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Interactive comment on "Silicon isotope fractionation and uptake dynamics of three crop plants: laboratory studies with transient silicon concentrations" *by* Daniel A. Frick et al.

Daniel A. Frick et al.

dfrick@gfz-potsdam.de

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Dear Dr. Delvigne

We greatly appreciate your time which you took to review our manuscript.

The manuscript "Silicon isotope fractionation and uptake dynamics of three crop plants: laboratory studies with transient silicon concentrations" by Daniel Frick et al. brings out two important points: (a) Si isotope fractionations during plant uptake are similar no matter the Si is taken up actively or passively with water flux; (b) contrasted Si isotopes fractionations at the root-shoot interface reveal

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different plant Si accumulation strategies. Until now, this could only be speculated from data in the literature and for once it is clearly demonstrated. This conclusion is of great interest for the community and I'm convinced that this study will be really helpful for a large number of studies. Also, I would like to thank the authors for the high quality of their study at all steps. The experiment is well-designed and fit-for-purpose, the dataset is of high quality, the manuscript is very well written and easy to follow. It's a pleasure to read this work that is perfectly adapted to Biogeosciences. Overall, there is very little to suggest in terms of improvements but here are some minor comments.

Thank you very much for the validation of our work. It means a lot. In the following we are responding to your questions and recommended improvements in detail. We will supply the improved manuscript with track changes in the later process after the discussion has ended.

Title: I'm not sure that the term "transient" is the best one. To me, it's not appropriate but I'm not a native speaker. I would prefer something like "exhaustible" or "finite" . Also, I would have loved a title less technical to attract more readers but it's a safe choice.

We agree that the title is a very technical description of the paper – after some intense discussions we have come up with a shorter title for the manuscript which still grasps the essence of our work:

Silicon stable isotope fractionation and uptake dynamics of crop species

Material and methods: I agree with Reviewer 2 that it would be useful to add details on how transpiration was measured.

We have added the information in a revised version of the manuscript. The following amendments were made in section 2.3 regarding the details how we measured the transpiration:

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“*Each week the pots were weighted without the lid and the plants, and the mass of transpired water was replenished with ultrapure water (18.2 $M\Omega \cdot cm$). The weight difference to the previous week is considered the mass of water transpired by the plants. The pots were closed with a lid, and we thus neglect evaporation.*”

Additionally, we have also given our definition of transpiration in *ch.* 2.6.1:

“*We define the plant transpiration as the amount of water taken up by the plants and successively transferred into the atmosphere. The transpiration is measured weekly by weighing the pots without the lids and plants, the weight difference to the previous week is considered the mass of water transpired by the plants. The gravimetrically determined transpiration does not account for the amount of water present in the plants at harvest and the negligible amount of guttation* (Joachimsmeier et al., 2012).”

L89: Have you checked the Si solubility limit at 15C? No sign of polymerization?

We have not spectroscopically searched for absence of polymerisation in the nutrient solutions. The solubility for amorphous silica at 25 ° C is reported to be ∼ 116 µg/g (Gunnarsson and Arnórsson, 2000), using their reported temperature dependence the solubility of SiO2 at 15 ° C is ∼ 95 µg/g and for 18 ° C ∼ 101 µg/g. Our starting concentration is slightly above the solubility limit between 15-18 ° C (by 2-5 µg/g Si). We did however not observe a significant change in the silicon isotope composition during the early course of the experiments. We would expect this when a significant amount of silicic acid polymerises. We have made an amendment to section 4.1 to describe this concern:

“*The initial concentration of Si at the start of the experiment (49.5 µg/g) was slightly above the solubility limits of amorphous silica at 15-18 °C (44.2 – 47.1 µg/g), part of the silicon could thus also be lost to polymerisation and precipitation.*”

Section 2.5.1 and 2.5.3. Why don’t you analyse Si isotopes of nutrient solutions directly after a cationic purification? The content of anions is too high? As

salts are not detailed in section 2.1 it's not obvious what could compromise the analysis. It's worth mentioning what you feared with these samples. I guess you did not choose the easy way for a reason.

We have followed the procedure of (Steinhoefel et al., 2017) due to two concerns: the possible interference of the organic content which could be excreted by the roots and the relative high content anions. High temperature NaOH fusion is our 'go-to-method' and we have not evaluated a direct cationic purification. We have rephrased this: see below for the improved passage.

L126: It might be useful to rephrase this sentence that is a bit confusing. I had to read the sentence a few times to understand that the important thing is the amount of NaOH/g Si and not the molarity of the solution. It's worth explaining why you add a solution and not a powder directly as for solid samples. I guess it's to recover Si left on the crucible sides.

Well observed, this is exactly the reason we use a solution of NaOH instead of the pellets/powder. We have rephrased this: see below for the improved passage.

Have you tried this protocol with dissolved references like a solution of BHVO-2? There are so many different protocols for solution with a complex matrix that a quality check is useful. Alternatively, it is worth mentioning that your protocol is equivalent to the one of Steinhoefel et al 2017 (excluding the destruction of DOC) as you both use 1mmol of NaOH / 100g Si (if my calculations are correct).

Throughout the NaOH fusion and chromatographic separation we have used BHVO-2 and ERM-CD281 as a quality control. However, for the drying step we could not find an appropriate reference sample in liquid form which could act as an independent control (dissolved but unpurified BHVO-2 would contain already a large amount of Na due to the fusion). We have however taken some measures to assure that the drying is not affecting the silicon isotope composition:

- We controlled the yield based on the amounts we dried down and the concentration measured after the NaOH fusion to assure no loss or gain.
- The overall blank levels were contributing less than 1% to the total amount of Si processed.

The passage 2.5.1 reads now:

"*The relative complex matrix (high nutrient content and organic acids) could interfere with the chromatographic purification of Si, thus the nutrient solution was digested following the "Sample preparation of water samples" by Steinhoefel et al., 2017 without the additional dissolved organic removal step. Briefly, based on the concentration measured, an aliquot of each nutrient solution containing approximately 1000 µg Si was dried down in silver crucibles on a hotplate at 80-95 ° C. The crucibles were then filled with 400 mg NaOH (Merck pellets, p.a. grade, previously checked for low Si blank levels) and ultrapure water to the initial fill level and dried down. This step ensured that Si adhered to the crucible walls was also covered with NaOH. A blank containing ultrapure water and NaOH was processed together with the samples to check for contaminations.*"

L 150: It would be useful to add some references (e.g., Savage et al., 2014 for BHVO-2 and Delvigne et al., 2019 for ERM-CD281) Camille Delvigne, Abel Guihou, Jan A. Schuessler, Paul Savage, Sebastian Fischer, Jade E. Hatton, Kate R. Hendry, Germain Bayon, Emmanuel Ponzevera, Bastian Georg, Alisson Akerman, Oleg Pokrovsky, Frank Poitrasson, Jean-Dominique Meunier, and Isabelle Basile-Doelsch (2019). An inter-comparison exercise of the Si isotope composition of soils and plant reference materials. Geophysical Research Abstracts, Vol. 21, EGU2019-18488, 2019.

I'm hesitant to cite a single selected publication for BHVO-2 since more than 27 publications (to my knowledge) have helped to characterise BHVO-2 for its silicon isotope composition, I have thus opted for the GeoReM database. Regarding ERMC-CD281, I am happy to include the tremendous effort you and your colleagues made to characterise plants and soils for their silicon isotope composition and cite your EGU abstract as a reference:

"*ERM-CD281 resulted in δ^{30}Si = 0.34 ± 0.20 ‰ 2s, n=13 and BHVO-2 in δ^{30}Si = -0.29 ± 0.09 ‰ 2s, n=40, in line with literature values (Jochum et al., 2005 for BHVO-2 and Delvigne et al., 2019 for ERM-CD281).*"

L338: It is hard to find its way with all these data as you mix 30/28 and 29/28. It would be less confusing for the reader if you stick only to 30/28 fractionation factors and just specify when it is recalculated from 29/28. Also, it may be useful to remind here your own 30/28 fractionation factors to directly see that your data are within the literature range. It's also worth mentioning that all species in your list are Si accumulators.

We agree that it is a very crowed section, we have taken your advice and only report 30/28 and indicate where we re-calculate the fractionation factor from a reported 29/28 ratio. Thank you also for pointing this out that we have likely measured the first Si fractionation factors for non-accumulating Si species, we have added this information:

"*Our new Si fractionation factors (tomato 0.33 ‰ and mustard 0.55 ‰ are the first to be reported for non Si accumulator plants and together with wheat (0.43 ‰ are similar to those measured in other Si accumulator species, including rice, 0.30 ‰ (Sun et al., 2008), -1.02 ± 0.33 ‰ * (* indicates results recalculated from $^{29/28}$Si to $^{30/28}$Si, Ding et al., 2005) and -0.79 ± 0.07 (Sun et al., 2016), banana, -0.77 ± 0.21 ‰ * (Opfergelt et al., 2006) and -0.68 ‰ * (Delvigne et al., 2009), and corn and wheat, -1.00 ± 0.31 ‰ * (Ziegler et al., 2005).*"

L384-392: The link with the previous section is a bit poor. It's too bad to end the discussion with a weak paragraph:

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We shortened this paragraph and tried to better link it to the discussion before:

"*This implies that Si which is liberated through weathering reactions, may be recycled multiple times through plants, re-dissolved into soil solution and precipitated into secondary minerals before being exported from the ecosystem. Based on plant and phytolith data aggregated by Frings et al., 2016 biogenic silica is unlikely one of the main export flux of Si from the ecosystems. Plants are thus an important factor for the internal ecosystem element cycling (Uhlig and von Blanckenburg, 2019), but not for the particulate Si export. The plant internal processes which distribute, and deposit Si have however, influence on the amounts and chemical form of Si which is cycled through the ecosystem, and these processes can be traced using stable isotopes to identify the mechanism.*"

L 394: It would be more careful with the "species-specific" term as your study demonstrates that your fractionation factors are rather similar despite your 3 plants have very different Si strategies. This might be confusing and sounds contradictory.

This is true and was not the intended meaning of species-specific. We have rephrased the sentence and hope this is now clearer:

"*We have confirmed that the amount of Si uptake into crop plants and the distribution within is species-specific and complex, involving uptake mechanism in varying proportions. However, regardless of the uptake strategy (active and rejective) all three crop species preferentially incorporate light silicon (^{28}Si) with a fractionation factor $1000 \cdot \ln(\alpha)$ for tomato 0.33 ‰ for mustard 0.55 ‰ and for wheat 0.43 ‰ . Within uncertainty, the fractionation factors between these species are indistinguishable.*"

We hope that these answers clarify your questions and thank-you for helping with the improvement of this manuscript.

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Best regards on behalf of all my co-authors,
Daniel A. Frick

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