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Interactive comment on “The contribution of tephra constituents during biogenic silica determination: implications for soil and paleoecological studies” by W. Clymans et al.

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Revision on interactive comment on “ The contribution of tephra constituents during biogenic silica determination: implications for soil and paleoecological studies” by W. Clymans et. al.

Dear Editor,

We are pleased that both reviewers and associate editor support publication and acknowledge the importance of our study. We have complied with all their requests, and where not, reasoning is detailed accordingly (see below). We hope the revised manuscript is ready for publication. Please feel free to contact us if additional explana-

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tions or revisions are necessary. Kind Regards, Wim Clymans et al.

Referee #1: D.J. Lowe The authors are pleased to receive positive comments on the relevance, content and writing style from D.J. Lowe (an expert within the field). His detailed suggestions to improve technical and language issues enhanced clarity and led to more correct presentation of the results. We greatly appreciated his annotated MS .

Referee #2: Anonymous The only critical comments that are made deal with the generality of the study: *Guidelines are good for caveats involved in volcanic soils, but one can question if general observations can be applied to other soils samples. *Impact of the paper is restricted to specific samples from which the role in a global context is quite small. We agree with the reviewer that we had to tone down some of our statements with respect to the generality of our results. However, we want to stress that although having a small spatial distribution, volcanic soils are suggested to coincide with an important biological control on the Si cycle (Derry et al., 2005 & Meunier et al., 1998). Therefore, those systems have received increased attention as being highly relevant systems to study the effect of biology on the Si cycle. Our observation that the non-biogenic fraction can significantly contribute to the SiAlk pool is also observed in other soil systems (see Barão et al., 2014. EJSS; Barão et al., 2015. LOM), and has equally important consequences for the interpretation of the BSi pool. This supports the relevance of our general observation with respect to increased critical interpretation of BSi estimates in soil profiles, and certainly in volcanic prone areas.

C1: Add a short description of sampling method and preservation for the samples referenced as unpublished data in Table 1. R1: For unpublished data a short description with basic information was added in the caption of table 1. Notice that we have changed the representation of the ages as some of them were not cal BP dates.

C2: Dampen following statement: "We formulate guidelines for the use of alkaline extraction techniques to determine BSi in soils and sediments." R2: We clarified that

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guidelines are primarily provided to aid sample analysis of soil and sediment samples prone to volcanic glass inputs. However, we would like to emphasize that one can easily see methodological advantages and application possibilities of the described approach (using Si:Al in combination with alkaline reactivity constants) to tackle contributions of other non-biogenic sources, such as clays and nanocrystalline fractions. This is also suggested in section 4.2.2 and 4.3.1, but we do agree that the absence of mineralogical information limits the generality of our interpretation regarding the contribution of other than volcanic non-biogenic fractions. We therefore refer to an extensive line of research performed by our co-author L. Barão (Barão et al., 2014. EJSS; Barão et al., 2015. LOM; Barão, 2015, thesis) who exemplifies the usefulness of the method for such cases.

C3: Rephrased p17 line 534 dealing with limited knowledge of mineralogical composition samples. R3: Rephrased

C4: The reactivity constant is not a standard, provide more detail on the rationale of its use. R4: Included in the methodology section 2.3.2

C5: Don't abbreviate MDS and provide unit. R5: Changed throughout the manuscript

C6: Would it be possible to define a very pure tephra sample as a standard? R6: Due to the large variation in the chemical composition of pure glass shards, as shown on the TAS diagram, it is difficult to use one standard with fixed dissolution parameters. However, we provide a clear framework based on their intrinsic Si:Al ratio (defined with EMPA) and dissolution characteristics to interpret the dissolution parameters of pure glass shards. Additionally, the heavy liquid separation was indeed performed to isolate glass shards from clays, nanocrystalline minerals and biogenic Si fractions, and to validate our proposed “typical” dissolution pattern obtained for fresh deposits (defined group 1 in the manuscript) depleted of such fractions. However, pre-treatment steps hampered straightforward interpretation.

C7 & R7: We agree that pretreatment need to be conducted with care, and suggest

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additional research focusing on delineating the exact effects and consequences for BSi determination.

C8: Fig 1, provide more info on TAS? R8: Additional information is provided in the figures captions. TAS is a standard way of classifying pyroclastic volcanic rocks based on non-genetic features, and commonly applied to classify tephra samples.

Additional changes based on the editor's suggestions:

C9: Alkaline extraction techniques are not the only used method to determine BSi. R9: We have included an overview of alternative methods.

C10: Presentation of results according to their origin (i.e. soil, peat or lake sediment). Do deposits represent the extreme in terms of percentage tephra in the samples. R10: We disagree as samples at the moment are ordered following a decreasing contribution of tephra, and increasing complexity of the samples composition. This corresponds with the observed patterns in dissolution properties and therefore makes it clearer for the reader to interpret the classification in three groups.

C11 Clarify to what extent heavy liquid separation aided this study? R11: Heavy liquid separation is used to obtain more 'pure' shard and diatom signatures for our more complex samples. These purified samples are used to validate the fraction modeling results of the continuous extraction. Our results indicate that purification was successful (single fraction left; section 3.2.2), but chemical pre-treatment during heavy liquid separation altered the dissolution properties. The heavy liquid separation does not provide additional quantitative information regarding the influence of tephra material on determinations of biogenic silica. As suggested, we have removed all such references. A good suggestion is made to construct an artificial sample series made of pure glass shard mixtures and BSi to optimize the suggested correction method (section 4.2.3). However one should be careful with chemical pre-treatment techniques as outlined in the manuscript.

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C12: Improve the presentation of the results. R12: We clarified the presentation of the results. The factor 2-5 compares 3-5h Na₂CO₃ and NaOH, not 20-24h Na₂CO₃ and NaOH. However, we indicated that also there we observe extreme differences (>10) for which we do not have a clear explanation.

C13: How might grain size influence the dissolution curves? R13: The method assumes complete dissolution of the biogenic Si fraction, this means SiAlk should be independent of grain size. However, our data indicates that for other contributors like volcanic glass incomplete dissolution leads to an apparent contribution to SiAlk measurements. Such partial dissolution depends on the reactive surface area, and therefore grain size. This probably partially explains the variation in k-factor for the slower fraction. It is, however, unlikely that grain size explains the whole range of dissolution parameters observed. Artificially reducing the grain size is likely to affect the contribution of non-biogenic SiAlk as grinding will enhance available reactive surface area. This needs to be avoided to exclude experimentally induced bias on the BSi estimate despite the probably improved comparability of the dissolution curves.

C14: Where does the Vedde Ash fit in? R14: Indeed, its weathered character (most probably of the basaltic component) led to the contribution of other non-biogenic Si fractions assumed to be the nanocrystalline weathering products (see figure 2, 3 and 5 for classification and section 4.2.3 for explanation).

C15: What is the detection limit of the alkaline extraction and what is the analytical uncertainty? R15: Detection limit depends on the method used, but for alkaline extraction values of 0.01 wt% SiO₂ are usually assumed to be the lower level of accuracy (i.e. soil studies). As shown in Table 2, the analytical uncertainty for tephra samples exceeds the detection limit. The within lab analytical uncertainty for pure biogenic samples and non-volcanic soil samples are normally very low (from negligible to 10%, Conley, 1998), but increase with the contribution of clays (see section 4.2.3 and also Barão et al. 2015. LOM). The incomplete dissolution after 3-5 hours in Na₂CO₃ probably explains the “higher” relative analytical uncertainty for our samples, and why they

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seem to decrease for the 20-24h set. For NaOH, the consistent agreement between measured alkaline extracted Si:Al ratios for shards and those based on the EMPA suggests accurate estimates. However we highlight the necessity to conduct an elaborate uncertainty analysis on the parameterization of the curve modeling in the concluding section.

C16: Correct value cited for Prokopenko et al. R16: Corrected

C17: The study was not really designed to infer implications for downcore variations in BSi content for paleorecords, or to detect the potential indirect effect of tephra deposition on diatom community and productivity in lakes. R17: We only partly agree with this comment. We understand the concern that our study design only allows to infer conclusions based on direct quantifiable effect of volcanic shard contribution, i.e. reconnaissance and significant contribution during alkaline extraction. We therefore reformulated (acknowledging previous recommendations) and reduced the discussion part concerning the indirect effect that tephra deposition might have on the diatom signature of lakes. We acknowledge that more studies are required to confirm the significance of the downcore effect of tephra contributions to BSi measurements in oligotrophic systems (the most sensitive systems). However, we believe that a simple comparison of the absolute contribution of volcanic shard and its weathering products with interpretable shifts in observed downcore variation in BSi gives already a clear indication of its potential consequences (first two paragraphs of section 4.3.2). Additionally, we would like to stress that although many authors have suggested this relationship; all have failed to quantify its effect. Therefore, we believe that our methodologically focused study provides new insights to what extent tephra deposition affects the interpretation of BSi records in paleo records. We believe this justifies the inclusion of section 4.3.2 in its reduced format in the final manuscript, and additionally included suggestions for future research to strengthen our findings.

Fig. 1 & Table 1 were updated, Fogo A is classified as a trachyte instead of dacite (see zip file attached).

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References: *Phd thesis: Lúcia Barão, 2015, Biogenic and non-biogenic Si pools in terrestrial ecosystems: results from a novel analysis method, University of Antwerp, Antwerp *Conley, D.: An interlaboratory comparison for the measurement of biogenic silica in sediments, MARINE CHEMISTRY, 63, 39-48, 1998. *Derry, L., Kurtz, A., Ziegler, K., and Chadwick, O.: Biological control of terrestrial silica cycling and export fluxes to watersheds, NATURE, 433, 728-731, 2005. *Meunier, J. D., Kirman, S., Strasberg, D., Nicolini, E., Delcher, E., and Keller, C.: The output and bio-cycling of Si in a tropical rain forest developed on young basalt flows (La Reunion Island), GEODERMA, 159, 431-439, 2010.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/12/C2340/2015/bgd-12-C2340-2015-supplement.zip>

Interactive comment on Biogeosciences Discuss., 12, 3505, 2015.

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