

## Author comments on bg-2012-467 - final response to reviewers' comments

M. Sommer on behalf of all co-authors, Müncheberg, 12.4.2013

First of all we would like to thank all reviewers for their very helpful comments which will increase the quality of our paper. Main concern of all three reviewers is our conclusion which finally is reflected in the title. We are aware that “perturbation / transient state” is inferred from the data. However, by going carefully through all alternative explanations for the phenomena observed – using multiple working hypothesis combined with the exclusion principle – we are (still) convinced of our interpretation. With the title we also would like to strengthen the system's perspective on Si cycling in biogeosystems<sup>1</sup>. As a compromise we suggest a slightly modified title: *Si cycling in a forest biogeosystem – the importance of transient state biogenic Si pools*. We hope the reviewers agree on our line of argumentation.

Detailed reply (black) to reviewers' comments (red):

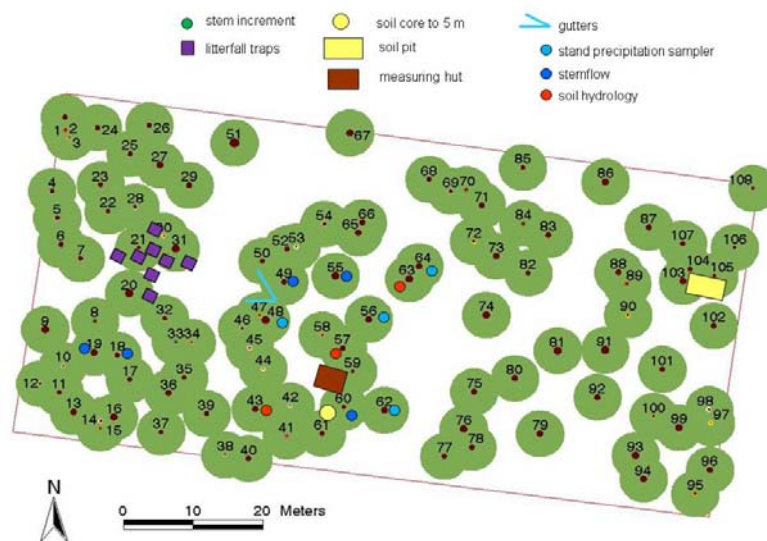
### Reviewer #1

- The introduction puts a lot of emphasis on Ge/Si and isotopes, but they are not actually used in this study. This part of the intro could be reduced, and the applicability of both techniques can be pointed to in discussion (where it is already touched upon). On the other hand, the 4 scenarios concerning weathering and climate limitation of Si cycling in Cornelis et al. 2011 should be better clarified.

Ge/Si and isotopes are skipped from the intro and shifted to discussion; the four scenarios of Cornelis are described in more detail

- It is difficult to assess where cores were taken. A map of the system could be very useful. Also the focus on only one core for sediment and soil is potentially limiting the applicability to the whole study site. It should be at least discussed what the lack of spatial distribution of sampling could imply for the results.

The following map is added to Chap. 2.1:



M. Lachmann (unpublished BSc thesis, 2002) augered soils in a 25m x 25m raster (down to 1m). The depth functions of soil texture (finger probes) were found to be very similar between the augerings (and the sampled soil pit). Therefore a uniform sediment stratification of that area seems reasonable. Despite evident topsoil heterogeneities (esp. in thickness of organic layers and related bulk densities), the soil pit represents a typical soil profile for the plot.

- Why was soil bulk density estimated and not determined? (18870, last line)

Bulk densities were measured in the soil pit (p.18870, 1.26-27) and estimated for the drilling core (1.2-2.5m) by the following equation:  $bulk\ density = (1 - total\ porosity) * density$ . Assuming a total porosity of 0.36 (36 Vol.%, reasonable for near surface glaciofluvial sands), and a quartz density of 2.65 g cm<sup>-3</sup> we get a BD of 1.7 g cm<sup>-3</sup>.

<sup>1</sup> By the way: this is actually discussed in carbon dynamics / balances as well: Schmidt et al. Nature 2011, Luo & Weng TREE 2011, Kasischke et al. JGR 2013.

- Was a correction applied for mineral Si release during Tiron extraction? Both NaOH and  $\text{Na}_2\text{CO}_3$  can extract significant amounts of mineral Si, and different correction methods have been suggested (e.g. Saccone et al. 2007). Why was no correction applied?

Tiron mainly extracts amorphous Si (biogenic, mineral), but also some crystalline Si, esp. from clay minerals. A correction for mineral Si release has not been applied, because we did not intend to separate biogenic from mineral Si by Tiron extraction. The results of a DeMaster like correction would still be ambiguous, because Tiron extracts both, the biogenic and pedogenic, amorphous Si (as fast reacting pools).

Nevertheless, the Tiron-Si depth functions give some hints on the distribution of different Si phases, when constraints are known. Example (referring to Fig.1): pH (proxy for weathering regime) is similar in the upper 35cm, clay content is slightly increased in the third horizon, but Tiron has a clear maximum in the SOC-rich first horizon (EA). From these findings we qualitatively conclude a decrease in biogenic Si with depth.

- The nomination “pedogenic silica” is what is supposed to be extracted with Tiron. But what does it stand for? Biogenic and amorphous phases? What was the coherence between phytolith Si pool (biogenic amorphous Si) and (corrected for minerals) Tiron Si pool?

Here we cited from literature, therefore quotation marks. We are aware that the phases which are extracted by Tiron are not well defined (see comment above); it is a proxy for the sum of biogenic  $\text{SiO}_2$  (not fully dissolved by Tiron) and amorphous, pedogenic  $\text{SiO}_2$ , ie coatings at mineral surfaces, Si adsorbed at iron oxide surface etc (Sauer et al. Biogeochemistry 2006)

- It is unclear how many times litterfall was sampled (one date – four months?)

Yes, phytoliths in litter fall were determined in one sample from a 4-months cumulative sampling period; sampling intervals for flux calculations are described in Chap. 2.3

- The quantifications for the zoogenic pool contains quite some assumptions. . . Why was Si content from another study used? What are implications?

The study of Aoki et al. (Geoderma 2007) is the only one which quantified Si content in (single) shells/tests of different testate amoebae species. We assumed a principal assignability of the results of Aoki. Own measurements of single tests were not planned for this study, but will be done in a recent DFG project on testate amoebae.

- Can borosilicate probes influence the dissolved Si concentration?

We also identified this question and initiated lab experiments: We adjusted the Si concentration in solution at 3.6 mg Si L<sup>-1</sup> and pumped solution through suction cups composed of different material. Borosilicate probes increased Si concentrations just by 0.2 mg Si L<sup>-1</sup> (compared to the Si concentration outside the cup). From these results we concluded a neglectible influence of borosilicate cups on measured Si concentrations in soil solution.

- The study of Struyf et al. (2010) on Si fluxes after soil disturbance and cultivation should be included in the intro and discussion. . . How do results fit in the conceptual model put forward in this study?

Struyf et al. (Nature Comm. 2010) adressed the effects of (drastic) land use changes (forest to agriculture, forest to human etc) on Si fluxes at catchment scale. We were analysing Si pools and fluxes at a site level with no historical LUC. In so far both studies are complementary. However, the conceptual model of Struyf et al. (Fig.3) does not cover vegetation changes by forest management, but a temporal sequence (“developing, climax, early deforested”).

- Line 22, page 18868: this is not a sentence as it contains no verb. Quite some of these “verb-less” sentences are found through the manuscript, please carefully check.

Verb-less sentence will be eliminated in the revised manuscript

- Page 18875, avoid stem near areas, please consider revising wording.

“Stem near” is replaced by “close to stem”

- Page 18882, line 15-17. This is a strong conclusion, as mainly taken from concentrations. However, fluxes and hydrology should be accounted for.

Sentence is skipped

## Reviewer #2

The reviewer was mainly concerned about the methods to identify phytoliths. Being aware of the methodological problems to identify the biogenic Si pool (esp. by physical separation) we did not intend to substitute phytolith determination with chemical extractions or vice versa - may be this was a misunderstanding(?). As recommended by the reviewer we now added percentages of phytoliths according to their shape characteristics in Table 2 (see below). We already did the shape characterization together with the counting for the four plant categories and dissolution features. We are convinced that is possible to assign at least part of the phytoliths to genus or family level as numerous studies have shown. We know that (i) the assignment is of some subjectivity (experience), and, (ii) 50-75% of the counted phytoliths were not assignable in our case. To minimise subjectivity we posted our phytolith micrographs at the internet platform “PhyTalk” (as stated in the acknowledgements) and asked for assignments to plants. The feedbacks confirmed our own assignments. With this quality check we would like to keep the 4 groups (grasses, beech, mosses, pine) in Table 2.

		depth	count-% of total phytolith number (10 SEM micrographs)									
		[cm]	globular	elongate	shortcells	vascular	n.a.	grasses	beech	mosses	pine	n.a.
litterfall (5-8/08)	leaves	-										
	bud scales	-										
	pericarps	-										
	branches	-										
soil	litter layer (L)		7	25	18	1	49	7	12	4	1	75
	AE	0-2	7	25	20	2	45	16	5	5	3	72
	Ah	2-10	0	38	15	0	47	44	0	1	2	53
	AB	10-20	0	27	8	0	64	45	0	0	1	54

We use these data as indicators for a vegetation shift: If no grasses grow at the plot (at least for the last 50years due to canopy closure) and there is a substantial amount of grass phytoliths one can conclude that this is a relictic biogenic Si pool - which is definitely a source for silica in soil solution (of unknown magnitude, of course).



Photo of the “Beerenbusch” site: no grasses in the understorey.

Technical comments:

- p. 18873/27: replace "method manual of Alexandre" by Alexandre et al., 1997.

done

- p. 18878/24 : give ranges or averages  $\pm$  SD for Si values;

rephrased to: Water soluble Si shows a decrease from 16 mg kg<sup>-1</sup> in the upper 2 cm to 4 mg kg<sup>-1</sup> in subsoil horizons and a recurring increase in sediments containing carbonates (Fig. 1)

- p. 18879/2: ..."the size of biogenic Si pool in different horizons": adsorbed Si can also explain the Si extracted by water; please comment

Right, water soluble Si exclusively extracts adsorbed Si; sentence has been skipped

- p. 18879/5: give ranges or averages  $\pm$  SD ; how do you explained that water extractable Si and Tiron Si have the same distribution in the soil profil (decrease down to 100-150 cm) ?

This may be a misunderstanding: There is only one value per horizon (3 lab replicates). By this sentence we just summarize the observed trend in the depth functions. We interpret the distribution as an effect of the biogenic Si pool distribution with depth. Higher values in both extractions can only be seen in topsoil horizons – the depth increment where most of the biogenic Si is located.

-p. 18879/18-20: the conclusion came too early in the text without a comprehensive evaluation of all the hypotheses ; for instance , 1) there is no evaluation of the validity of the values of Si extracted by Tiron. Because Tiron is known to dissolved crystalline silicate it can over estimate the measurement of the biogenic Si pools ; 2) the extraction by heavy liquid flotation can lead to loss during the procedures but without replicates, this hypothesis cannot be assessed; 3)the loss during the removal of the < 2 fraction has already been discussed (ex ; Saconne et al., 2007) but is not fully assessed here; assuming that all their BSi is concentrated. in this fraction it should have been detected using various techniques (XRD, IR, chemical extraction. . .) ; I also recommend to separate the discussion from the results.

The question about mineral Si release by Tiron was already stressed in our reply on reviewer 1 (see page 1-2). Further we fully agree: even with replicates the extraction by heavy liquid flotation cannot give any hints to losses of the < 2 $\mu$ m fraction. As we did not apply other techniques results and discussion should be separated here. We shifted the data interpretation (l. 16-28) into the discussion part.

-p.18880/1... and fig 2: the authors should present the shapes of phytoliths before assigning them to plant type. done (in Table 2 and text), see general comments

-p.18880/25: you mean "compared to Si (phytolith) given by physical extraction but 3 orders of magnitude less that Si (phytolith) given by Tiron extraction"?

here we would like to compare the calculated Si pool in testate amoebae with phytolith Si pool given by physical extraction (not Tiron); sentence is rephrased

-p. 18881/ 5: no data from dust (solid) input ?

unfortunately not

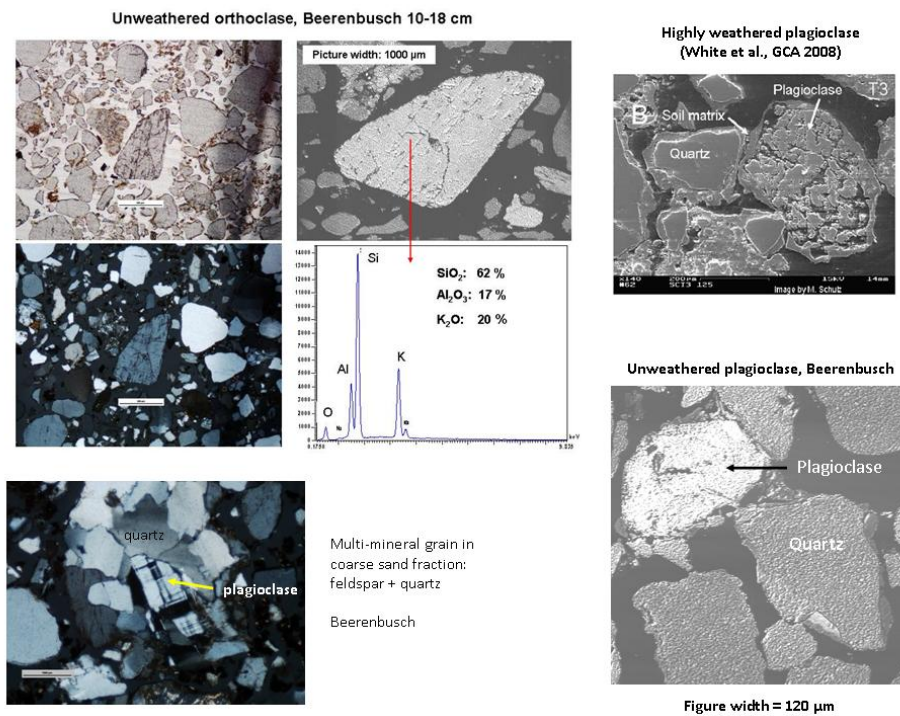
-p. 18884/13: you mean (high) Si concentration in the waters (6 mg/L) or in the plants ? because in both cases the concentration are low compared to other systems

sentence is skipped

-p. 18884/21: this statement is not robust if we consider the kinetics ; at acid pH the rate of quartz dissolution is an order of magnitude less than the one for albite for instance so the Si release from 3 % Albite should be equivalent to the Si release from 30 % quartz.

This consideration is valid for controlled lab experiments with sieved and grounded soil. It does not apply to in-situ situations like ours due to several reasons: (i) the mineral distribution in a soil horizon is inhomogenous; consequently, the accessibility of feldspar to soil solutions is hampered as water flow is not homogenous in soils (preferential flow paths), (ii) a lot of mineral grains are coated as can be seen in Figure 5a (2b, 3b); this also means less water access to the mineral (chemical reactions mainly take place in the coatings), (iii) a lot of feldspars are included into small rock remnants in the coarse sand fraction (see photo next page); here water access and chemical weathering is very limited. All these arguments fits to our observation that (iv) feldspars in our soil show almost no signs of weathering (surface etching, solutional caverns), compared with feldspar weathering in White et al. (GCA 2008) (see photo next page). Therefore we still consider our conclusion as valid.





-p. 18884/25 : the composition of the waters are not enough constrained to support the conclusion. The recent study of White et al (2012, GCA) shows that at the level of the weathering front the concentration of DSi can be controlled by dissolution of primary minerals whereas at the surface, DSi is controlled by phytolith. Here, the concentration of other elements such as Na, Cl Al would have been useful to constrain the weathering processes.

The study of White et al. (GCA 2012) differs substantially in its environmental setting from our site: high content of feldspar (in part feldspar > quartz) and kaolinite (up to 45%), mediterranean climate and grassland. It is not surprising that they find different sources for Si in soil solution, because there are a lot weatherable minerals in the subsoil. Our site shows very low feldspar content throughout the profile (with almost no signs of chemical weathering), very low clay content, and podzolization as the main pedogenic process. Further, the concentrations of Na, Cl, and Al do not support the hypothesis of a “weathering front”. Al and DOC rather supports the morphological evidence for podzolization. Here we present average concentrations in soil solution for a 11 year observation period (2001-2012) (all in mg L<sup>-1</sup>):

20cm: Na=5.8, Cl=7.9, Al=1.5, DOC=23.6

70cm: Na=5.5, Cl=7.4, Al=0.5, DOC=15.1

250cm: Na=5.9, Cl=8.7, Al=0.03, DOC=6.7

p.18886/17: "high DSi concentrations" compared to what ? compared to similar environmental settings, which means low content of weatherable minerals, podzolization humid climate

the sentence is rephrased: In summary, we conclude feldspar weathering to be of minor influence on silica concentrations in soil solutions.

-p.18886/22: not enough constrained by the data unless the description of the phytoliths is more rigorously done and the pools of BSi are more clearly evaluated ;the change of the vegetation 20 years ago may have changed the weathering rates and the biogeochemical cycle but no historical data are presently available to support the conclusion for the moment ; the model should have been discussed with the recent papers presenting evidenced for anthropogenic impact (Conley et al., 2008; Stuyff et al., Casey and Fulweiler ; Guntzer et al.)

Description of phytoliths have been done more rigorously (see general comment at p.3). Furthermore we used standard methods for BSi quantification and added testate amoebae; the main pedogenic process is podzolization - rates should even be lower compared to the situation when pine dominated the plot (as pine needles release more complexing, organic acids compared to beech leaves). Our study adds another aspect of anthropogenic impact on Si cycling to the studies cited in the reviewer’s comment – that is forest mangement in a permanent forest without LUC.

### Reviewer #3

- P2; Lines 17-21: this conclusion is not supported by your data. These observations aren't compared to a system with no land use change, ie a pine forest. So you cannot talk about anthropogenic perturbations. To our mind perturbations should be looked at in a broader sense. In terms of Si cycling we regard changes in forest management, ie a shift from pine to beech, as an anthropogenic perturbation; mainly, because this management action leads to a concomitant disappearance of grasses (at the latest with canopy closure more than 50 yrs ago) which built up a substantial phytolith pool.

With your dataset you aren't able to know which type of phytoliths (from pine or beech forest) govern the DSi concentration in aqueous phase.

Right. What we would like to say here is that we do not assume a steady state Si cycling at our plot. Instead the site is in a transient state due to an additional, relictic, biogenic Si pool, which mainly comes from a former understorey (grasses). This pool is not in an equilibrium between upbuilding and dissolution, but just diminishing by dissolution.

- P3; line 2: Could you please very briefly explain why many studies are currently focusing on the biogeochemical Si cycle?

Si is recognized as an important element in global biogeochemical cycles. Especially its linkage to global C cycle leads to an increased significance (diatoms in marine biogeosystems, C conservation in phytoliths, etc). Further a (suspected) Si depletion in arable soils – with a consequence of lower yields – puts Si cycling on the agenda.

- P3; line 3: please replace “quantification of Si pools” by “understanding of Si pathways”  
done

- P3; lines 4-7: I don't get why you mention Si isotopes here? What's the link with the objectives? Furthermore, could you explain briefly why natural Si fractionation is useful to understand the Si pathways in soil-plant systems?

The Si isotopes are skipped from the intro and shifted to the discussion part. For the general importance of isotopic studies see review of Opfergelt & Delmelle, Comptes Rendus Geoscience 344 (2012): 723-738

- P3; line 12: Could you please refer also to the Struyf's studies on the impact of land use on ASi pool  
done

- P3; line 14: Please insert also the studies in forest ecosystems.  
done

- P4; lines 3-5: could you further explain the four scenarios. How the definition of these scenarios is important for your study? Moreover, it might be a good idea to explain in more details the terminology used in Cornelis et al. 2011 and the meaning of climate weathering limited system. I think you're more between soil weathering-limited and climate-weathering limited systems as the weathering ability of the biogeosystem is low due to climate and low content of weatherable minerals (>95% quartz).  
Yes, scenarios are explained in more detail (see reply to reviewer #1, p.1).

- P5; line 15: replace “podsolization” by “podzolization”.  
done

- P6; line 2: a personal communication is allowed by BG?  
Why not?...

- P6; line 8: “assuming a principally similar sediment layering” How can you assume this?  
The genesis of a sandur is a large scale regional process. Although there is a local, small scale heterogeneity, the principal stratification of the glaciofluvial sediments is similar in a plot of 100m x 50m. This is supported by the work of Lachmann (unpublished BSc thesis, 2002) who augered soils in a 25m x 25m raster (down to 1m). The depth functions of soil texture (finger probes) were very similar between the augerings as well as in relation to the soil pit.

- P6; line 14: How did you estimate BD for sediments? And what do you mean in line 15?

Bulk densities were estimated by this equation:  $bulk\ density = (1 - total\ porosity) * density$ . Assuming a total porosity of 0.36 (36 Vol.%, reasonable for near surface glaciofluvial sands), and a quartz density of 2.65 g cm<sup>-3</sup> we get a BD of 1.7 g cm<sup>-3</sup>.

- P7; line 8: What is that you extract? Is it similar to the plant-available Si extracted using CaCl<sub>2</sub> solution or DSi measured using lysimeter?

The procedure extracts mainly adsorbed Si. Water extractable Si is (i) higher than DSi, because of using disturbed and sieved soil in the lab (elimination of structural effects), and, (ii) lower than CaCl<sub>2</sub>, because of the lower ionic strength of H<sub>2</sub>O. We did not analyse water from lysimeter, but suction cups.

- P7; line 20: please replace “pedogenic silica” by amorphous silica (=pedogenic opal + phytoliths and microorganisms remains). What about the dissolution of imogolite-type materials which are not suspected to be present in your soil given the soil pH < 4.9.

This is a citation and therefore set in quotation marks. Tiron might extract imogolite as well. However, we are not aware of any published study on that.

- P9; line 1: Are you able to quantify with a microprobe of SEM/EDX?

By using EDX we can quantitatively determine element composition, sure. May be we did not get the question?

- P9; line 19. . . : please rephrase without using paragraph. Could you be a little more critical about the method as some authors showed that the gravimetric separation using heavy liquid is not accurate, albeit this method is helpful for microscopic analysis.

Rephrased without using paragraphs. We are aware of the shortcomings of this method (see comments to reviewer #2). However, it is still the standard procedure to quantify (part of the) phytogenic Si (e.g., Blecker et al. GBC 2006, Alexandre et al. GPC 2011, Steinhöfel et al CG 2012) as accepted alternatives are missing.

- P12; lines 11-13; Did you avoid measuring Aeolian dust deposit on the surface of leaves?

Litter fall was not washed in order to avoid leaching of mobile elements. We used the standards given by ICP Forest for Level II plots in Europe and - by doing so - cannot avoid dust influence. However, we are aware of this problem and recently started an experiment comparing un-/washed beech leaves in terms of total Si, phytolith content, including SEM.

- P14; line 14: this oxalate extractable Fe and Al contents could reveal other soil components such as organo-metallic complexes.

Yes, it is well known that organo-metallic compounds are extracted, esp. in podzolized soil horizons. sentence is rephrased: “Organically complexed Fe, Al and pedogenic oxides....”

- P14; line 18: . . . And given the pH value in the subsoil (<4.9). However how can you explain the increase of Si<sub>ox</sub> between 0-25cm? Adsorption onto Fe oxides?

We do not have an explanation for the increase in Si<sub>ox</sub>. Adsorption onto Fe oxides might occur, but we do not know its proportion relative to organically complexed Fe. (Fe<sub>ox</sub> is decreasing almost linear from 0 to 25cm).

- P14; lines 23-24: that’s an interpretation for the discussion. Could you please further explain?

Sentence is deleted (see comments to reviewer #2)

- P15; line 1: “uppermost meter” What do you mean? Besides the differences in terms of mineral solubility in the soil profile, is it plausible to explain this observation by an active Si uptake in the topsoil with high content of roots?

We are not explaining this number, e.g., by active Si uptake. It is just a quantification of the most mobile Si pool in the first meter. Taking the first meter (0-1m) is somewhat arbitrary.

- P15; line 6: that’s for the discussion. . . need to be detailed

Rephrased: The highest content can be observed in the uppermost horizon (AE).

- P15; line 7: that’s surprising given the high content of ASi in topsoil. . . but BD is lower.

Yes, BD is lower and thicknesses of topsoil horizons is low compared to total soil.

- P15; line 10: could you please clarify how you quantify phytoliths?

See chap. 2.2.4

- P15; line12: you're talking about Si pools in your tables and introduction(. . .) and presenting results in SiO<sub>2</sub> here. Could you be consistent?

We consistently use Si, but phytoliths consists of SiO<sub>2</sub>, not Si. In order to convert phytolith masses into Si masses we need to use SiO<sub>2</sub>.

- P15; lines 16-21: this part must be clarified. In my own opinion, 2.4 and 4.4 g/kg cannot be compared.

Rephrased: "Comparing the calculated Si content of phytoliths with measured Si content of leaves supports this consideration: ... "

- P16; line 1: replace Table 2 by Fig 2.

We added Fig.2

- P16; line 5: maybe due to weathering/partial dissolution of beech phytoliths in soils, which become morphologically indistinguishable, compared to pine phytoliths. The 50-75% unrecognized phytoliths should be due to weathering features

Yes, we agree.

- P16; line 21: cite a reference

Done: Anderson, Protoplasma 181 (1994), 61-77.

- P18; line 5: Is it possible that this short-time scale Si pool significantly influences the Si isotopic signature in soil?

Not significantly and not permanently to our mind, because of the low masses of tests and high turnover rates

- P18; lines 11-13: very surprising. Could you further discuss this in your discussion?

In this article we did not focus on temporal dynamics of Si in soil solution. This would require a sound dynamic process modelling like in Gerard et al. (Geoderma 2002, GCA 2008). Therefore we skip this sentence.

- P 18; lines 15-17: That's for the discussion. Could you please further discuss these observations

Sentence is skipped (see comments to reviewer #2)

- P19; lines 12-14: Could you please make the relation with the DSi concentration in soil solution.

We do not understand this comment.

- P20; line 9: Could you please further discuss this observation and its impact on Si dynamic in soil, and more particularly in your biogeosystem?

The impact on Si dynamics is mentioned in the sentence before. Coatings reduce soil solution access to minerals. In consequence feldspars or quartz are protected from weathering and dissolution, because chemical interactions between solution and solid phases mainly take place at the surface of coatings. See also reply to reviewer #2, p.4/5

- P20; line 12: Why specifically kaolinite? And not other crystalline or poorly-crystalline aluminosilicates?

Kaolinite is characterized by high Al and low K, Mg. This fits to the chemical composition given in Figure5 (lower). Other clay minerals, like smectite or illite, would show clearly higher K and Mg contents. Bulk chemical analysis (Al:SiO<sub>2</sub>, pH) make poorly crystalline aluminosilicates very unlikely.

- P20; lines 17-18: and what about adsorption/coprecipitation of organo-Fe complexes or neoformation of Al-Si phases on the surface of quartz grains.

Yes, precipitation of organo-Fe complexes must be included (podzolization). Which Al-Si phases?

- P20; lines 22-23: How can you conclude this? A low proportion of weatherable minerals doesn't mean



that this pool of minerals in the climate & soil weathering-limited system cannot significantly influence Si dynamics.

There might be systems where a low proportion of weatherable minerals influence Si dynamics.

Rephrased: “in principal” is replaced by “at our site”

- P21; line 4: “pedochemical environment” Could you specify which environmental conditions can influence acidolyse/acidocomplexolyse?

Yes: an environment showing a high input of inorganic and organic acids (proton donors), like in podzols or podzolized soils (see reply to reviewer #2 and numbers on DOC at p.5)

- P21; lines 1-7: I’m not really convinced by your assumptions. . .

We try to convince the reviewers with our reply on their comments...

- P21; lines 15-17: I agree but could you please further explain a little more in term of a likely impact on Si dynamic and pedogenesis.

The impact on Si dynamics is on a much smaller time scale than adressed in this study which clearly focusses on (multi-)annual budgets.

- P22; line14: “parallel increase. . .” except in deep soil where we observe an increase of Si(H<sub>2</sub>O).

Yes, we add “... observed in the upper 25cm.” The further increase in DSi concentrations with greater depth is marginal and obviously not related to the clear increase of Si(H<sub>2</sub>O).

- P23; lines 9-10: how can you conclude this? We know that pine uptake is lower and so could influence the ASi pool in soil through litterfall. The dissolution of beech phytoliths can also play a key role.

Si uptake by pine is not necessarily lower. It depends on site conditions, like soils or parent material. Si fluxes by litterfall has been monitored at some ICP-Level II sites in Germany, e.g., at plot “1607 Holzland” in Thuringia. Here they measured an average Si flux (6 years of observation) of 20 kg Si ha<sup>-1</sup> y<sup>-1</sup> by litterfall of pine needles (Ines Chmara, Thüringenforst Gotha, pers. comm.). Of course beech phytoliths play a key role due to the mechanical instability & higher solubility of its phytoliths. But we argue the beech phytolith pool to be in equilibrium (upbuilding ≈ dissolution) as our beech stand is already 125 years old. We agree that pine was/is not the major contributor to recent biogenic Si pool in the soil, but grasses are (see Table 2). They disappeared with canopy closure (> 50 years ago) - a process which is related to the removal of pine trees. Therefore grass phytolith pool is in disequilibrium (no more upbuilding, only dissolution) and contributes to silica in soil solution.

- Figure 2: the EDX spectra is not discussed

The EDX spectra confirms that phytoliths consist almost exclusively of pure SiO<sub>2</sub>. A reference is added at p.15, l. 12

- Figure 5 upper: I don’t see the arrows pointing to amoebae. How can you say that’s a Fe oxide or clay coating in figure b? What about OC coating or organo-Fe coating?

Figure 5 upper gives an overview of the thin sections at low resolution. Here we did not place arrows, because amoebae cannot identified at this resolution. Fe oxides / clay coatings are inferred from brownish colour. Any coating containing considerable amount of OC would be much darker, see photo below (taken from Stoops, G.: Guidelines for analysis and description of soil and regolith thin sections, Soil Sci. Soc. Am., Madison, WI, 2003)

