for some samples [no amorphous silica visible on the slides]--but the fraction did have a measurable weight due to the presence of soil minerals and clays that were present in the "biogenic" fraction.

The maximum value in Table 1 was from the surface control soil sample from 36FA1603; all other samples were below 0.50 weight percent. Relatively lower Poaceae phytolith recoveries do occur in non-grassland settings with variable amounts of tree cover which restrict Poaceae community growth (c.f., Evett et al. 2006; Piperno 2006:123-125; Bozarth 1993). However, the visible particle damage (i.e., surface pitting from chemical dissolution in the bulliform cells) and the absence of some particles (most conspicuously diatoms, but also frequently some categories of short cell phytoliths [and the short cell specimens which are still present often show surface damage]) in the samples this series of sites suggests that the issue resulting in low biogenic content is almost certainly at least in part due to the basic pH soil environment and ongoing amorphous silica particle dissolution. This preservation issue in turn makes changes in environmental tree cover over time difficult to assess.

Table 4
Biogenic Silica Recoveries from all Sites Studied (Wt% of Soil)

	Carbonate Present	Biogenic Concentration (Wt% of Soil)[4]	Cam-bic	Cal-cic	Soil Type	Data from Table:
USLR	**+**	0.02-0.34	**?**	**?**	? (multiple sites)	1
5MT10647, 5MT10736	**+**	0.01-0.17		**+**	Aridic Halplustalf	
41MS69	**+**	0.03-0.05	**+**		Cumulic Haplustoll	
41BL278	**+**	0.03-0.07		**+**	Udic Calciustoll	
41TV2161	**+**	0.04-0.16		**+**	Udic Calciustoll	
41RB112	**+**	0.05-0.35	**?**	**?**	?	
41LM50, 41LM51	**+**		**+**		Udifluventic Haplustept	
Dempsey mixedgrass	**+**	0.03-0.14	**+**		Typic Halpustept	
36FA1603	**+**	0.04-0.96	**?**	**?**	?	
34HP42	**+**	?	**?**	**?**	?	
34WO69		0.80-4.11			Pachic Argiustoll	2
41YN452		0.94-1.60	**+**		Fluventic Halpustept	
34BV176	**+**	0.24-2.77			?	
34NW132		0.46-4.60			Fluventic Hapludoll	3
34WN107		1.31-2.87			Cumulic Hapludoll	
34CD76		0.12-1.15			Udic Haplustept	
Manning tallgrass prairie		0.14-0.63			Udic Argiustoll	
5GN2404, 5GN2262		0.13-0.81			?	
34CN176		?			?	

In the samples with better preservation, the weight percent data for the sites presented in Tables 2 (some carbonates present damage) and Table 3 (no carbonates and no appreciable damage dissolution evident) overlap considerably--but are always higher than the values reported for the sites Table 1 (Table 4). Several of the sites in Table 2 did have a dearth of diatoms, but overall the phytolith assemblage was in a reasonably good state of preservation and provided adequate short cell counts suitable for environmental reconstruction. The sites listed in Table 3 all had excellent diatom and phytolith preservation.

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[4] In some samples, no biogenic silica was present. The weight % "biogenic" fraction recovered was due to the presence of soil mineral contamination in the biogenic isolate. There were 0% biogenic content in some samples from 41TV2161,41MS69, and the Dempsey Divide mixedgrass prairie control samples)

Most of the Table 4 biogenic isolate concentration data for the sites presented in Tables 2 and 3 came from analysis of soil profiles at various sites.[5] Generally, the surface A-horizon had the highest biogenic silica concentration, and the concentration decreased down profile (example phytolith concentration plot in Figure 11). At locations where buried A-horizons were present, additional phytolith concentration peaks were present down-profile. Diatom concentrations were often elevated in the surface A-horizon; however, at Carnegie Canyon diatoms also peaked in a buried A-horizon [where the phytoliths also peaked], and indicated the presence of welded A-horizons (Figure 12).

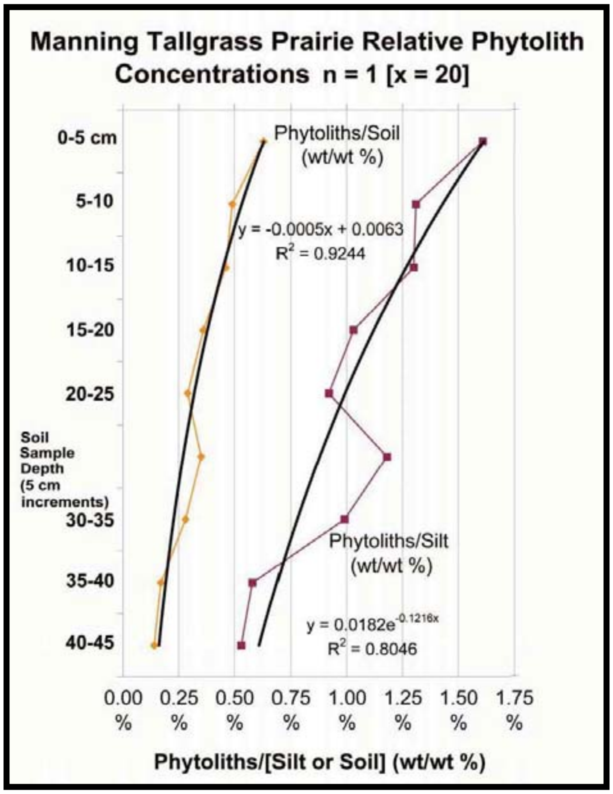

Figure 11. Phytolith isolate concentration at Manning tallgrass prairie (Sudbury 2011a: 106, Figure 66). Manning tallgrass prairie is a "virgin" [never been plowed] tallgrass prairie remnant.

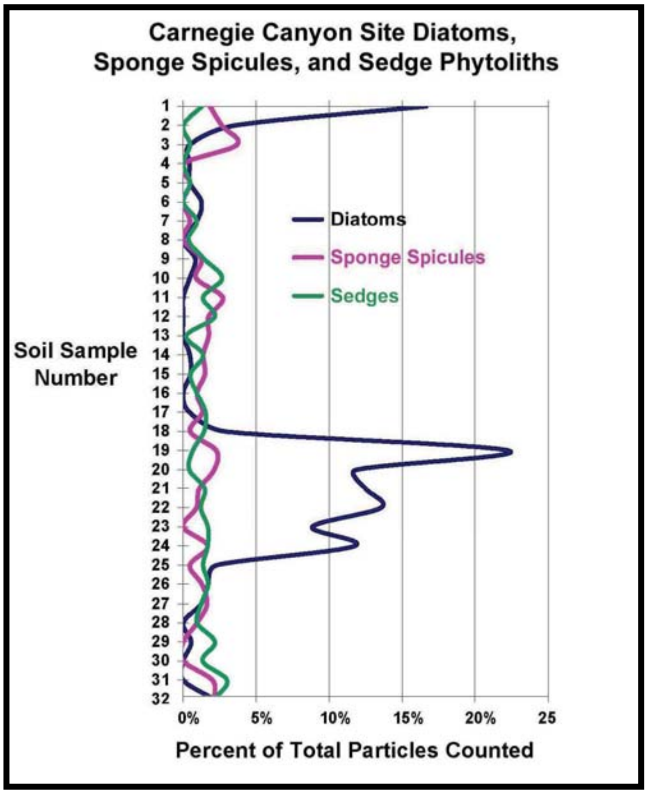

Figure 12. Profile diatom concentration at Carnegie Canyon relative to total biogenic particle counts (Sudbury 2011a:147, Figure 91). Diatom concentrations peaked at the surface, and also in the buried A-horizons. Diatom preservation was excellent.

The biogenic samples from non-basic soils are generally much better preserved and higher concentration that those recovered from very basic soils. There is concentration variability in acidic soil profile samples, with concentrations generally peaking when stable landscapes developed (i.e., A-horizons).

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[5] Samples from 41YN452, 5GN2404, 5GN2262, and 34CN176 were primarily feature samples rather than soil profiles. The samples from 34BV176 were primarily buried A-horizons.

There is still a lot of variability in biogenic concentration at the well-preserved sites. The rate of soil deposition will certainly influence the biogenic load in the samples (i.e., the faster the aggradation, the more the biogenic fraction is diluted by the more rapidly accumulating soil). Another variation in the biogenic weight percent concentration can be due to the assemblage itself; for instance, sponge spicules were abundant in the two highest weight percent samples (34WO69 and 34NW132) which likely contributed to their relatively high gravimetric biogenic content.

Conclusions:

The presence of soil carbonate often--but not always--can be used to predict biogenic silica preservation issues, due to impacts on soil pore water pH which can increase the dissolution rate of amorphous biogenic silica. All of the "calcic" sites evaluated in this summary had preservation issues, whereas at least one "cambic" site only had minor issues. Thus, although a suggestive indicator, soil description information alone is not enough to predict biogenic silica stability/survival.

There is apparently a threshold concentration at which pH-enhanced particle dissolution occurs, which has not yet been delineated. Based on this limited data set, it appears that this threshold may lie between >0 and 20% total carbonate equivalent. However, this value remains to be determined, and it is likely there is not a single threshold value. Rather it is probable that the final answer will have many contributing factors and will depend on the specific site setting. Thus, there is no simplistic cut and dried answer to the question: "should these samples be processed for biogenic silica recovery or not?"

In a number of cases, abundant charcoal has been present in samples with poor biogenic preservation; this was previously hypothesized to possibly be due to charcoal absorbing ions that might otherwise be protective of the biogenic particle surface (Drees et al. 1989:951-952; Sudbury 2007:16-18). The graph in Figure 1 is dissolved amorphous silica concentration at steady state; on an active stream bank with occasional flood events, and soil with active soil pore water movement, silica dissolution could reasonably be expected to accelerate. It has also been noted that a basic pH excursion will cause the solution to temporarily be supersaturated before returning to the steady state concentration (Iler 1979:41)--that occurrence combined with increased soil pore water movement would greatly accelerate particle dissolution. Botanical origin of phytoliths can also influence dissolution rate (Bartoli and Wilding 1980). Potentially other local soil environmental parameters not yet considered could also impact biogenic particle stability. Measuring current soil pH does not necessarily indicate that the soil pH has been stable throughout soil development. Also, it has been noted that pH measurements taken in the field can differ from those later taken in the lab as much as 2 pH units (Matthiesen 2004).

One interesting aside to this discussion is that calcareous soils often contain a large assemblage of snails which are generally absent in acidic soils. Snails have been abundant in the sand fractions of the Texas carbonate-rich samples processed over the last few years (Sudbury 2014a, 2014b, 2014c, 2013b). Conventional soil processing routinely crushes soil samples prior to texture analysis, and some conventional published phytolith extraction procedures sieve the soils to remove organic materials, often separate the sand fraction for the silt and clay by sieving, and may also acid treat the samples. All of these mechanical and chemical treatments will destroy the snail assemblage. Thus, if those mechanical techniques are employed for biogenic fraction isolation, it is recommended that a duplicate sample be processed without crushing in order to obtain an undamaged sand fraction that can be examined for snails and other large particles--this step should definitely be implemented when analyzing calcareous soils. Snails represent a very useful environmental proxy benefit of calcareous soils which is relatively unrecognized and greatly underutilized. The JSE phytolith preparative method (ibid.) has moved beyond the physically and chemically damaging procedures, and recovers intact snails as well as much larger phytoliths and spicules (300+ microns) than are normally reported by other analysts.

This data review led to recognition and assessment of particle damage that was not previously understood at the original time of analysis, resulting in the addition of Table 2 after the initial draft (and the relocation of some sites to Table 1 status that initially were assumed would be assigned to Table 3). This retrospective evaluation of the overall biogenic preservation data from the twenty-two sites summarized in Table 4 resulted in the following observations:

1. The absence or near absence of diatoms in biogenic soil isolates appears to indicate amorphous silica preservation issues (Table 1). Conversely, abundant diatom concentrations correlate with excellent overall biogenic silica preservation and concentrations (Tables 3, 4; Figure 12). Diatoms may be absent in biogenic isolates that otherwise appear to be well-preserved (Table 2). This suggests that diatoms are likely the first biogenic fraction component to dissolve in response to soil pH issues.
2. Spicules occasionally show slight weathering, but overall tend to be well-preserved at nearly all sites (however, they were totally absent from some samples at the sites noted in footnote 4). Spicules appear to be the last biogenic particle category to dissolve.
3. Phytoliths show variable degrees of preservation in samples with relatively low diatom numbers. Generally, some but not all, bulliform cells show surface pitting and in some cases partial particle dissolution (Figures 3-9). Short cells tend to dissolve more quickly than bulliform cells, which is presumed to be due to their relatively high surface area to volume ratio (but may also be in part due to relative particle hydration states). The sequence of short cell morphologies which disappear via dissolution from the assemblage appears to be variable, and requires additional data to fully delineate and understand. Cucurbits and phytoliths of tree origin appear to show more resilience than other phytoliths.
4. Assessment of statospore occurrence is not relevant to this discussion as statospores are only present on some sites in certain environmental settings involving desiccation.

Based on this information, the relative biogenic particle solubility in a basic pH soil matrix can generally be summarized as follows:

diatoms >> short cell phytoliths > bulliform phytoliths > tree phytoliths >> sponge spicules

with diatoms being most soluble and sponge spicules being the least soluble. Thus, if a biogenic isolate does not contain diatoms, that is a likely indicator of possible soil pH/carbonate-related biogenic preservation/dissolution issues. Biogenic silica solubility is dependent on a number of factors as discussed elsewhere (Iler 1979; Sudbury 2014a). These factors include particle density and the influence of protective ions on the silica surface as well as solution pH. Charcoal and relative particle sizes also likely have a significant impact, as well as site setting (i.e., rate of soil pore water movement and residence time).

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