Reviewer 1:

Review of manuscript egusphere-2025-78 submitted to EGUsphere by Sofía López-Urzúa and colleagues: Quantifying the agricultural footprint on the silicon cycle: Insights from silicon isotopes and Ge/Si ratios

With apologies to the authors and editor for this late review.

López-Urzúa and colleagues present the results of a comprehensive Si (isotope) budget for a small agricultural budget in France. Using different mass-balance approaches to quantify the amount of Si exported from the catchment in harvested crops, they find that it exceeds by a large amount the export of dissolved Si in streamwater, providing a demonstration of anthropogenic impacts on catchment Si cycling.

In general, I find this a solid manuscript worthy of publication after minor revisions. It is well written with clear figures and appropriate referencing, and deals with a topic that I think will be interesting to many in the community. The methods used are appropriate and the data seem of good quality. I have some suggestions or questions the authors may wish to consider in a revised version of the manuscript, that I detail in rough order of appearance.

Response: We thank Reviewer 1 for their thoughtful and constructive review. We greatly appreciate this recognition of the manuscript's overall quality, and we welcome the opportunity to improve our work further.

The two main concerns raised were:

- Inconsistencies across the manuscript regarding the assumption of congruent versus incongruent dissolution.
- The assumption that all primary minerals share the same Si isotope and Ge/Si signatures.

To address these points, we have revised the manuscript to consistently assume incongruent bedrock dissolution, considering quartz as inert. This change required correcting the Si isotope composition (δ^{30}Si) and Ge/Si ratio of the initial solution after mineral dissolution, which in turn necessitated the use of mineral-specific signatures. Because the bedrock in our catchment consists of fine-grained siltstone, it was not possible to physically separate and analyze individual minerals to determine their specific signatures. Therefore, we compiled a mineral-specific dataset of δ^{30}Si and Ge/Si values from the literature, that will be included in the Supplementary Material. These mineral-specific signatures were also used to correct the signatures of secondary clays minerals in the clay-sized fraction and were consistently applied throughout both the elemental and isotopic mass balance calculations. To assess the impact of estimates of mineral-specific isotope signatures on our flux calculations, we conducted a sensitivity analysis, that will be included in the appendix.

The revised results show that, although we now obtain a slightly lower fraction of Si exported via harvesting using the isotope-based mass balance model and a similar one using the regolith-based mass balance model , our main conclusion remains unchanged: Si export through crop harvesting continues to be an important flux—exceeding the dissolved Si flux and comparable to the erosion flux—underscoring the strong anthropogenic imprint on the silicon cycle in agricultural catchments.

Below, we provide point-by-point responses to the reviewer's detailed comments and clarify our methodology and interpretations accordingly.

Perhaps the weakest part of the dataset – as acknowledged by the authors (e.g. around L595) is the small number of total plant and clay samples, and that they are limited to only the leaves and not the full plant biomass. Much of the data interpretation relies on the plant and clay Si isotope fractionations/differences between fractionations for the difference species, but I feel these are not so well constrained. If there is the possibility to provide more data here this would greatly help strengthen the paper.

Response: We appreciate the reviewer's thoughtful comment and fully acknowledge the limitations of our dataset, particularly the small number of leaf (n = 4) and clay (n = 2) samples, as noted in the manuscript. Despite these constraints, we have taken several measures to integrate uncertainty and ensure our interpretations remain robust, particularly with regard to plant Si isotope signatures.

- Using Method 1 (section 5.2: Determining Si export from the catchment as biomass using an isotopic mass balance of Ge/Si and δ³⁰Si: e_{org}^{Si}), we implemented a conservative approach in Scenario 1 by applying a uniform distribution across the full range of measured plant δ³⁰Si values (−0.40‰ to +0.83‰) as an input for our Monte Carlo estimates of uncertainty. This ensures that the modeled outcomes reflect the full range of natural variability observed in our dataset.
- Using Method 3 (section 5.5: quantifying Si export through harvesting using Si loss indexes and isotopic fractionation: $h_{regolith}^{Si}$), we calculated the isotopic fractionation for each type of leaf sample. These are consistent with published values in literature. To incorporate uncertainty, we again applied a uniform distribution, assigning equal probability to the full range of observed fractionation values among species.

While our analysis includes only two maize and two wheat samples, these represent the dominant crops grown in the catchment. Moreover, Si isotopic fractionation is more strongly influenced by plant functional type than by intraspecific variability (Frick et al., 2020). Thus, we believe the selected species capture the relevant functional variability for the purpose of this study.

Regarding the clay samples, we analyzed two samples from contrasting soil conditions—one from a hydromorphic soil and one from a well-drained soil. Both exhibited very similar δ³⁰Si signatures, suggesting that the isotopic composition of secondary clays remains relatively consistent across variable soil environments in the studied catchment. This observation supports our use of a representative value for clays contributing to the erosion flux.

We agree that expanding the dataset—especially with more comprehensive plant and soil sampling—would further strengthen our conclusions. Nonetheless, we are confident that our conservative modeling strategy, use of scenario testing, and reliance on published values for comparison provide robust and defensible constraints on Si isotope behavior and fluxes in this catchment. In the revised manuscript, we will include a brief discussion before introducing the scenarios to clarify that the modeled outcomes capture the full range of natural variability observed in our dataset.

Related – in some cases the uncertainty propagation seems unrealistically small, in particular for the clay fractionation (Table 4 gives it as ±0.07‰; presumably 1sd?), but I can't make this fit with the data from table 1. Also, an uncertainty of only 0.01‰ is used for the secondary clay itself, but this is after a series of corrections for the 'contamination' of the clay size fraction with primary minerals. How is it possible that this correction process (detailed in appendix B) results in a narrower uncertainty? And is it justifiable that a single clay sample taken at ca. 60cm depth (Fig. 2) is representative of the clay that will eventually be eroded?

Response: We thank the reviewer for pointing out the issue with the uncertainty propagation in Table 4. There was an error in the original calculation. As pointed out earlier, in the revised manuscript we will apply mineral-specific signatures to correct the clay-sized fraction from the contribution of primary minerals, which will result in the updated values in Table 4. Additionally, to better capture uncertainty in this correction process, we revised our approach as follows:

- We first estimated the mineralogical composition of the clay-sized fraction through a mixing model and implemented a Monte Carlo simulation to propagate uncertainties. We assumed normal distributions for Si, Al, and K concentrations with a standard deviation of 5%, consistent with the long-term analytical precision of elemental analysis (<5%).
- We then corrected Si and Al concentrations to account for kaolinite contributions through Gaussian uncertainty propagation.

- Finally, for δ³⁰Si and Ge/Si ratio corrections, we performed a second Monte Carlo simulation using mineral-specific δ³⁰Si and Ge/Si values compiled from the literature for primary minerals (quartz, muscovite, and microcline). This updated procedure significantly larger and more realistic uncertainties (e.g., ±0.17‰ for δ³⁰Si and ±0.74 for Ge/Si) compared to the previously underestimated ±0.04‰:

Sample	δ^{30}Si (‰)	Ge/Si (µmol mol-1)
240 clay	-1.20 ± 0.16	4.78 ± 0.41
288 clay	-1.25 ± 0.17	8.31 ± 0.74

Regarding Table 1, the previously reported uncertainty of ±0.01‰ for secondary values is now updated to ±0.04‰. This uncertainty corresponds to the standard deviation of the mean calculated from the two corrected δ³⁰Si values (−1.20 ± 0.16‰ and −1.25 ± 0.17‰) but it does not incorporate the uncertainties from the correction procedures applied in Appendix B. To avoid confusion, we have added a footnote in Table 1 to clarify that the reported uncertainty represents the descriptive variation (mean ± SD) between corrected values, not the total analytical or propagated uncertainty used in modeling.

Concerning the representativeness of the clay sample taken at ~60 cm depth: we analyzed two clay samples from contrasting pedological conditions—one from a hydromorphic soil and one from a well-drained soil. Both yielded very similar δ³⁰Si values, suggesting minimal isotopic variation in secondary clays across soil types and depths. Moreover, the mineralogical and geochemical profiles of the sampled soils are relatively homogeneous, supporting the assumption that these clays are representative of those being mobilized via erosion from more superficial horizons. While we agree that expanding the dataset would be ideal, we are confident that the revised methodology and expanded uncertainty analysis now provide a more accurate and defensible treatment of the clay corrections and their influence on the mass balance model.

The mass-balances approaches detailed here explicitly or implicitly require steady-state, but I wonder how justifiable that is for this heavily anthropgenised catchment. E.g. the Clymans et al. reference that is cited details how the soil pools of Si change over decadal to centennial tiemscales in response to land cover change. This is a bit of an easy criticism to make but perhaps some discussion on how transient increases or decreases in the size of internal soil pools of Si (phytoliths, amorphous Si, clays, …) might impact the interpretation would be warranted?

Response: Thank you for raising this point. We acknowledge that strict steady-state conditions may not always hold, particularly in a catchment with significant anthropogenic influence. Transient changes in soil Si reservoirs —such as phytoliths, amorphous silica, and clays—could indeed influence short-term mass-balance interpretations. However, we argue that a quasi-steady-state framework is appropriate for our study for several reasons:

1) Temporal integration and isotopic consistency of dissolved Si export across multi-year time scales: Our silicon isotope dataset spans multiple hydrological years and seasons (2015, 2017, 2021, 2022, 2023; see Zenodo dataset). Despite differences in sampling time and discharge conditions, δ³⁰Si values in soil solution, groundwater, and river water remain consistent in both absolute values and isotopic trends. This temporal coherence indicates that our estimates of the Si element and isotope dissolved efflux averages over short-term (i.e., seasonal and inter-annual) represents a steady state. Our reasoning aligns with that of Bouchez et al. (2013), who argue that time-integrated datasets (e.g., sediment depth profiles, multi-year average fluxes) provide a solid basis for applying a quasi-steady-state assumption.
2) Long-term (multi-decadal) changes in Si content and isotope composition in secondary phases: Over long time scales, the additional removal of Si through harvesting will likely progressively deplete all "solid" compartments of the Critical Zone in Si, in particular in the lightest Si isotopes. As a result, today's soil solutions are isotopically heavier than in the past. However, solid phases such as clay minerals and organic matter formed partly under pre-agriculture conditions still retain an "inherited", lighter isotopic composition. Consequently, clay minerals sampled today as a whole integrate inherited Si isotope composition that is lighter than what would be expected if they had formed solely from present-day water-rock

interactions. A similar reasoning might apply to soil organic matter. Note that it does not apply to the plant pool, which in this environment is harvested yearly, leaving the possibility for this pool to “reset” its isotopic composition as time passes and as water itself evolves. If this legacy effect were fully corrected for (i.e., if solids were in equilibrium with today’s heavier waters), the isotopic signature of soil solutions would likely be even heavier, further reinforcing our conclusion that harvesting is a major driver of light Si isotope export.

In light of these points, we recognize that the system may not be in perfect steady state, but we consider a quasi-steady-state approach both justifiable and robust for our mass-balance interpretation. In the revised manuscript, we will include a brief discussion before Section 5.2 to explicitly acknowledge these limitations and clarify the assumptions underlying our approach.

Regarding the vertical gradients in [Si] and d30Si, there doesn’t seem to be much discussion of a simple mixing between Si-deplete rainwater and Si-rich ‘weathering’ water. Could this be part of the interpretation?

Response: While mixing between Si-depleted rainwater and Si-rich weathering-derived water could explain some of the vertical gradients in [Si], it cannot fully account for the observed δ^{30}Si signatures. To our knowledge, no silicon isotope values for rainwater have been reported in this region. If mixing were the dominant process, it would require rainwater to have a significantly heavier δ^{30}Si signature to explain the enrichment in soil solutions. Instead, the observed δ^{30}Si enrichment is best explained by biological processes, particularly plant uptake and subsequent harvesting, which preferentially remove lighter Si isotopes from the system. We will add a sentence in the manuscript to clearly explain that rain water cannot be a significant Si input to the soil system and thus cannot contribute to the establishment of the Si concentration and isotope composition profiles.

The authors assume that the bedrock is dissolving congruently (e.g. L311, but somewhat contradicted on L541), and that all primary minerals have the same Si isotope signature (e.g. Appendix B, L682). But how justifiable are these assumptions? A growing body of work demonstrates that minerals have specific d30Si signatures. Probably of minor importance here, but perhaps worth considering.

Response: Thank you for highlighting this important point. As noted earlier, we acknowledge an inconsistency in our original approach. In Section 5.1 (L311), we initially assumed congruent bedrock dissolution—i.e., that the water released reflects the bulk rock Si/Al ratio (7.54), δ^{30}Si (-0.13 ± 0.05‰), and Ge/Si ratio (1.33 µmol mol^{-1}). However, in our calculation of $h_{regolith}^{Si}$ we treated quartz as inert, implying incongruent dissolution.

To address this, we revised the manuscript to consistently reflect incongruent bedrock dissolution, assuming that only muscovite, albite, and chamosite actively dissolve. We also now consider mineral-specific δ^{30}Si and Ge/Si signatures, based on a literature compilation:

Mineral	**δ^{30}Si (‰)**	**Comments**	**Ge/Si (µmol mol^{-1})**	**comments**
Quartz	-0.06 ± 0.10 n=11	Mean of data heavier than -0.13 (bedrock)	0.72 ± 0.30 n=5	Mean of all quartz values
Microcline and albite	-0.29 ± 0.14 n=17	Mean for feldspars and plagioclase	2.55 ± 0.77 n=8	Mean for feldspars and plagioclase
Muscovite	-0.49 ± 0.11	Estimated as mean between biotite and feldspar	2.13 ± 0.21 n=3	Mean of available values
Chamosite	-0.68 ± 0.18 n=6	Estimated using biotite values	4.55 ± 1.24 n= 6	Estimated using biotite values

For δ^{30}Si, we selected only quartz data with heavier values than the bedrock average (–0.13 ± 0.05‰), since including lighter quartz values would not reproduce the bulk bedrock signature, given that other minerals exhibit even lower δ^{30}Si. This “filtered” literature compilation yielded a quartz δ^{30}Si of –0.06 ± 0.10‰. For microcline and albite, we adopted the average value reported for feldspars and plagioclases (–0.29 ± 0.14‰). For chamosite, a member of the chlorite group, we used values from biotite (–0.68 ± 0.18‰), and for muscovite, where direct data are lacking, we applied the average between biotite and feldspar (–0.49 ± 0.11‰), based on known trends relating δ^{30}Si fractionation to polymerization (Douthitt, 1982; Savage et al., 2014) and interlayer cation effects (Méheut et al., 2009; Méheut and Schauble, 2014).

For Ge/Si ratios, we used 0.72 ± 0.30 μmol mol^{-1} for quartz, 2.55 ± 0.77 μmol mol^{-1} for albite and microcline, 2.13 ± 0.21 μmol mol^{-1} for muscovite, and 4.55 ± 1.24 μmol mol^{-1} for chamosite.

We acknowledge that there are uncertainties in the mineral-specific δ^{30}Si and Ge/Si values, and that we rely on literature data compiled from other sites. However, this is currently the best approach available, as we only have one bulk bedrock sample and mineral-specific data are scarce. These kinds of assumptions are common in geochemical modeling, and we have taken care to test that our main outcomes are not overly sensitive to these choices.

Using these revised values, we recalculated the composition of the dissolving fluid, obtaining a Si/Al = 1.8, δ^{30}Si = –0.44 ± 0.08‰ and Ge/Si = 2.8 μmol mol^{-1}. These corrections do not affect the main trends or interpretations of our δ^{30}Si and Ge/Si dynamics in the catchment.

There are three different approaches applied here: 1) a d30Si+Ge/Si mass balance, 2) a mass balance based on river Si fluxes, and 3) a mass balance based on soil geochemistry. Although they are designed to predict slightly different aspects of Si export, I was surprised not to see a more explicit comparison (e.g. in a table or a figure).

Response: We appreciate the reviewer's suggestion to more explicitly compare the three different approaches used to estimate Si export. We agree that a clearer side-by-side comparison would strengthen the manuscript. To address this, we will move Tables 2 and 5 to the appendix and include a new summary table in the main text that directly compares the estimates from all three approaches.

The fractional export value for e_Si in approach 2 (stream water + sediment based) is 0.36 (L498). As far as I understand, this includes E_org, E_sec and E_prim - but is this inconsistent with a bedrock dominated by quartz? (which they assume elsewhere to be inert, e.g. 541 – if quartz is not dissolving then a minimum value for e_Si would be the quartz fraction of the bedrock)

Response: We thank the reviewer for this thoughtful observation. It is correct that if quartz is assumed to be inert, the minimum theoretical value for e_{river}^{Si} should reflect the quartz fraction of the bedrock. Given that quartz comprises approximately 62% of the bedrock, this suggests a lower bound for e_{river}^{Si} around 0.62.

The lower value we obtained (0.36) using the stream water + sediment approach likely reflects methodological limitations. Our "gauging" estimate is based on turbidity-derived suspended sediment concentrations, which primarily capture the fine sediment fraction. Coarse and dense minerals such as quartz are more likely to be transported as bedload and are thus underrepresented in turbidity-based estimates. This grain-size bias in suspended sediment sampling has been well documented (Bouchez et al., 2011; Lupker et al., 2012). In addition, it is also possible that some portion of the quartz is retained within the soil profile. Quartz is resistant to weathering and may accumulate over time in the regolith, particularly if it is not being mobilized either in dissolved form or as suspended or bedload particles. This would further reduce the fraction of Si exported via the river system, relative to the bulk rock composition.

As a result, this part of our methodology likely underestimates the total solid-phase Si export from primary minerals. However, even assuming a more conservative value of e_{river}^{Si} = 0.62—matching the quartz fraction of the bedrock—the amount of Si exported via harvesting (h_{river}^{Si}) remains larger than the dissolved Si flux, supporting our conclusion that agricultural harvesting is a major component of Si export in the system. We will include a discussion of this issue and the associated references in the revised manuscript.

Minor comments:

L56: Either more recent revisions of the Si budget (e.g. Treguer et al) and/or the 'original' river Si flux estimates (e.g. Dürr et al/Beusen et al) might be appropriate here.

Response: Thank you for the suggestion. We have added Dürr et al. (2011) and Beusen et al. (2009) for the values of dissolved Si (6.2 ± 1.8 Tmol Si yr-1), Frings et al. (2016) for the values of dissolvable amorphous silica (1.9 ± 1.0 Tmol Si yr-1), and Tréguer et al. (2021) for the most recent review. Additionally, we have removed the reference to groundwater to better align with the cited studies.

L84: To avoid overstating the novelty of this contribution, maybe already mention here that some previous work has identified that plant biomass as a whole doesn't seem to discriminate against Ge as much as the phytolith-based estimates cited here would suggest.

Response: We have modified the text to acknowledge this broader perspective "While some studies suggest that Ge is discriminated against Si during vascular plant uptake (Blecker et al., 2007; Delvigne et al., 2009; Derry et al., 2005; Lugolobi et al., 2010; Meek et al., 2016), other research indicates that plant biomass as a whole does not exhibit as strong a discrimination (Delvigne et al., 2009; Frings et al., 2021; Kaiser et al., 2020; Rains et al., 2006; Sparks et al., 2011)".

L158: if the bedrock comprises bedding of different lithologies, is this one sample enough to capture the heterogeneity? Even in plutonic rocks variability in 'immobile' element content can be large (which becomes important for e.g. the mass-balances and the 'tau' values later).

Response: We acknowledge that relying on a single bedrock sample is not ideal for capturing potential lithological heterogeneity. To address this limitation, we incorporated data from Denis and Dabard (1988), who compiled chemical analyses (n = 9) from the same geological unit that underlies our study basin. These samples, collected along a transect approximately 32 km southeast of our site, report TiO_2 concentrations with a mean of 0.71 ± 0.19 wt.% (SD), which closely matches the TiO_2 concentration measured in our own bedrock sample (0.74 ± 0.04 wt.%).

To better account for both natural variability and analytical uncertainty in the bedrock Ti concentration, we implemented a Monte Carlo simulation when calculating τ_{prim}, e_{sec}^{Si} and e_{org}^{Si}. Specifically, we modeled the Ti concentration in the bedrock as a normal distribution with a mean of 0.74 wt.% and a standard deviation of 0.19 wt.%, reflecting the variability reported by Denis and Dabard (1988). For soil samples, we assumed a 5% relative uncertainty in Ti concentration. This approach integrates both measurement uncertainty and spatial heterogeneity in schist bedrock, thereby improving the robustness of our mass-balance calculations.

Importantly, despite this more rigorous treatment of uncertainty, the resulting values are nearly identical to those previously reported. This is because τ_{prim}, e_{sec}^{Si} and e_{org}^{Si} in Eq. 10 were already calculated using the mean values across all soil profile samples, which inherently incorporate substantial natural variability, some of it being most likely the result of variability in bedrock composition. The original values were τ_{prim} = –0.42 ± 0.15, e_{sec}^{Si} = 0.088 ± 0.042, and e_{org}^{Si} = 0.0064 ± 0.0033, while the updated Monte Carlo-derived estimates are τ_{prim} = –0.42 ± 0.15, e_{sec}^{Si} = 0.088 ± 0.043, and e_{org}^{Si} = 0.0065 ± 0.0035. These consistent results lend support to the robustness of our initial estimates and demonstrate that the updated method supports the same conclusions, while providing a more comprehensive representation of uncertainty.

L180: What is precision/long term reproducibility on the elemental data? Were any secondary reference materials included in the analyses?

Response: Yes, the river water standard SLRS-5 (National Research Council, Canada) was systematically analyzed, with a long-term analytical precision of better than 5%. This will be added in the method section

Fig 2: presumably cmbs on the y-axis, not mbs. Greek letter mu (not u) on Ge/Si x-axis.

Response: Thank you for pointing out this error. In the new manuscript we have corrected “mbs” to “cm b.s.” on the y-axis and replaced “umol mol^{-1}” with “µmol mol^{-1}” on the Ge/Si x-axis.

L286: “compared”

Response: Thank you for pointing out this error. In the new manuscript we will correct this mistake.

345: ‘show a positive correlation’ / ‘are positively correlated’

Response: Thank you for pointing out this error. In the new manuscript we will correct this mistake.

L415 – also Baronas et al 2020 GBC would be appropriate to cite here?

Response: Thank you for the suggestion. We have added Baronas et al. (2020) to acknowledge their findings that a significant portion of Si is taken up by vegetation fbioSi = 39 ± 14%, which aligns with the range reported by Frings et al. (2021). “These contributions are also higher than those observed in four other non-agricultural catchments, where $e_{org-iso}^{Si}$ ranged from 0.20 ± 0.1 to 0.42 ± 0.23 (Baronas et al., 2020; Frings et al., 2021).”

L483 – actually relatively high?

Response: We are not sure what the reviewer is referring to here — is it that the fraction of Si exported in the dissolved form (0.12 ± 0.06) is high compared to the value determined by the isotopic mass balance? If so, we underline that the isotopic mass balance approach yields values ranging from 0.15 ± 0.08 to 0.22 ± 0.11, which are within the uncertainties of the value obtained by the gauging method. Assuming this is what the reviewer is suggesting, we will add: “The mean fraction of Si exported from the catchment in the dissolved form is 0.12 ± 0.06, which is consistent with the values calculated using the isotopic mass balance when considering their respective uncertainties (0.15 ± 0.08 to 0.22 ± 0.11).”

L519: eSi_sec repeated here – presumably should be eSi_org?

Response: Thank you for catching this error. We have corrected e_{sec}^{Si} to e_{org}^{Si} in the revised manuscript.

L520: If this is a schist bedrock, how variable is the Ti content, and how are uncertainties propagated?

Response: We thank the reviewer for this related comment. As discussed in our response to Comment L158, we addressed the potential variability in Ti content within schist bedrock by incorporating external geochemical data from Denis and Dabard (1988), who reported TiO_2 concentrations (n = 9) with a mean of 0.71 ± 0.19 wt.% in the same geological unit underlying our study site. This variability was integrated into our calculations through a Monte Carlo simulation that models Ti concentration in the bedrock as a normal distribution (mean = 0.74 wt.%, SD = 0.19 wt.%) and includes a 5% relative uncertainty for the soil Ti concentrations. This framework allowed us to propagate uncertainties in Ti through all downstream calculations of τ_{prim}, e_{sec}^{Si} and e_{org}^{Si}, ultimately providing a more comprehensive assessment of uncertainty. As noted previously, this improved treatment does not significantly change the final estimates, reinforcing the robustness of our original results.

L530: What is the justification for using stream water rather than soil solutions to define e_prec?

Response: We chose to use stream water rather than soil solutions because it integrates contributions from the entire catchment, providing a more representative estimate of ε_{prec}^{Si} at the catchment scale rather than reflecting localized variations. We will add a sentence justifying this choice.

L544: “to be inert”

Response: Thank you for correcting this error.

L567: Why are these values so low compared to previous two estimates?

Response: First, we would like to clarify that the values e_{org}^{Si} and $e_{org-iso}^{Si}$do not represent the same quantity. The term $e_{org-iso}^{Si}$ refers to the fraction of silicon that is both eroded naturally and exported through harvesting. In contrast, term e_{org}^{Si} specifically represents the silicon associated with soil organic matter—i.e., the phytoliths that remain in the soil after harvesting. This distinction, which stems from the way the different mass balance equations are set up, explains why the value of e_{org}^{Si} is lower than that of $e_{org-iso}^{Si}$.In the revised manuscript, we will rename e_{org}^{Si} to make this distinction clearer and include a sentence to explicitly state the difference between the two terms.

Regarding $e_{clay-iso}^{Si}$ and e_{sec}^{Si}, these metrics are intended to represent the same process but determined with different approaches. In particular, estimating e_{sec}^{Si} based on elemental metrics (eq. 15) is particularly challenging due to the complexity and spatial heterogeneity of soil processes. For instance, the preferential erosion of fine-grained, clay-rich material can remove a significant portion of the secondary Si pool from the soil. As e_{sec}^{Si} is calculated using $[Si]_{sec}$, reflecting the amount of soil Si contained in secondary minerals, any Si loss by clay erosion leads to an underestimation of $[Si]_{sec}$. Consequently, the resulting e_{sec}^{Si} value is biased toward lower estimated. We will include a discussion about these potential issues, acknowledging in particular that an ideal approach would require a more detailed characterization of the soil profiles and mineralogy.

L595: fractionation factors are not ‘heavy’ or ‘light’; better to talk about magnitude. In general, fractionation factor normally refers to so-called ‘alpha’ notation, and just ‘fractionation’ alone to ‘epsilon’ notation – see Coplen 2011 DOI: 10.1002/rcm.5129.

Response: Thank you for providing clarification on the use of fractionation factor for alpha notation and isotopic fractionation for the epsilon notation. We have corrected to talk about the magnitude of the isotopic fractionation. Additionally, we have revised the sections 5.5.1 and 5.5.4 replacing the “fractionation factor” by “isotopic fractionation”.

L634: See also Vandervenne et al 2013 Proc Royal Soc B.

Response: Thank you for the suggestion. We have now included Vandevenne et al. (2013) as a reference to highlight the role of grazing animals in accelerating the return of biogenic Si to the soil and enhancing its reactivity and dissolvability.

L708: Does the very low number of acceptable iterations (e.g. 0.2% for scenario 2) simply imply that an assumption underpinning the mass-balance or endmember assignments is incorrect?

Response: Thank you for your thoughtful comment. You are correct that the very low number of acceptable iterations in Scenario 2 (e.g., 0.2%) originally suggested a potential issue with our mass-balance assumptions or endmember assignments. In our initial approach, we assumed congruent dissolution of the bedrock. We have now revised the model to consistently reflect incongruent dissolution, assuming that only muscovite, albite, and chamosite actively contribute to weathering. This update includes the use of mineral-specific $\delta^{30}Si$ and Ge/Si signatures based on a literature compilation.

As a result, the $\delta^{30}Si$ value assigned to the dissolving rock has changed significantly, leading to a much higher number of valid iterations across all scenarios. Previously, out of 6 million iterations, only 78,658 were valid for Scenario 1, 13,524 for Scenario 2, and 1,541,432 for Scenario 3. In the revised model, approximately 590,000 iterations are now valid for Scenario 1, 464,000 for Scenario 2, and 1,603,000 for Scenario 3. These improvements result in a more robust and internally consistent set of model outputs, indicating that mass balance is “more likely” to be achieved using these updated values for the solution produced by rock dissolution

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