Peer Review File

Two-stage oxidation of petrogenic organic carbon in a rapidly exhuming small mountainous catchment

Corresponding Author: Professor Li-Hung Lin

This file contains all editorial decision letters in order by version, followed by all author rebuttals in order by version.

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Decision Letter:

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Dear Professor Lin,

Your manuscript titled "Two-stage oxidation of petrogenic organic carbon in a rapidly exhuming small mountainous catchment" has now been seen by 3 reviewers, and we include their comments at the end of this message. They find your work of interest, but some important points are raised. We are interested in the possibility of publishing your study in Communications Earth & Environment, but would like to consider your responses to these concerns and assess a revised manuscript before we make a final decision on publication.

We therefore invite you to revise and resubmit your manuscript, along with a point-by-point response that takes into account the points raised. Please highlight all changes in the manuscript text file.

We also request that you move some of the information from the main text into the methods and supplement because, currently, the manuscript is too long (see article guidelines), and the reviewers also request additional information on your methods and approach, which will require additional space.

Please submit your point-by-point responses as a separate file, distinct from your cover letter where you can add responses to the Editors' comments that you do not want to be made available to the reviewers. Word files are preferred.

Important: The response to reviewers must not include any figures, tables or graphs. If you wish to respond to the reviewer reports with additional data in one of these formats, please add them to the main article or Supplementary Information, and refer to them in the rebuttal. Due to current technical limitations, any figures, tables, or graphs embedded in your rebuttal will not be included in the peer review file, if published.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

Please use the following link to submit your revised manuscript, point-by-point response to the referees' comments (which should be in a separate document to any cover letter), a tracked-changes version of the manuscript (as a PDF file) and the completed checklist:
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We hope to receive your revised paper within six weeks; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we may close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Earth & Environment or published elsewhere in the meantime.

Please do not hesitate to contact us if you have any questions or would like to discuss these revisions further. We look

forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Joshua Dean, PhD
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orcid.org/0000-0001-9058-7076

Carolina Ortiz Guerrero, PhD
Associate Editor
Communications Earth & Environment

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Please refer to our data policies at http://www.nature.com/authors/policies/availability.html.

REVIEWER COMMENTS:

Reviewer #1 (Remarks to the Author):

Please see attached review file

Reviewer #2 (Remarks to the Author):

General Comments:
This manuscript uses a gradient of rock to soil to submarine samples to quantify the amount of OCpetro which is either oxidized or re-buried during export from the mountain catchment to off-shore burial. This is a very interesting result and a well written manuscript, there are several issues that need to be addressed before publication.

One thing is the direct link between the ramen data and the OCpetro oxidation, this is not clear in the given data. The direct continuum of degradation is not clear and could be explained by other sources. Additionally, the analysis of the mineral associated OCpetro needs clarification and re-assessment.

Specific line comments:
58: Make sure to cite this paper instead of or with the Torres et al. 2014 paper : The role of sulfur in chemical weathering and atmospheric CO2 fluxes: evidence from major ions, δ13CDIC, and δ34SSO4 in rivers of the Canadian Cordillera; J Spence, K Telmer; Geochimica et Cosmochimica Acta, 2005
60: Which earth system model? Or do the authors mean the models in general?
61: Look at work done by M. Ogric as well for OCpetro oxidation.
72: Is it well established that highly graphitized OCpetro is related to low microbial oxidation in laboratory studies?
87: Make sure to specify that this refers to Taiwanese rivers not all rivers or POC.
97-98: What do the authors mean by "lumping nature of OC entities through various treatments?" Sampling treatments? Please be specific and clarify what is meant by this statement.
157-158: What different metrics were used to assess the different degrees of weathering? Is major element or tau values included here?
171: What is the rational for only measuring the fine particulate fractions?
200-201: please report all radiocarbon values as either Fm (Fraction modern) as is the convention or delta 14C (14C).
258: What are the conventional methods?
269-271: How were the weathered materials calculated or quantified?
277-279: This needs to be re-accessed, OCpetro by definition is not biospheric, ie it is from the rock and is incorporated into the rock during sedimentation during the geological past. The timescale must be defined here, because it is very unclear how it is currently written.
302-309: This would be useful to point to the work by Petsch et al. 2001 which showed direct biological assimilation
331: Be careful with these assumptions, "old refractory organic matter" age does not necessarily mean refractory.
351: Is there evidence from these data to suggest this is true?
427: There is not an intrinsic recalcitrance of organic matter. The reactivity of OC is environmentally derived. Hemingway et al. 2019.
439-448: it is unclear to me how the determination of the "within minerals", "attached" and "non-attached" are determined. This is essential to understand if OCpetro is accessible to microbes for oxidation. However, it seems (to me) that any OCpetro is inherently intertwined with minerals, It IS the mineral because it is the weathered rock material. This is a very interesting topic but needs to be fully flushed out in the discussion and needs more explanation how these categories are created.
450-454: in the weathered materials what about clay minerals? It seems strange that there is preservation of mica in these phases. If that is not the case, I would suggest some alteration of these categories.
446: Is rutile assumed to be associated with OCpetro? This doesn't make sense, there is not well documented accounts of Ti based minerals being associated with organic matter or carbon, potentially this is just a consequence of both phases resisting both transport and weathering but are not actually associated with one another.
471-473: This doesn't make sense to me, potentially the authors meant that the pattern is "inconsistent" not consistent, because the mica is likely to be weathered quickly, the OCpetro is unlikely to be protected by this mineral phase, because it is susceptible to "abrasion and biodegradation". It is also interesting to me that the mica phases are in the weathered materials, could this be an "interference of clay minerals". Is there independent XRD data to confirm or calibrate the ramen mineral data?
473-479: This does not make sense to me. Feldspar is less resistant to weathering than mica in this study (Not in the literature). There is some discrepancy in these statements that is very confusing?
485-486: This statement is only consistent if the OC is from the vegetation, but the OCpetro is inherently in the mineral phase already, because it IS the mineral! It is from the rock. The next sentence is correct, but these ideas need to be better, more consistently integrated within this argument.
492: destructed is not used correctly here
500: while pMC is technically correct, it is an outdated notation, and should be changed to either Fm or 14C.
502: Where did this biospheric endmember come from? Can the authors cite it or say from which samples it was calculated for?
520: These are large ranges of OCpetro oxidation, what other studies show this large of a range? Can there be a better

justification for the fox used in each of these catchments? This is a huge range in exhumation rate and in the derived CO2 flux. Is it likely all of the OCpetro which is "weathered" is fully oxidized to CO2?

530: What does the phrase "adopting the data" mean here? Please clarify.

541: What about in the Amazon flood plains? Even in this low erosion rate area there are significantly increased OCpetro oxidation occurring: Dellinger et al. 2023 PNAS

557: Could this not be the other way around, that the more disordered graphite is actually because the highly ordered graphite was never formed, rather than it is being broken down?

Figure comments:

While the figures are clear and well organized, I have a few suggestions that could make the story clearer.

Fig 1. Is there a way to maybe create a different color for the formations and the water? The bathymetric map when first glancing at it, is hard to distinguish from the Tanano Complex. I know it is labeled, but a more distinct color could eliminate any confusion.

Fig 2. The caption needs to be more descriptive. If one is not an expert in Ramen then the different axis doesn't mean much, it would be helpful to add some method explanation, such as what each axis means in a fundamental sense. What is the reader supposed to take away from this figure? It seems like that the weathered material is fundamentally different than the other sampled materials.

Fig 3. Please expand the axis to be across the two bottom plots and the three upper ones. Additionally, the two different blue colors are extremely hard to distinguish. Is it necessary to have the Di (Disorder OCpetro? Since only one sample total falls into this range?). The calculated temperature what does this mean in this figure and what is the total width? From the ramen experiments? Please be more descriptive in the caption? In d and e, how is an Estuary a site lithology? Should this just be a sediment derived from wither schist or slate?

Fig 4: Maybe the best way to show these data is to compare across the gradient of samples. A very important question that doesn't necessarily come through in this figure is the trying to understand what is transported to the marine sediments. Isn't it a little odd that the weathered material does not seem to reflect what is in the bedload, suspended load to marine sediments. Is the mildly graphitized and intermediate grade OCpetro different in crystallinity? Or just the absence of graphite in the IG samples? What is the real difference in crystal structure between these two and does it relate to reactivity? In A. what does this reflect? What is the %OC or the %graphite in these samples, these as relatives without context make these data hard to interpret.

Fig 6. pMC is an outdated metric for radiocarbon reporting. Please convert to FM or 14C (‰).

Reviewer #3 (Remarks to the Author):

This manuscript by Lien et al report new Raman spectroscopy, carbon content, carbon isotope and radiocarbon data to characterize, through a source-to-sink perspective, the pathway and oxidation of petrogenic organic carbon (OCpetro) across the Beinan River catchment from Taiwan. They found a two-stage oxidation process is soils and in submarine canyon and calculate a global OCpetro oxidation rate of 7-137 tC.km-2.yr-1 which is a significant CO2 source to the atmosphere.

Overall, the manuscript is well-written, and the conclusions are well supported by the data. There are still very few papers with detailed characterization and quantification of petrogenic carbon oxidation and so this contribution will be of interest to the research community. Hence, I recommend publication of this manuscript in Communications Earth & Environment with minor revisions. Below I explain the main two points where I think the current manuscript can be improved (see also detailed comments below): i) give more details on how the OCpetro oxidation rate (and the large uncertainty) is calculated, because it is lacking sufficient explanation in the current manuscript. This can be added in the supplementary materials and not necessarily in the main text; ii) Add a synthesis or recap figure (figure 7) showing: the pathway of OCpetro, the two stages OCpetro oxidation, where microbial oxidation takes place, the respective contribution of soil (with disordered graphitic carbon) vs. bedrock (highly mature graphitized OCpetro) and CO2 release fluxes. That would help the reader to visualize the whole picture.

Detailed comments:
- Line 63: Not that the most recent and accurate estimate is 68 Mt/yr (Zondervan et al., 2023)

- Lines 64 and 65: CO2 drawdown by silicate weathering is 140 Mt/yr before carbonate precipitation in the ocean and 70 Mt/yr after carbonate precipitation (on timescales longer than 10^4 years). Biospheric OC burial is estimated to be 170 Mt/yr in the present-day (Hilton and West, 2020). Please correct the 40-75 MtC/yr number or indicate more precisely what does it correspond to?

- Line 87: according to Galy et al., (2015), "global biospheric and petrogenic POC fluxes of 157 and 43 megatonnes of carbon per year, respectively" so no the majority of exported particulate OC is composed of OCbio, not OCpetro. Please correct here

- Line 275: what is "in-situ diagenesis"? and what is "exotic"? Define the terms or use terms that are more accurate

- Lines 367-368: when you say "negligible" is it possible to give a quantitative constraint or not? (<1%, <5%, <10%?)

- Lines 368-370: how does it compare with data and interpretation from Hilton et al., (2010)?

- Lines 507-509: this is not very clear, why the « fitting results were reliable only when the OCpetro from different profiles were degraded at the same pace »? And why "This prerequisite is nearly impossible to accomplish at natural sites"?

- Line 524: what is the calculated catchment average TOCbedrock and fox? Also could you give here the average fox value for each rock type? (or after Line 520)

- Line 527: why such a large range of value (and uncertainty)? I suggest to give the details of the calculation in the supplementary materials (add one section). Maybe you could report two values, i.e. one calculated with 10Be erosion rate and one calculated with sediment gauging data?

Also, this calculation is based on soil data (weathered materials), but you show that this material is a "negligible" contribution to the suspended sediment load where intermediate and medium grade graphite dominates (indicating low OCpetro oxidation intensity). Is that not a bias in the calculation of total CO2 emission to extrapolate the f ox values from highly weathered soil to the rest of the catchment area? You use the most highly weathered setting to calculate CO2 emission, but these settings do not contribute much actually.

Version 1:

Decision Letter:

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Dear Professor Lin,

Your revised manuscript titled "Two-stage oxidation of petrogenic organic carbon in a rapidly exhuming small mountainous catchment" has now been seen by our original reviewer #1, whose comments appear below. In light of their advice we are delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Earth & Environment.

We therefore invite you to revise your paper one last time to address the remaining concerns of our reviewers. At the same time we ask that you edit your manuscript to comply with our format requirements and to maximise the accessibility and therefore the impact of your work. Specifically, please clarify the technical parts of the figure captions for Figs 2 and 3, for which things like "bands" and "positions" are not easy to interpret for someone unfamiliar with the topic area.

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We hope to hear from you within two weeks; please let us know if you need more time.

Best regards,

Carolina Ortiz Guerrero, Ph.D.
Associate Editor
Communications Earth & Environment

Joshua Dean, PhD
Editorial Board Member
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REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

I appreciate the efforts that the authors have made to address the review comments.
The clarifications and additional information provided, in both the text and figures, is sufficient.

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Review by Robert Sparkes

Lien and co-authors have produced an important study assessing the potential for petrogenic organic carbon (OCpetro) to oxidise during exhumation, weathering and erosion in a highly tectonically active mountain belt. The short time and distance between exhumation and submarine burial would previously have led to assumptions that OCpetro oxidation is minimal between source and sink, but these authors present Raman spectroscopy data that suggests OCpetro degrades due to biological priming in the soils. They then use TOC data to provide estimates of the flux of CO2 due to this weathering.

The Raman spectra are acquired and processed robustly and competently, using techniques comparable to other studies in Taiwan and worldwide. The authors have carefully collected a large dataset which is commendable. Thermometry testing via multiple Raman techniques, plus isotopes, is robustly presented, and discussions exploring reasons for the observed distribution pattern of spectra are clear.

There are, however, areas which could be improved prior to publication. The conclusions regarding CO2 fluxes are not based on the Raman spectra but on organic carbon data collected alongside the spectroscopic measurements. This aspect of the study is not explained or explored in as much detail as the Raman, and there are several clarifications identified below that need to be addressed.

Overall, this is an interesting study that, with changes, would be appropriate for publication in Communications Earth & Environment.

Major Comments

How were OC samples prepared for EA and IRMS? The manuscript and supporting information lack detail on the methods used to generate the TOC and TN data, beyond naming the instrument used. TOC measurements via EA require separation of organic and inorganic carbon, for example by acidic removal of inorganic carbon prior to analysis. IRMS also requires removal of inorganic carbon to avoid isotopic bias. If acid was used to leach out carbonate, what type, strength and reaction conditions were used? Did the authors consider loss of organic matter during this stage? Raman and isotopic results are used to claim that weathered material makes a "negligible" contribution to fluvial bedload sediments (Line 368), and that in-river degradation is minimal (Supplement Lines 175-177). TOC data was then used to calculate OCpetro oxidation, seemingly independent of the Raman data that makes up the majority of the study, in section "Implications for carbon cycle", and claims that the catchment is responsible for a globally significant amount of carbon dioxide release, which must be in the rock and soil profiles prior to fluvial erosion. To support this, two things are required. First, a thorough description of the TOC methodology to match that of the Raman approach. Second, a more integrated approach to the discussion of C-cycle implications. Currently, the two halves of the manuscript are quite disjointed – the headline figures regarding OC oxidation rates are based on a minor component of the work carried out. For example, the authors could compare the "f-ox" oxidation fraction and Raman data for individual samples and see whether there is a link between the spectra collected and "f-ox".

The uncertainty in "f-ox" and therefore the carbon fluxes is very high, more than an order of magnitude. Can the authors recommend further work which would narrow the range of possible values?

As the authors concede, TOC data from the canyon is not presented, despite it forming a significant part of the Raman discussion and potentially responsible for further OCpetro oxidation and CO2 release. At minimum, the authors' estimate of 1% OCpetro oxidation offshore should be supported by data or a literature comparison.

The section discussing mineral association and protection from oxidation can only deal with particulate organic matter that is susceptible to Raman analysis. Protection of carbon films and other highly disordered and/or molecular-scale carbon is not something that can be easily interrogated with the Raman, yet these will be present in the EA and IRMS datasets. The authors could consider discussing this fact.

Minor comments

Lines 63-65   It is not clear how 40-100 MtC oxidation can offset 140 MtC silicate weathering and/or 40-75 MtC biospheric OC burial. The numbers do not seem to match up (e.g. 40-100 becoming 40-75, what is the scaling factor here? Is this sentence a combination of findings from multiple studies? Consider rewriting or explaining in greater detail.

Lines 81-83   The authors mention progressive degradation of the recalcitrant pool during transfer through large river systems. Consider making a comment here about whether this progressive degradation targets specific parts of the recalcitrant pool.

Lines 97-98   Do you have a citation or further details about "lumping nature of OC entities"?

Lines 130-131 What are the typical residence times prior to flushing into rivers? Do the authors have a reference for this? This is calculated later in the manuscript, is it the same value as line 346?

Line 146   How many rock samples were collected?

Lines 476-479 There is scope to add a further level of discussion here, having identified the differences between mica and feldspar resistivity to dissolution and physical abrasion.

Fig 2   How confident are the authors in the G positions of weathered samples? Is the G position truly the centre of the graphitic peak, or an artefact of the fitting process?

Fig 3   What happens to the Highly Graphitised OCpetro that is seen in the bedrocks but few other samples? It would likely be the least degradable form of carbonaceous material present in the system.

Fig 5   How were the bounding boxes for sample types defined? The coloured shapes are irregular, were they drawn automatically or by hand?

Fig S1   Some samples have error bars – how many repeated measurements were made in order to generate these standard deviations?

Typographical errors

Throughout   Check the use of past and present tense

Line 138   There seems to be a typographical error in the sentence "For river sediments…". Do you mean "For" or "Four"? The sentence works without either word, but not as currently written.

Line 140   Missing word "at **the** estuary"

Lines 311-312   There appears to be an error in the phrase "favors the release of old refractory organic matter freed from mineral susceptible to the leaching of organic acid"

Lines 463-464   Phrase "relatively recalcitrant to resist intensive biodegradation" could perhaps be clearer.

Lines 472-473   "consistent with its vulnerability of platy structure susceptible to the abrasion and biodegradation" could be clearer

Responses to reviewers' comments

Review #1 by Robert Sparkes

Comment 1-01: How were OC samples prepared for EA and IRMS? The manuscript and supporting information lack detail on the methods used to generate the TOC and TN data, beyond naming the instrument used. TOC measurements via EA require separation of organic and inorganic carbon, for example by acidic removal of inorganic carbon prior to analysis. IRMS also requires removal of inorganic carbon to avoid isotopic bias. If acid was used to leach out carbonate, what type, strength and reaction conditions were used? Did the authors consider loss of organic matter during this stage?

Response 1-01: Thanks for the reminder. Indeed, the preparation methods for TOC and TN was accidentally omitted in the supplementary information. The methods adopted in this study proceeded with gently grounding (only for rocks), drying, sieving to less than 63 μm and homogenized so the potential heterogeneity of sampled material batch could be minimized. About 0.5 g of each sample aliquot was mixed with 5 mL of 2 N HCl thoroughly in a centrifuge tube using a vortex mixer to digest carbonate minerals. The mixture was incubated (at least overnight) at room temperature until no bubble was generated. Samples were centrifuged at 5000 rpm for 5 minutes to remove the acid solution. If bubbles were generated vigorously during the incubation, additional 1–2 mL of 2 N HCl was added again to ensure that all carbonates had been eliminated (no bubble was generated). Regardless of acid digesting for carbonate removal one or two times, samples were washed with 8 mL of deionized water for 4–5 times until the pH of solutions returned to neutral (confirmed by pH test paper). Suspended loads with limited sample volume that could not be scraped from the filter were processed by immersing the filter in the acid solution for several hours until no bubble was generated and washing it with deionized water multiple times. After carbonates removal, all samples were dried at 50 °C. Samples in centrifuge tubes were further ground gently to reduce particle aggregation and avoid potential geochemical heterogeneity. Although acid-soluble organic carbon (e.g., fulvic acids) could be lost during acid leaching, loss of organic matter during acid leaching and washing has been reported to be only 1.1–4.0% for soil, algae and sediments[1]. Furthermore, the differences in $\delta^{13}C$ and Fm (Fraction modern) values after pretreatment have been reported to be less than 0.6‰[2] and between 0.0006 and 0.1457[3], respectively. Therefore, potential loss of leachable organic acids and its effect on isotopic composition were assumed to be small, and no further quantitative assessment was performed. We have added this part to Method.

Comment 1-02: Raman and isotopic results are used to claim that weathered material

makes a "negligible" contribution to fluvial bedload sediments (Line 368), and that in-river degradation is minimal (Supplement Lines 175-177). TOC data was then used to calculate OCpetro oxidation, seemingly independent of the Raman data that makes up the majority of the study, in section "Implications for carbon cycle", and claims that the catchment is responsible for a globally significant amount of carbon dioxide release, which must be in the rock and soil profiles prior to fluvial erosion. To support this, two things are required. First, a thorough description of the TOC methodology to match that of the Raman approach. Second, a more integrated approach to the discussion of C-cycle implications. Currently, the two halves of the manuscript are quite disjointed – the headline figures regarding OC oxidation rates are based on a minor component of the work carried out. For example, the authors could compare the "f-ox" oxidation fraction and Raman data for individual samples and see whether there is a link between the spectra collected and "f-ox".

Response 1-02: Thanks for the comment. The first part regarding the methodology for the processing and compositional analysis of organic matters is provided in response 1-01. For the second part of comment, we are aware of the fact that the Raman and isotopic data are likely not referred to the same structural or chemical entities. The Raman spectroscopy qualitatively characterizes the ordering status of graphitic carbon; therefore, the change of Raman maturity is primarily attributed to the residual graphitic carbon that experienced abrasion and weathering processes. In particular, broadened and stronger defect bands (e.g., D1–D4 bands described in the main text) are generally interpreted as the formation of functional groups or alteration of graphitic structures. For example, previous experimental studies on the oxidation of highly-ordered graphite at high temperature (≥ 200 °C) suggest that D bands become more evident with the formation of transitional functional groups (e.g., C=O and C–O) and the mass loss over a course of temperature increase[4,5]. The introduction of initial defects and functional groups further lowers the starting temperature corresponding to significant mass loss and leads to more rapid and significant weight loss. In addition, soot (a highly disordered form of graphitic carbon) could be readily oxidized with concurrent CO_2 production over a heating course[6]. The soot with less ordered structure also tends to be oxidized at a faster pace than the rather ordered one, leaving the residual soot characterized by more ordered structure. Although lab-scale experiments are conducted under the dry condition at high temperature, the experimental results provide lines of evidence that may be further extrapolated to the biologically mediated scenario under ambient conditions. First, the increasing intensity of D bands over the heating process points directly to the conversion of highly crystalline graphite into the disordered form, a pattern resembling the weathering of OC_{petro} along the rock-soil transition. The experimental spectroscopic shift combined with the mass loss further suggests that the

OC_{petro} could have been altered with the production of volatiles. Considering that oxygen-containing functional groups are also concomitantly produced during the experimental oxidation, CO_2 appears to be the most viable and probable candidate for volatile phase even though corresponding validation still lacks. Second, the experiments on soot lead to a higher abundance of more mature graphitic carbon and co-production of CO_2. Both preconditioned graphite and soot with less ordered structure are susceptible to faster mass losses than the ordered graphite and soot. This experimental data pattern is analogous to our observations for marine sediments where the abundance of disordered OC_{petro} decreases with the increasing transport distance from the shoreline.

The analogy drawn between our field observations and experimental constraints suggests that in addition to the feasibility of OC_{petro} oxidation, the OC_{petro} degradability and the resultant form of graphitic carbon preserved in soils or marine sediment are intimately related to the initial maturity of OC_{petro}, and that CO_2 is very likely the end product of OC_{petro} oxidation. What remains unclear is how the OC_{petro} weathering prevails under the conditions that are totally different from the experimental setup (e.g., biotic catalysis/high water activity versus dry O_2 at temperatures up to 800 ℃). Equally important is the extent to which the degraded component is converted to CO_2 or other forms of intermediate state, and how alike and the proportion of residual total organic carbon could be attributed to graphitic carbon.

On the other hand, the isotopic compositions illustrate the ^{13}C and ^{14}C abundances of total organic matters that could be sourced from residual graphitic carbon, newly introduced labile OC, and any other uncharacterized form of organic carbon (e.g., biofilm). Similar to the results of this (Figs. 6 and S3) and previous studies[7], the isotopic results could be further fed into the quantitative assessment that constrains the loss of organic carbon during soil development.

In summary, neither of these methodologies delineates any form of transitional organic compound other than graphitic carbon, nor do they resolve whether and to what extent CO_2 is produced during the transformation of highly mature graphitic carbon in rocks to the disordered form in soils or during the elimination of the disordered form in marine sediments.

Nevertheless, to assess whether Raman parameters can be quantitatively correlated to compositional data, the correlation between f_{ox} and Raman data is examined as the reviewer advised (Fig. S5). These parameters include the derived temperature based on the relative area of D and G bands, the total width of D and G bands, and the Raman distance based on the maturity difference assessed by the total width and derived temperature between individual analyzed particle versus the averaged rock characteristics. No correlation is found between these two datasets, suggesting

compositional complexity of the entire OC entity. Since Raman data provide the ordering status of individual OC_{petro} particles, both datasets may be better correlated only when the graphitic carbon dominates the OC pool. In summary, the current model for OC_{petro} oxidation is limited by the lack of detailed characterization of the target organic entities using various spectroscopic and compositional analyses. It is also essential to experimentally resolve the reaction pathway and kinetics for the oxidation of graphitic carbon under ambient conditions, and to validate the collected parameters in field observations. We have added this part to Discussion, Supplementary Note 3 and Supplementary Discussion 1.

Comment 1-03: The uncertainty in "f-ox" and therefore the carbon fluxes is very high, more than an order of magnitude. Can the authors recommend further work which would narrow the range of possible values?

Response 1-03: The large uncertainty of carbon flux is primarily related to a large range of $TOC_{bedrock}$, f_{ox} and denudation rate reported previously and derived in this study for the investigated catchment. In particular, the denudation rate used for the flux calculation was set at a range (1.5 to 10 mm yr^{-1}) that covered the reported values. Therefore, the derived flux would correspondingly span near an order of magnitude. To refine the flux estimate, individual derived parameters are examined. First, f_{ox} is susceptible to localized characteristics of soil, plant, landscape, bedrock and climate that can vary over a considerable range within a small spatial scale in the investigated mountainous catchment. To investigate their possible variation, the modeling for f_{ox} is performed on individual samples using their corresponding $TOC_{bedrock}$. The resultant f_{ox} values are further categorized in accordance with lithology and averaged to yield 0.65 ± 0.12 for slate and 0.49 ± 0.29 for schist. For the second parameter, the erosion/denudation rate varies substantially, depending on the time scale inherited by individual methodologies. On a decadal time scale, the erosion rate based on riverine sediment yield has been estimated to be 20.9 mm yr^{-1} [8]. This rate could have been further refined to a range of 4–5 mm yr^{-1} using the alternative rating curve that has been considered to better cover the possible discharge range[9]. Over a millennium time scale, the denudation rate based on the exposure age derived from cosmogenic ^{10}Be has been reported to be 4.54 ± 1.86 mm yr^{-1} [10]. For comparison, the sediment accumulation rate constrained by zircon U-Pb ages has been estimated to be 5.14 mm yr^{-1} over the recent ~2 Ma [11]. The million-year scale exhumation rate based on fission-track thermochronology has been estimated to be 1.5–10 mm yr^{-1} [8]. In this regard, the erosion rate of 4.5 ± 1 mm yr^{-1} is arbitrarily chosen to accommodate a considerable range of rates derived from different methodologies across the contemporary-geological time scales. Considering that OC_{petro} oxidation is also strongly tied to the landscape and

climate that have been comparable with modern characteristics in the investigated catchment for thousands of years, the designated rate (4.5 ± 1 mm yr^{-1}) may be even more reliable. Using these two parameters and the average TOC$_{\text{bedrock}}$, the carbon fluxes are calculated to be 23 ± 7 tC km^{-2} yr^{-1} for slate and 33 ± 21 tC km^{-2} yr^{-1} for schist. If the variation in TOC$_{\text{bedrock}}$ ($0.28 \pm 0.23\%$ for slate and $0.53 \pm 0.39\%$ for schist) is taken into account, the oxidation flux would exhibit a much broader range. At this stage, the computed flux is still variable primarily owing to the availability and spatial coverage of individual parameters. More data would be helpful to determine whether the consensus of computed fluxes could be reached. We have added this part of discussion to Supplementary Note 4.

Comment 1-04: As the authors concede, TOC data from the canyon is not presented, despite it forming a significant part of the Raman discussion and potentially responsible for further OCpetro oxidation and CO2 release. At minimum, the authors' estimate of 1% OCpetro oxidation offshore should be supported by data or a literature comparison.

Response 1-04: Thank you for the reminder. The compositional data from marine sediments collected along the canyon levee were presented in Figs. 5 and S1 and Table S1. The 1% OC$_{\text{petro}}$ oxidation originally assumed in the main text represents a conservatively educated guess on the lowest bound. To evaluate and justify the percentage of OC$_{\text{petro}}$ in marine sediments that might have been oxidized during transport to the deep sea, three independent constraints using different parameters obtained in this or previous studies are assessed. The first approach is to quantify the change in the ratio of the disordered to total OC$_{\text{petro}}$ from sediments near the estuary (NOR3-1) to the deep sea (MD18-3538). The threshold of the Raman parameter used to discriminate the ordered from disordered OC$_{\text{petro}}$ is placed at the calculated temperature of ≥ 330 °C and total width of ≤ 140 cm^{-1}. The OC$_{\text{petro}}$ with Raman parameters above this threshold (also the common range for bedrocks) is categorized as the ordered form, and vice versa as the disordered form. The ratios of the disordered to total OC$_{\text{petro}}$ decrease from 66% (31/47) at NOR3-1 near the estuary, 36% (9/25) at OR1-960-C5, 27% (6/22) at OR1-967-S1, to 18% (5/28) at MD18-3538, the most distant site from the shoreline. This 48% decrease in the ratio is interpreted as the loss of disordered OC$_{\text{petro}}$ during transport. The estimate is susceptible to the uncertainty that the grain count provided above cannot be directly translated into mass difference. To provide a conservative assessment, this estimate could be considered as an upper bound for the oxidation of OC$_{\text{petro}}$. The second constraint presented in the main text is to configure the mass balance and mixing process based on the abundance and isotopic composition of OC and OC$_{\text{petro}}$. This approach yields the f_{ox} values of 0.65 ± 0.12 for slate and 0.49 ± 0.29 for schist. As stated in Discussion, soil development has been

estimated to last for tens of years, which is comparable with the time scale for transport from the estuary to the distal abyssal plain. Considering a higher oxidative driver associated with atmospheric oxygen, this range of f_{ox} could also be regarded as the upper bound for the oxidation of OC_{petro} during marine transit. Finally, the previous study based on Re proxy has revealed the flux of riverine Re and derived OC_{petro} oxidation ranged from 11 to 22 tC km^{-2} yr^{-1} in two tributaries of the current investigated catchment[12]. Using the catchment area, a sediment yield of 20 Mt yr^{-1} [9], TOC_{petro} content of 0.36% (this study), the fraction of OC_{petro} oxidized during soil development and river transit is calculated to be 20–33%. Again, this estimate could have been larger than that for marine transit, serving as the upper bound for the OC_{petro} oxidation. In summary, the assessments framed by three different approaches enable the placement of the upper bound for the fraction of OC_{petro} oxidation to be less than 20%. For a conservative estimate, the oxidation flux along marine transit is constrained by using an oxidation fraction of 1% to demonstrate that the magnitude of OC_{petro} oxidation in marine environments cannot be neglected. We have added this part of discussion to Supplementary Discussion 2.

Comment 1-05: The section discussing mineral association and protection from oxidation can only deal with particulate organic matter that is susceptible to Raman analysis. Protection of carbon films and other highly disordered and/or molecular-scale carbon is not something that can be easily interrogated with the Raman, yet these will be present in the EA and IRMS datasets. The authors could consider discussing this fact.

Response 1-05: Thank you for the suggestion. As stated in response 1-02, we have extended more discussion on the fact that the Raman and isotopic data are likely not referred to the same structural or chemical entities. Raman spectroscopy qualitatively characterizes the ordering status of graphitic carbon; therefore, the change in Raman maturity is primarily attributed to the residual graphitic carbon that experienced abrasion and weathering processes. Broadened and stronger defect bands are generally interpreted as the formation of functional groups or alteration of graphitic structures. Raman spectroscopy can also identify the bonding characteristics of inorganic materials. By combining a suite of spectroscopic characteristics, specific minerals surrounding or attached with the OC_{petro} particles can be identified. On the other hand, the isotopic compositions illustrate the ^{13}C and ^{14}C abundances of total organic matters that could be sourced from the residual graphitic carbon, newly introduced labile OC, and any other uncharacterized form of organic carbon. For comparison, biofilms and other natural organic materials are amorphous and composed of complexly structured compounds. They may also emit fluorescence when subject to the laser excitation[13-15].

Therefore, both effects of complex matrix and fluorescence could render the Raman characterization of naturally assembled organic matters from soils and sediments and the relationships between biofilm with OC_{petro} challenging. We have added the limitation of instrumental capability and matrix complexity to Method and Supplementary Discussion 1.

Comment 1-06: Lines 63-65: It is not clear how 40-100 MtC oxidation can offset 140 MtC silicate weathering and/or 40-75 MtC biospheric OC burial. The numbers do not seem to match up (e.g. 40-100 becoming 40-75, what is the scaling factor here? Is this sentence a combination of findings from multiple studies? Consider rewriting or explaining in greater detail.

Response 1-06: Thank you for the suggestion. This sentence describes that the large quantity of CO_2 flux produced by OC_{petro} oxidation (40–100 MtC yr^{-1}) is comparable with other geological sinks (140 MtC yr^{-1} for silicate weathering and 40–75 MtC yr^{-1} for sedimentary burial of biospheric OC) [16-18]. We have rephrased this sentence as "With the approaches such as isotopic mass balance model or riverine Re proxy, the global oxidation flux of OC_{petro} has been estimated to be 68^{+18}_{-6} MtC yr^{-1}, a quantity comparable with other geological sinks (140 MtC yr^{-1} for silicate weathering and 40–75 MtC yr^{-1} for sedimentary burial of terrestrial biospheric OC)" to avoid confusion.

Comment 1-07: Lines 81-83: The authors mention progressive degradation of the recalcitrant pool during transfer through large river systems. Consider making a comment here about whether this progressive degradation targets specific parts of the recalcitrant pool.

Response 1-07: The OC_{petro} oxidation in large river systems proceeds in multiple compartments along the transit. The best example probably lies in the Amazon system. Using the Re proxy for OC_{petro} oxidation, Dellinger, et al. [19] quantified the riverine Re fluxes from the upstream Andean catchments to the midstream floodplain and converted them to the fluxes of OC_{petro} oxidation. Their results demonstrate that the flux of OC_{petro} oxidation for the floodplain constitutes 40% of the overall oxidative flux and is only slightly less than that from the mountainous catchments (46%), suggesting that the long-term storage in the low-relief riparian zone of the big river system facilitates further degradation of OC_{petro} drained from high-relief mountainous regions. Such a flux pattern may greatly exceed that for small catchments in high standing islands (like that in this study) due to different spatial and time scales for the sediment storage in floodplain and/or delta. We have added this part to Discussion.

Comment 1-08: Lines 97-98: Do you have a citation or further details about "lumping

nature of OC entities"?

Response 1-08: This description was originally used to state the fact that compositional analyses integrate the abundance and isotopic characteristics of the entire OC entity. Potential biases could arise because OC subject to various treatments and analyses could be attributed to a spectrum of structural and compositional entities. As raised in response 1-02, the isotopic compositions illustrate the ^{13}C and ^{14}C abundances of total organic matters, including remaining graphitic carbon after oxidation and newly introduced labile OC (e.g., biofilms). We have rephrased this sentence as "potential biases could arise due to the fact that OC subject to various treatments and analyses described above is attributed to a spectrum of structural and compositional entities." to avoid confusion.

Comment 1-09: Lines 130-131: What are the typical residence times prior to flushing into rivers? Do the authors have a reference for this? This is calculated later in the manuscript, is it the same value as line 346?

Response 1-09: The description in lines 130-131 is the same as that in line 346. The connection has been denoted in the manuscript.

Comment 1-10: Line 146: How many rock samples were collected?

Response 1-10: A total of 16 rock samples were collected in this study. We have added the sample number to Method.

Comment 1-11: Lines 476-479: There is scope to add a further level of discussion here, having identified the differences between mica and feldspar resistivity to dissolution and physical abrasion.

Response 1-11: Our results reveal a strong dissociation of mica-OC$_{petro}$ relationship but comparable abundances of feldspar during the sediment transport. The pattern is inconsistent with the dissolution rate determined from theoretical calculations with experimental constraints through which plagioclase dissolves at a rate about one, or even up to three[20], order(s) of magnitude greater than that of mica group (e.g., muscovite and phlogopite)[21]. Even considering that feldspar may be falsely identified as laumontite (zeolite group) with similar spectral characteristics, their dissolution rates are comparable to each other[22]. The chemical weathering processes cannot account for the observed patterns of mineralogical abundances across different compartments. Instead, the selective elimination of mica may result from the vulnerability of platy structure susceptible to the physical abrasion and grinding associated with sediment transport across river and marine environments. We have amended further discussion to the manuscript.

Comment 1-12: Fig 2: How confident are the authors in the G positions of weathered samples? Is the G position truly the centre of the graphitic peak, or an artefact of the fitting process?

Response 1-12: The Raman spectrometer used in this study was constantly calibrated with a silicon standard before each measurement batch to ensure the wavenumber did not drift. Two commonly used Raman thermometry established by Beyssac, et al. [23] and Lahfid, et al. [24] were adopted in this study to quantitatively evaluate the alteration of both ordered and disordered OC_{petro}. In order to retrieve Raman parameters for the two thermometers, the spectra with asymmetric composite D band were fitted into five bands (G, D1–4 bands) [24], whereas the rest of the spectra were deconvoluted into four bands (G, D1–3 bands) [23]. The fitting was manually conducted and iterated until the results converged. The peak position of fitted D3 band was inspected to be always lower than 1550 cm^{-1} while the G band was retained. As the D2 band was mostly fitted, the position of G band was well constrained to be between those of D2 and D3 bands. Finally, the position of fitted G band was not fixed at a constant value but instead deviated from 1580 cm^{-1} for the well crystalline graphite upon the presence of disordered OC_{petro}. Their position variation is well correlated with the so-called Raman band separation (RBS; Fig. S6) that describes the position distance between the G and D1 bands. In this study, the degree of disorder in OC_{petro} is negatively correlated with RBS. Such a relationship between disordering and RBS has also been observed for kerogen[25]. The description about the signal processing has been amended to Method.

Comment 1-13: Fig 3: What happens to the Highly Graphitised OCpetro that is seen in the bedrocks but few other samples? It would likely be the least degradable form of carbonaceous material present in the system.

Response 1-13: The Highly Graphitized OC_{petro} in bedrocks was mostly retrieved from DLKW with only one exception where such a particle measurement was performed on black schist from WL. The black schist at DLKW was collected near the contact with a slightly ellipsoidal intrusive metagranite body with a diameter of ~1 km from the aerial perspective. The coverage area of black schist in the contact with metagranite at DLKW was volumetrically smaller than bedrocks distributed elsewhere. Therefore, the occurrence of Highly Graphitized OC_{petro} was scarce in bedrock, and became even much fewer or absent in weathered materials or downstream sediments. The presence of Highly Graphitized OC_{petro} might be diluted or degraded during the transport to the depositional basin.

Comment 1-14: Fig 5: How were the bounding boxes for sample types defined? The

coloured shapes are irregular, were they drawn automatically or by hand?

Response 1-14: The bounded boxes were manually drawn by outlining the data range for individual categories. Therefore, readers can better visualize the variation of each sample category.

Comment 1-15: Fig S1: Some samples have error bars – how many repeated measurements were made in order to generate these standard deviations?

Response 1-15: The TOC and TN contents were determined from duplicate aliquots of each sample. If the variations of replicates were larger than 5%, additional duplicate measurements were conducted. The standard deviation of all repeated measurements of each sample was calculated to represent the error bar. The TOC contents for samples with limited sample size were measured once by IRMS. Error bars for these samples were derived from the error percentage of standards. Errors of C/N ratio were propagated from the errors of TOC and TN contents. All the sample error bars were drawn on the plot with some of them smaller than the symbol (details in Table S1). The description of error bars has been added as "The TOC and TN contents and standard deviations were determined by at least duplicate aliquots of each sample depending on the variation of replicates. All the error bars ($\pm 1\sigma$) were drawn on the plot with some of them smaller than the symbol (details in Table S1)."to the figure caption.

Comment 1-16: Throughout: Check the use of past and present tense

Response 1-16: Thank you for the reminder. The logic of using past or present tense in this study is to distinguish the analyses and results obtained in this study from the interpretation and inference made based on the results. Therefore, the description of our results was reported by using the past tense, whereas the discussion part was written in the present tense. We have gone through the use of tense in the manuscript and made some correction.

Comment 1-17: Line 138: There seems to be a typographical error in the sentence "For river sediments…". Do you mean "For" or "Four"? The sentence works without either word, but not as currently written.

Response 1-17: Thank you for the reminder. We have revised the sentence as "River sediments, suspended and bed loads, were retrieved from the main stem in the mountain front to the river mouth, and from main tributaries in July 2019." to reduce the confusion.

Comment 1-18: Line 140: Missing word "at **the** estuary"

Response 1-18: Thank you for the reminder. The sentence has been revised.

Comment 1-19: Lines 311-312: There appears to be an error in the phrase "favors the release of old refractory organic matter freed from mineral susceptible to the leaching of organic acid"

Response 1-19: Thank you for the reminder. The sentence has been revised as "…favors the release of refractory organic matter from minerals by leaching with organic acid produced by microorganisms and plant roots" to reduce the confusion.

Comment 1-20: Lines 463-464: Phrase "relatively recalcitrant to resist intensive biodegradation" could perhaps be clearer.

Response 1-20: Thank you for the reminder. The sentence has been revised in accordance with the suggestion.

Comment 1-21: Lines 472-473: "consistent with its vulnerability of platy structure susceptible to the abrasion and biodegradation" could be clearer

Response 1-21: Thank you for the reminder. The sentence has been revised as shown in response 1-11.

Reviewer #2 (Remarks to the Author):

Comment 2-01: One thing is the direct link between the ramen data and the OCpetro oxidation, this is not clear in the given data. The direct continuum of degradation is not clear and could be explained by other sources.

Response 2-01: Thank you for the comment. Indeed, we are aware of the fact that the Raman and isotopic data are likely not referred to the same structural or chemical entities. Raman spectroscopy qualitatively characterizes the ordering status of graphitic carbon; therefore, the change in Raman maturity is primarily attributed to the residual graphitic carbon that experienced abrasion and weathering processes. In particular, broadened and stronger defect bands (e.g., D1–D4 bands described in the main text) are generally interpreted as the formation of functional groups or alteration of graphitic structures. For example, previous experimental studies on the oxidation of highly-ordered graphite at high temperature (≥ 200 °C) suggest that D bands become more evident with the formation of transitional functional groups (e.g., C=O and C–O) and the mass loss over a course of temperature increase[4,5]. The introduction of initial defects and functional groups further lowers the starting temperature corresponding to significant mass loss and leads to more rapid and significant weight loss. In addition, soot (a highly disordered form of graphitic carbon) could be readily oxidized with concurrent CO_2 production over a heating course[6]. The soot with less ordered structure also tends to be oxidized at a faster pace than the rather ordered one, leaving the residual soot characterized by more ordered structure. Although lab-scale experiments are conducted under the dry condition at high temperature, the experimental results provide lines of evidence that may be further extrapolated to the biologically mediated scenario under ambient conditions. First, the increasing intensity of D bands over the heating process points directly to the conversion of highly crystalline graphite into the disordered form, a pattern resembling the weathering of OC_{petro} along the rock-soil transition. The experimental spectroscopic shift combined with the mass loss further suggests that the OC_{petro} could have been altered with the production of volatiles. Considering that oxygen-containing functional groups are also concomitantly produced during the experimental oxidation, CO_2 appears to be the most viable and probable candidate for volatile phase even though corresponding validation still lacks. Second, the experiments on soot lead to a higher abundance of more mature graphitic carbon and co-production of CO_2. Both preconditioned graphite and soot with less ordered structure are susceptible to faster mass losses than the ordered graphite and soot. This experimental data pattern is analogous to our observations for marine sediments where the abundance of disordered OC_{petro} decreases with the increasing transport distance from the shoreline.

The analogy drawn between our field observations and experimental constraints

suggests that in addition to the feasibility of OC_{petro} oxidation, the OC_{petro} degradability and the resultant form of graphitic carbon preserved in soils or marine sediment are intimately related to the initial maturity of OC_{petro}, and that CO_2 is very likely the end product of OC_{petro} oxidation. What remains unclear is how the OC_{petro} weathering prevails under the conditions that are totally different from the experimental setup (e.g., biotic catalysis/high water activity versus dry O_2 at temperatures up to 800 °C). Equally important is the extent to which the degraded component is converted to CO_2 or other forms of intermediate state, and how alike and the proportion of residual total organic carbon could be attributed to graphitic carbon.

On the other hand, the isotopic compositions illustrate the ^{13}C and ^{14}C abundances of total organic matters that could be sourced from residual graphitic carbon, newly introduced labile OC, and any other uncharacterized form of organic carbon (e.g., biofilm). Similar to the results of this (Figs. 6 and S3) and previous studies[7], the isotopic results could be further fed into the quantitative assessment that constrains the loss of organic carbon during soil development.

In summary, neither of these methodologies delineates any form of transitional organic compound other than graphitic carbon, nor do they resolve whether and to what extent CO_2 is produced during the transformation of highly mature graphitic carbon in rocks to the disordered form in soils or during the elimination of the disordered form in marine sediments.

Nevertheless, to assess whether Raman parameters can be quantitatively correlated to compositional data, the correlation between f_{ox} and Raman data is examined as the reviewer advised (Fig. S5). These parameters include the derived temperature based on the relative area of D and G bands, the total width of D and G bands, and the Raman distance based on the maturity difference assessed by the total width and derived temperature between individual analyzed particle versus the averaged rock characteristics. No correlation is found between these two datasets, suggesting compositional complexity of the entire OC entity. Since Raman data provide the ordering status of individual OC_{petro} particles, both datasets may be better correlated only when the graphitic carbon dominates the OC pool. In summary, the current model for OC_{petro} oxidation is limited by the lack of detailed characterization of the target organic entities using various spectroscopic and compositional analyses. It is also essential to experimentally resolve the reaction pathway and kinetics for the oxidation of graphitic carbon under ambient conditions, and to validate the collected parameters in field observations. We have added this part to Discussion, Supplementary Note 3 and Supplementary Discussion 1.

Comment 2-02: Additionally, the analysis of the mineral associated OCpetro needs

clarification and re-assessment.

Response 2-02: Thanks for the suggestion. We have revised the categorization for the relationships between minerals and OC_{petro} and the presentation (Fig. 4) for the frequencies of associated minerals across different compartments in the investigated catchment by plotting the abundances of attached minerals in the order of material transport (from source rock to weathered materials, river sediments and marine sediments). The variation in mineral abundance can be better visualized and discussed in the context of physical transport.

To clarify the mineral-OC_{petro} relationships, only two categories are defined and used here with each embedded with testable criteria for the application to other studies. The first one is the "attached" category, which corresponds to the direct mineral-OC_{petro} association with minerals identifiable by current instrumentation setting. Two potential occurrences are assigned to this category: (1) The target OC_{petro} particle is surrounded by or covered with minerals. For most analyzed spots, the identified minerals are transparent. Even if the mineral overlays completely on OC_{petro} particle, the Raman spectra for both mineral and OC_{petro} can still be acquired. (2) The target OC_{petro} particle is present without any clear, visible association with minerals. However, the Raman spectra of mineral in addition to OC_{petro} can be acquired. For this occurrence, it is suspected that the mineral is too small to be microscopically visible but detectable by the laser beam with a size of ~1 μm. Therefore, the mineral-OC_{petro} signal acquired from the same laser spot is interpreted as the mineral attached with OC_{petro}. If no signal or signals other than minerals are detected, the OC_{petro} is classified as "non-attached" category. Three potential occurrences of OC_{petro} are classified into this category: (1) The target OC_{petro} is a free particle. (2) The target OC_{petro} is underlain by minerals. Because OC_{petro} is microscopically and spectroscopically opaque, the underlain mineral phase could not be resolved. (3) The target OC_{petro} is microscopically attached with materials unidentifiable under current instrument setting. These materials might include minerals with indiscernible weak Raman signals and organic materials (e.g., biofilm) as inferred by the brownish appearance of OC_{petro} and/or high spectral background. As soils and sediments are commonly enriched with organic matters, organics-induced fluorescence may generate a high background that can impede the identification of specific organic compounds and organics-incorporated clay minerals[13-15,26].

Additionally, while the clay fraction (<2 μm) exported from the Beinan River to offshore sediments has been reported to comprise 58% of illite, 35% of chlorite, 5% of smectite and 2% of kaolinite[27], their summed fraction is supposed to be a small fraction considering the median grain size of 24.9 μm at the river mouth[28]. The diluted fraction combined with the small size of clay render the detection of OC_{petro}-clay association (only particles with a size between 20–60 μm were measured in this study) challenging.

Overall, the four most prevalent minerals identified in this study include three common rock-forming minerals (quartz, mica, feldspar) and a widely distributed accessory mineral (rutile) in metamorphic rocks. Clay minerals that have been reported as an efficient agent for the protection of organic matters[29,30] were not found because of the potential interference of high spectral background, diluted fraction, and small size that was excluded from the microscopic screening. We have amended further description to Method.

Comment 2-03: 58: Make sure to cite this paper instead of or with the Torres et al. 2014 paper: The role of sulfur in chemical weathering and atmospheric CO2 fluxes: evidence from major ions, δ13CDIC, and δ34SSO4 in rivers of the Canadian Cordillera; J Spence, K Telmer; Geochimica et Cosmochimica Acta, 2005

Response 2-03: Thank you for the suggestion. We have added the citation to the manuscript.

Comment 2-04: 60: Which earth system model? Or do the authors mean the models in general?

Response 2-04: Here we described that OC_{petro} was neglected in the past when considering the major pathways involved in global carbon cycle. "The Earth system model" has been removed to avoid confusion.

Comment 2-05: 61: Look at work done by M. Ogric as well for OCpetro oxidation.

Response 2-05: Thank you for the reminder. We have added the citation to the manuscript.

Comment 2-06: 72: Is it well established that highly graphitized OCpetro is related to low microbial oxidation in laboratory studies?

Response 2-06: To our knowledge, the biodegradability and reaction rate of highly graphitized OC_{petro} as compared to the disordered OC_{petro} have not been tested in the laboratory likely because the reaction is slow and the potential strains or natural assemblages responsible for the degradation of graphite have not been identified or cultivated. Previous studies, as described in response 2-01, have revealed that the introduction of defects and functional groups lowers the temperature corresponding to significant oxidation of graphite and leads to more rapid and significant weight loss[4,5]. In addition, the soot with less ordered structure tends to be oxidized at a faster pace than the rather ordered one, leaving the residual soot characterized by more ordered structure[6]. Although lab-scale experiments proceed under the dry condition at high temperature, the experimental results provide lines of evidence that may be further

extrapolated to the biologically mediated scenario under ambient conditions. In this regard, highly graphitized OC_{petro} could be inferred to be more resistant to weathering and microbial activities than the disordered one.

Comment 2-07: 87: Make sure to specify that this refers to Taiwanese rivers not all rivers or POC.

Response 2-07: Thank you for the reminder. We have rephrased the sentence and added other citations in the manuscript as "While OC_{petro} contributes a large fraction to exported particulate OC in small mountainous rivers in Tawian, New Zealand and the Andes (could be up to 70–80%[31-33]; often by definition of zero radiocarbon activity)..." to avoid confusion.

Comment 2-08: 97-98: What do the authors mean by "lumping nature of OC entities through various treatments?" Sampling treatments? Please be specific and clarify what is meant by this statement.

Response 2-08: This description was originally used to state the fact that compositional analyses integrate the abundance and isotopic characteristics of the entire OC entity. Potential biases could arise because OC subject to various treatments and analyses could be attributed to a spectrum of structural and compositional entities. As raised in response 2-01, the isotopic compositions illustrate the ^{13}C and ^{14}C abundances of total organic matters, including remaining graphitic carbon after oxidation and newly introduced labile OC (e.g., biofilms). We have rephrased this sentence as "potential biases could arise due to the fact that OC subject to various treatments and analyses described above is attributed to a spectrum of structural and compositional entities." to avoid confusion.

Comment 2-09: 157-158: What different metrics were used to assess the different degrees of weathering? Is major element or tau values included here?

Response 2-09: The degree of weathering was differentiated based on observations conducted in the field. Along the weathering gradient, the sample with the least weathering degree was composed of fragmented and fine-grained bedrock which was interbedded with its relatively intact parent counterpart. By contrast, the most weathered sample was collected from a vegetated soil profile composed of dark brownish humic substances. Although measurements of major and trace elements and derived tau values can assess the degree of soil development and mineralogical loss through weathering, these parameters are not specifically relevant to the transformation or loss of OC_{petro}. Additionally, while the weathering front can be defined by the strong variation in tau value, the same principle may not be applicable to the weathered

materials associated with talus deposit generated by the landslide. The precursors to the current weathered materials may have experienced different degrees of weathering and even multiple events of landslides. In active tectonic region like Taiwan, the subsequent soil development is often not long enough (see Discussion on soil residence time) to re-develop a typical profile of elemental loss through weathering. Therefore, tau values will be invalid for samples collected from different profiles susceptible to repeated landslide events.

Comment 2-10: 171: What is the rational for only measuring the fine particulate fractions?

Response 2-10: Sediment organic compositions and concentrations vary with different size fractions[3,34,35]. In general, finer sediments have higher total organic contents primarily because higher surface area enables higher absorptive capacity of organic matters[36,37]. The complexation between organic compounds and clay minerals is known to even generate better organic protection against biodegradation. In contrast, large sediment particles tend to be composed of rock detritus with low organic contents and biological remnants (e.g., plant or animal tissues). In this regard, the selection of size fraction for analyses was set to balance the maximum extraction of specific target and the efficiency in sample processing and analyses. The study utilized the materials sieved to less than 63 μm to capture the spectroscopic and compositional characteristics of OC_{petro}. Additionally, in order to enable representative and comparable spectroscopic measurements between each sample, extremely small particles were avoided.

Comment 2-11: 200-201: please report all radiocarbon values as either Fm (Fraction modern) as is the convention or delta 14C (14C).

Response 2-11: Thank you for the reminder. We have revised the notation in all the texts, tables and figures.

Comment 2-12: 258: What are the conventional methods?

Response 2-12: The conventional method is to acquire the Raman spectra of graphitic carbon below a transparent mineral on polished thin sections cut perpendicular to the foliation rather than raw sediments randomly oriented. The conventional method is used to avoid the potential spectroscopic interference by mineral orientation and artificial defects generated by polishing. Therefore, the derived temperature based on G and D bands can be compared between samples. Such an approach has been validated and adopted in studies focusing on the acquisition of metamorphic P-T conditions. For sediment samples like in this study, the oriented thin section is practically infeasible to prepare. While the derived temperature is still a useful parameter to describe the

maturity of graphitic carbon, it would be a priori to validate the utility of the derived temperature for randomly oriented sediments (or graphitic carbon). Our results demonstrate that the derived temperature ranges of rocks obtained from this study are comparable with those for the same catchment from previous studies, suggesting that the derived temperature can potentially differentiate the relative maturity of graphic carbon. Still, it should bear with great caution to use the derived temperature described here to infer or discuss the metamorphism condition and cooling history.

Comment 2-13: 269-271: How were the weathered materials calculated or quantified?
Response 2-13: The degree of weathering was differentiated based on observations in the field and consistent with the degree of soil development as raised in response 2-09.

Comment 2-14: 277-279: This needs to be re-accessed, OCpetro by definition is not biospheric, ie it is from the rock and is incorporated into the rock during sedimentation during the geological past. The timescale must be defined here, because it is very unclear how it is currently written.
Response 2-14: We are clearly aware of the fact that OC_{petro} is not biospheric OC. What we have tried to address or argue for the first scenario here is whether the graphitic carbon in the investigated rock-soil profiles can be derived from the conversion of biospheric carbon to disordered/ordered OC_{petro} through diagenesis or even metamorphism over a geological time scale on site. Such a scenario is opposite to the common perception that the observed pattern is more likely related to the degradation on the metamorphically-derived highly ordered OC_{petro} in active orogens, and has been demonstrated with a 5-km thick marine sediment core where extremely disordered OC_{petro} in the upper core was transformed to relatively ordered OC_{petro} at the core bottom extending from Oligocene to Miocene [38]. The in situ deposition scenario is ruled out by assessment using the data of geology and tectonic activity in the region. The sentence has been revised as "To address the first mechanism, diagenesis/metamorphism converts biologically derived OC (e.g., plants and algae) into OC_{petro} at >50 °C over geological time scales (e.g., tens of thousands of years)." to avoid confusion.

Comment 2-15: 302-309: This would be useful to point to the work by Petsch et al. 2001 which showed direct biological assimilation
Response 2-15: Thank you for the reminder. Indeed, the work by Petsch, et al. [39] establishes the foundation of further investigations in OC_{petro} oxidation. We have added the citation to the section ahead of the statement of priming effect.

Comment 2-16: 331: Be careful with these assumptions, "old refractory organic matter" age does not necessarily mean refractory.

Response 2-16: Thank you for the reminder. We are aware of the fact that the terms "old" and "refractory" are used on the basis of different approaches and principles. Structurally and chemically complex entities cannot be clearly defined with a single analytical approach. However, as compared to the newly introduced labile organic carbon, the old organic carbon generally has experienced a history of diagenesis and metamorphism at high temperatures and pressures, both of which enable the polymerization and volatilization of organic compounds. Therefore, the old organic carbon is generally considered to bear greater resistance (or be more refractory) to weathering. As any of these terms has been used mostly in a qualitative fashion, only the definition of "old" OC_{petro} is clearly provided in the modeling of f_{ox}. The context has been revised more clearly in the manuscript.

Comment 2-17: 351: Is there evidence from these data to suggest this is true?

Response 2-17: No, there is no any solid evidence available to support this assertion. However, as raised in response 2-01, the abiotic oxidation of graphite is conducted at high temperature with preexisting defects[4-6]. Unlike extreme conditions employed in lab experiments[40], the involvement of microorganisms in ambient degradation of OC_{petro} could be deduced from the alteration of spectral characteristics accompanied with the modeled oxidation fraction of OC_{petro} manifested by radiocarbon analyses.

Comment 2-18: 427: There is not an intrinsic recalcitrance of organic matter. The reactivity of OC is environmentally derived. Hemingway et al. 2019.

Response 2-18: The sentence states previous findings and our observations that organic matters with complex and ordered structures (e.g., OC_{petro}, lignin and aliphatics) are more resistant to weathering than labile ones (e.g., simple sugar and amino acid)[41]. This intrinsic nature can cause selective degradation of organic matters under the same environmental condition. To avoid confusion, the sentence has been removed.

Comment 2-19: 439-448: it is unclear to me how the determination of the "within minerals", "attached" and "non-attached" are determined. This is essential to understand if OCpetro is accessible to microbes for oxidation. However, it seems (to me) that any OCpetro is inherently intertwined with minerals, It IS the mineral because it is the weathered rock material. This is a very interesting topic but needs to be fully flushed out in the discussion and needs more explanation how these categories are created.

Response 2-19: Thanks for the suggestion. We note that the original criteria for

mineral-OC$_{petro}$ categorization is not sufficiently clear and applicable. We have revised it and described the details in response 2-02. In short, only two categories are defined and used here with each embedded with testable criteria for the application to other studies. The first one is the "attached" category, which corresponds to the direct mineral-OC$_{petro}$ association with minerals identifiable by current instrumentation setting. The second one is the "non-attached" category where no signal or signals other than minerals are detected.

Comment 2-20: 450-454: in the weathered materials what about clay minerals? It seems strange that there is preservation of mica in these phases. If that is not the case, I would suggest some alteration of these categories.

Response 2-20: The detection of clay minerals from weathered materials and sediments appears to be challenging under the current instrumental setting. For one aspect, clay minerals often tend to associate with organic matters due to its higher absorptive capability and capacity[29,30]. However, as being described in response 2-02, organic compounds may induce high fluorescence background, potentially masking the spectra of clay minerals. Another aspect is that particles with a small size (<20 um) were heterogeneously distributed among samples and difficult to resolve the authenticity of OC$_{petro}$ and the mineral-OC$_{petro}$ relationships, and, therefore, were excluded from spectral analyses (only particles with a size between 20–60 μm were measured in this study). Finally, the small size of clay fraction can easily suffer from the great dilution factor contributed by other major minerals (e.g., quartz and feldspar). While clay minerals are prevalent in various compartments of the catchment and marine sediments, this fraction of fine particles is often excluded from spectroscopic characterization.

Identification of mica by the Raman spectra bears with very limited uncertainty. Therefore, our abundance pattern for mica and other minerals depicts their combinative capability against chemical weathering and physical destruction (abrasion and pulverization). Our results reveal a strong dissociation of mica-OC$_{petro}$ relationship during the sediment transport. The selective elimination of mica may result from the vulnerability of platy structure susceptible to the physical abrasion and grinding associated with sediment transport across river and marine environments. Further description for these two parts has been added to Method and Discussion.

Comment 2-21: 446: Is rutile assumed to be associated with OCpetro? This doesn't make sense, there is not well documented accounts of Ti based minerals being associated with organic matter or carbon, potentially this is just a consequence of both phases resisting both transport and weathering but are not actually associated with one another.

Response 2-21: Please refer to response 2-02 where the categorization for mineral-OC_{petro} is defined and applied. In brief, the physical association between OC_{petro} and rutile has been observed in various samples. The fact that the association survives from gentle grounding during sample processing suggests the authenticity of rutile-OC_{petro} relationships. Rutile is indeed more resistant to transport and weathering. The rutile-OC_{petro} abundances do not vary substantially across different compartments (except for elevated abundances for Intermediate grade in weathered materials and Mildly Graphitized carbon in marine sediments), attesting its resistance to various geological processes. The high abundance of rutile might also imply a specific occurrence related to the preservation of OC_{petro}. How this association relationships could be translated into the protection mechanism remains uncertain.

Comment 2-22: 471-473: This doesn't make sense to me, potentially the authors meant that the pattern is "inconsistent" not consistent, because the mica is likely to be weathered quickly, the OCpetro is unlikely to be protected by this mineral phase, because it is susceptible to "abrasion and biodegradation". It is also interesting to me that the mica phases are in the weathered materials, could this be an "interference of clay minerals". Is there independent XRD data to confirm or calibrate the ramen mineral data?

Response 2-22: Thank you for the suggestion. Our results reveal a strong dissociation of mica-OC_{petro} relationship but comparable abundances of feldspar during the sediment transport. The pattern is inconsistent with the dissolution rate determined from theoretical calculations with experimental constraints through which plagioclase dissolves at a rate about one, or even up to three[20], order(s) of magnitude greater than that of mica group (e.g., muscovite and phlogopite) [21]. Even considering that feldspar may be falsely identified as laumontite (zeolite group) with similar spectral characteristics, their dissolution rates are comparable to each other[22]. The chemical weathering processes cannot account for the observed patterns of mineralogical abundances across different compartments. Instead, the selective elimination of mica may result from the vulnerability of platy structure susceptible to the physical abrasion and grinding associated with sediment transport across river and marine environments. We have amended further discussion to the manuscript

Identification of mica by the Raman spectra bears with very limited uncertainty. Clay minerals that have been reported as an efficient agent for the protection of organic matters[29,30] were not found because of the potential interference of high spectral background, diluted fraction, and small size that was excluded from the microscopic screening as discussed in response 2-02. Current experimental setting might not be able to generate identifiable clay mineral spectra. Since the protection provided by clay

minerals is beyond the scope of this study, therefore, further analyses targeting at clay fraction are not performed.

Comment 2-23: 473-479: This does not make sense to me. Feldspar is less resistant to weathering than mica in this study (Not in the literature). There is some discrepancy in these statements that is very confusing?

Response 2-23: Thank you for the reminder. In order to clarify the discussion, we have reorganized this paragraph as shown in response 2-22.

Comment 2-24: 485-486: This statement is only consistent if the OC is from the vegetation, but the OCpetro is inherently in the mineral phase already, because it IS the mineral! It is from the rock. The next sentence is correct, but these ideas need to be better, more consistently integrated within this argument.

Response 2-24: OC_{petro} is generally considered as carbonaceous materials transformed from the biospheric OC through diagenesis or metamorphism. Spectroscopically, OC_{petro} resembles graphite to various degrees. However, its exact structure and composition are neither clarified nor fixed (response 2-01), thereby rendering it not eligible to be a mineral by strict definition. In this regard, we prefer to treat OC_{petro} as OC and differentiate the association with surrounding minerals (response 2-02).

Comment 2-25: 492: destructed is not used correctly here

Response 2-25: Thank you for the reminder. We have changed it to "eliminated" and added the "physical abrasion".

Comment 2-26: 500: while pMC is technically correct, it is an outdated notation, and should be changed to either Fm or 14C.

Response 2-26: Thank you for the reminder. We have revised the notation in all the texts, tables and figures.

Comment 2-27: 502: Where did this biospheric endmember come from? Can the authors cite it or say from which samples it was calculated for?

Response 2-27: The biospheric endmember for radiocarbon activity came from wax fatty acids from vascular plant in soils measured by Hemingway, et al. [7]. We have added the citation.

Comment 2-28: 520: These are large ranges of OCpetro oxidation, what other studies show this large of a range? Can there be a better justification for the fox used in each of these catchments? This is a huge range in exhumation rate and in the derived CO2

flux. Is it likely all of the OCpetro which is "weathered" is fully oxidized to CO2?

Response 2-28: The large uncertainty of carbon flux is primarily related to a large range of $TOC_{bedrock}$, f_{ox} and denudation rate reported previously and derived in this study for the investigated catchment. In particular, the denudation rate used for the flux calculation was set at a range (1.5 to 10 mm yr^{-1}) that covered the reported values. Therefore, the derived flux would correspondingly span near an order of magnitude. To refine the flux estimate, individual derived parameters are examined. First, f_{ox} is susceptible to localized characteristics of soil, plant, landscape, bedrock and climate that can vary over a considerable range within a small spatial scale in the investigated mountainous catchment. To investigate their possible variation, the modeling for f_{ox} is performed on individual samples using their corresponding $TOC_{bedrock}$. The resultant f_{ox} values are further categorized in accordance with lithology and averaged to yield 0.65 ± 0.12 for slate and 0.49 ± 0.29 for schist. For the second parameter, the erosion/denudation rate varies substantially, depending on the time scale inherited by individual methodologies. On a decadal time scale, the erosion rate based on riverine sediment yield has been estimated to be 20.9 mm yr^{-1} [8]. This rate could have been further refined to a range of 4–5 mm yr^{-1} using the alternative rating curve that has been considered to better cover the possible discharge range[9]. Over a millennium time scale, the denudation rate based on the exposure age derived from cosmogenic ^{10}Be has been reported to be 4.54 ± 1.86 mm yr^{-1} [10]. For comparison, the sediment accumulation rate constrained by zircon U-Pb ages has been estimated to be 5.14 mm yr^{-1} over the recent ~2 Ma [11]. The million-year scale exhumation rate based on fission-track thermochronology has been estimated to be 1.5–10 mm yr^{-1} [8]. In this regard, the erosion rate of 4.5 ± 1 mm yr^{-1} is arbitrarily chosen to accommodate a considerable range of rates derived from different methodologies across the contemporary-geological time scales. Considering that OC_{petro} oxidation is also strongly tied to the landscape and climate that have been comparable with modern characteristics in the investigated catchment for thousands of years, the designated rate (4.5 ± 1 mm yr^{-1}) may be even more reliable. Using these two parameters and the average $TOC_{bedrock}$, the carbon fluxes are calculated to be 23 ± 7 tC km^{-2} yr^{-1} for slate and 33 ± 21 tC km^{-2} yr^{-1} for schist. If the variation in $TOC_{bedrock}$ (0.28 ± 0.23% for slate and 0.53 ± 0.39% for schist) is taken into account, the oxidation flux would exhibit a much broader range. At this stage, the computed flux is still variable primarily owing to the availability and spatial coverage of individual parameters. More data would be helpful to determine whether the consensus of computed fluxes could be reached. We have added this part of discussion to Supplementary Note 4.

Comment 2-29: 530: What does the phrase "adopting the data" mean here? Please

clarify.

Response 2-29: The sentence described that the previous estimate was based on the same approach and the data for this and other geologically different catchments. We have revised the sentence as "The results are in the same order of magnitude as the previous estimate based on the same approach and the data for this and other geologically different catchments…".

Comment 2-30: 541: What about in the Amazon flood plains? Even in this low erosion rate area there are significantly increased OCpetro oxidation occurring: Dellinger et al. 2023 PNAS

Response 2-30: Thank you for the reminder. The OC_{petro} oxidation in large river systems proceeds in multiple compartments along the transit. The best example probably lies in the Amazon system. Using the Re proxy for OC_{petro} oxidation, Dellinger, et al. [19] quantified the riverine Re fluxes from the upstream Andean catchments to the midstream floodplain and converted them to the fluxes of OC_{petro} oxidation. Their results demonstrate that the flux of OC_{petro} oxidation for the floodplain constitutes 40% of the overall oxidative flux and is only slightly less than that from the mountainous catchments (46%), suggesting that the long-term storage in the low-relief riparian zone of the big river system facilitates further degradation of OC_{petro} drained from high-relief mountainous regions. Such a flux pattern may greatly exceed that for small catchments in high standing islands (like that in this study) due to different spatial and time scales for the sediment storage in floodplain and/or delta. We have revised the discussion and comparison with the Amazon study accordingly.

Comment 2-31: 557: Could this not be the other way around, that the more disordered graphite is actually because the highly ordered graphite was never formed, rather than it is being broken down?

Response 2-31: This and previous studies[42] both reveal that maturities of ordered OC_{petro} for rocks are similar regardless of the sample preparation (response 2-12) and in agreement with the metamorphic grade based on isotopic fractionation and thermogeochronology[43,44]. No disordered OC_{petro} has been found in bedrocks. Therefore, the potential occurrences for disordered OC_{petro} have been discussed. These processes include on-site early diagenesis, entrainment of exogenous OC_{petro}-alike carbons, and the degradation of highly ordered OC_{petro}. The first two possibilities have been ruled out as discussed in the manuscript.

Comment 2-32: Fig 1. Is there a way to maybe create a different color for the formations and the water? The bathymetric map when first glancing at it, is hard to

distinguish from the Tanano Complex. I know it is labeled, but a more distinct color could eliminate any confusion.

Response 2-32: Thank you for the suggestion. We have revised the map to ensure the clarity.

Comment 2-33: Fig 2. The caption needs to be more descriptive. If one is not an expert in Ramen then the different axis doesn't mean much, it would be helpful to add some method explanation, such as what each axis means in a fundamental sense. What is the reader supposed to take away from this figure? It seems like that the weathered material is fundamentally different than the other sampled materials.

Response 2-33: Thank you for the suggestion. We have added further explanation to the figure caption as the following, "Raman spectroscopic characteristics with sample types color coded. Plots of (a) D1 vs. G positions (cm⁻¹) and (b) FWHM (full width at half maximum) of D1 vs. G (cm⁻¹). FWHM is an alternative parameter to evaluate the maturity of graphitic carbon (decreases with increasing maturity). Raw deconvoluted data can be found in Supplementary Materials."

Comment 2-34: Fig 3. Please expand the axis to be across the two bottom plots and the three upper ones. Additionally, the two different blue colors are extremely hard to distinguish. Is it necessary to have the Di (Disorder OCpetro? Since only one sample total falls into this range?). The calculated temperature what does this mean in this figure and what is the total width? From the ramen experiments? Please be more descriptive in the caption? In d and e, how is an Estuary a site lithology? Should this just be a sediment derived from wither schist or slate?

Response 2-34: Thank you for the suggestion. As the criteria for categorization follows the approach described in Sparkes, et al. [45], we tend to keep all the categories in the figure for data comparisons. The figure has been revised in accordance with the reviewer's suggestion (Fig. 3). The figure caption has also been expanded to be more explanatory for general readers.

Comment 2-35: Fig 4: Maybe the best way to show these data is to compare across the gradient of samples. A very important question that doesn't necessarily come through in this figure is the trying to understand what is transported to the marine sediments. Isn't it a little odd that the weathered material does not seem to reflect what is in the bedload, suspended load to marine sediments. Is the mildly graphitized and intermediate grade OCpetro different in crystallinity? Or just the absence of graphite in the IG samples? What is the real difference in crystal structure between these two and does it relate to reactivity? In A. what does this reflect? What is the %OC or the

%graphite in these samples, these as relatives without context make these data hard to interpret.

Response 2-35: Fig. 4 has been revised in accordance with the reviewer's suggestion. For detailed illustration, please refer to response 2-02. Raman spectroscopy measures the maturity/crystallinity of graphitic carbon rather than the percentage of graphite in each sample. The maturity of graphitic carbon is related to the abundances of defects and functional groups, and therefore to reactivity as raised in response 2-01. Between rock and weathered materials, the ratio of each OC_{petro}-mineral group remains at nearly a constant at Mildly graphitized level, suggesting the original resistance of ordered OC_{petro} to weathering processes regardless of mineral association. For comparison, the abundances of mica-OC_{petro} association at both graphitization levels decrease substantially from rock to river and marine sediments, suggesting the less resistance of mica against the physical abrasion and pulverization along the river and marine transits. The detailed description and interpretation for the observed data pattern have been revised and added to the manuscript.

Comment 2-36: Fig 6. pMC is an outdated metric for radiocarbon reporting. Please convert to FM or 14C (‰).

Response 2-36: Thank you for the reminder. We have revised the notation in the text, figure and table.

Reviewer #3 (Remarks to the Author):

Comment 3-01: Below I explain the main two points where I think the current manuscript can be improved (see also detailed comments below): i) give more details on how the OCpetro oxidation rate (and the large uncertainty) is calculated, because it is lacking sufficient explanation in the current manuscript. This can be added in the supplementary materials and not necessarily in the main text; ii) Add a synthesis or recap figure (figure 7) showing: the pathway of OCpetro, the two stages OCpetro oxidation, where microbial oxidation takes place, the respective contribution of soil (with disordered graphitic carbon) vs. bedrock (highly mature graphitized OCpetro) and CO2 release fluxes. That would help the reader to visualize the whole picture.

Response 3-01:

(i) Thank you for the suggestion. The OC_{petro} oxidation flux is estimated as the following equation:

$$Oxidation\ flux = TOC_{bedrock} \times f_{ox} \times \rho \times r$$

where $TOC_{bedrock}$ represents the average of total organic content for slate (0.28%) and schist (0.53%), and f_{ox} is the oxidation fraction of OC_{petro} (0.65 ± 0.12 for slate and 0.49 ± 0.29 for schist), ρ represents rock density (assumed to be 2.8 g cm^{-3}), and r is erosion rate. The error of each variable is propagated to generate the uncertainty of the oxidation flux. The large uncertainty of carbon flux is primarily related to a large range of $TOC_{bedrock}$, f_{ox} and denudation rate reported previously and derived in this study for the investigated catchment. In particular, the denudation rate used for the flux calculation was set at a range (1.5 to 10 mm yr^{-1}) that covered the reported values. Therefore, the derived flux would correspondingly span near an order of magnitude. To refine the flux estimate, individual derived parameters are examined. First, f_{ox} is susceptible to localized characteristics of soil, plant, landscape, bedrock and climate that can vary over a considerable range within a small spatial scale in the investigated mountainous catchment. To investigate their possible variation, the modeling for f_{ox} is performed on individual samples using their corresponding $TOC_{bedrock}$. The resultant f_{ox} values are further categorized in accordance with lithology and averaged to yield 0.65 ± 0.12 for slate and 0.49 ± 0.29 for schist. For the second parameter, the erosion/denudation rate varies substantially, depending on the time scale inherited by individual methodologies. On a decadal time scale, the erosion rate based on riverine sediment yield has been estimated to be 20.9 mm yr^{-1} [8]. This rate could have been further refined to a range of 4–5 mm yr^{-1} using the alternative rating curve that has been considered to better cover the possible discharge range [9]. Over a millennium time scale, the denudation rate based on the exposure age derived from cosmogenic ^{10}Be has been reported to be 4.54 ± 1.86

mm yr^{-1} [10]. For comparison, the sediment accumulation rate constrained by zircon U-Pb ages has been estimated to be 5.14 mm yr^{-1} over the recent ~2 Ma [11]. The million-year scale exhumation rate based on fission-track thermochronology has been estimated to be 1.5–10 mm yr^{-1} [8]. In this regard, the erosion rate of 4.5 ± 1 mm yr^{-1} is arbitrarily chosen to accommodate a considerable range of rates derived from different methodologies across the contemporary-geological time scales. Considering that OC_{petro} oxidation is also strongly tied to the landscape and climate that have been comparable with modern characteristics in the investigated catchment for thousands of years, the designated rate (4.5 ± 1 mm yr^{-1}) may be even more reliable. Using these two parameters and the average $TOC_{bedrock}$, the carbon fluxes are calculated to be 23 ± 7 tC km^{-2} yr^{-1} for slate and 33 ± 21 tC km^{-2} yr^{-1} for schist. If the variation in $TOC_{bedrock}$ (0.28 ± 0.23% for slate and 0.53 ± 0.39% for schist) is taken into account, the oxidation flux would exhibit a much broader range. At this stage, the computed flux is still variable primarily owing to the availability and spatial coverage of individual parameters. More data would be helpful to determine whether the consensus of computed fluxes could be reached. We have added this part of discussion to Supplementary Note 4.

(ii) Thank you for the suggestion. We have added a schematic diagram to illustrate the two-stage oxidation of OC_{petro} (Fig. 7).

Comment 3-02: Line 63: Not that the most recent and accurate estimate is 68 Mt/yr (Zondervan et al., 2023)

Response 3-02: Thank you for the suggestion. We have revised this sentence as "With the approaches such as isotopic mass balance model or riverine Re proxy, the global oxidation flux of OC_{petro} has been estimated to be 68_{-6}^{+18} MtC yr^{-1}, a quantity comparable with other geological sinks (140 MtC yr^{-1} for silicate weathering and 40–75 MtC yr^{-1} for sedimentary burial of terrestrial biospheric OC)".

Comment 3-03: Lines 64 and 65: CO2 drawdown by silicate weathering is 140 Mt/yr before carbonate precipitation in the ocean and 70 Mt/yr after carbonate precipitation (on timescales longer than 10^4 years). Biospheric OC burial is estimated to be 170 Mt/yr in the present-day (Hilton and West, 2020). Please correct the 40-75 MtC/yr number or indicate more precisely what does it correspond to?

Response 3-03: Thank you for the suggestion. Because we focus on the terrestrial weathering process and its contribution to carbon cycling through rivers, the total volume of OC burial in the ocean (170 MtC yr^{-1}) is not quoted in the manuscript. Instead, the burial flux of biospheric OC derived from land (40–75 MtC yr^{-1}) [18] is compared with other geological carbon fluxes. We have added the citation and rephrased this

sentence as "With the approaches such as isotopic mass balance model or riverine Re proxy, the global oxidation flux of OC_{petro} has been estimated to be 68^{+18}_{-6} MtC yr^{-1}, a quantity comparable with other geological sinks (140 MtC yr^{-1} for silicate weathering and 40–75 MtC yr^{-1} for sedimentary burial of terrestrial biospheric OC)" to avoid confusion.

Comment 3-04: Line 87: according to Galy et al., (2015), "global biospheric and petrogenic POC fluxes of 157 and 43 megatonnes of carbon per year, respectively" so no the majority of exported particulate OC is composed of OCbio, not OCpetro. Please correct here

Response 3-04: The sentence is referred to the context of small mountainous rivers, which export large amounts of OC_{petro} to the ocean. We have rephrased the sentence as "While OC_{petro} contributes a large fraction to exported particulate OC in small mountainous rivers in Tawian, New Zealand and the Andes (could be up to 70–80%[31-33]; often by definition of zero radiocarbon activity)..." to avoid confusion.

Comment 3-05: Line 275: what is "in-situ diagenesis"? and what is "exotic"? Define the terms or use terms that are more accurate

Response 3-05: "In situ diagenesis" means that OC experiences early diagenesis on site. What we have tried to address or argue for the first scenario here is diagenesis/metamorphism converts biologically derived OC (e.g., plants and algae) into OC_{petro} at >50 °C over geological time scales (e.g., tens of thousands of years). Such a scenario has been demonstrated with a 5-km thick marine sediment core where extremely disordered OC_{petro} in the upper core was transformed to relatively ordered OC_{petro} at the core bottom extending from Oligocene to Miocene[38]. However, considering the geothermal gradient in the orogens (29–35 °C km^{-1}) [46], the depth required for the conversion of biospheric carbon to OC_{petro} would be ~1.5 km below the surface. Such on-site deposition scenario is ruled out by the lack of thick and stable depositional environments in the region under dynamic tectonic activity. "Exotic low-maturity OC_{petro}" is attributed to the graphitic carbon that was imported from the source other than rock (e.g., soot). We have added the above discussion and revised the sentence as "Three potential mechanisms might be involved in such spectroscopic transformation, including: (1) on-site early diagenesis of non-graphitic OC, (2) entrainment of exogenous OC_{petro}-alike carbons into weathered materials, and (3) in situ degradation of high-maturity OC_{petro}." to avoid confusion.

Comment 3-06: Lines 367-368: when you say "negligible" is it possible to give a quantitative constraint or not? (<1%, <5%, <10%?)

Response 3-06: Only OC_{petro} with highly disordered structures from weathered materials can be unequivocally recognized by Raman parameters, while the origin of ordered OC_{petro} between rock detritus and weathered materials cannot be distinguished. In lines 367–368, the contribution of weathered materials to river sediments was specifically referred to disordered OC_{petro} and considered to be negligible based on the scarcity of disordered OC_{petro} in river sediments. For comparison, the percentage of the disordered to total OC_{petro} near the estuary at NOR3-1 is 66% (31/47), suggesting that instead of accumulating in river sediments, weathered materials tend to rapidly transit through fluvial systems and deposit in marine sediments. We have revised the sentence and added further discussion to the manuscript.

Comment 3-07: Lines 368-370: how does it compare with data and interpretation from Hilton et al., (2010)?

Response 3-07: Our compositional data pattern (C/N ratios and $\delta^{13}C$ values) is similar to that reported in the previous study[47]. This and previous studies both suggest a mixture of heterogeneous rock sources for river sediments. We have added the comparison to Discussion.

Comment 3-08: Lines 507-509: this is not very clear, why the « fitting results were reliable only when the OCpetro from different profiles were degraded at the same pace »? And why "This prerequisite is nearly impossible to accomplish at natural sites"?

Response 3-08: The original model treated the oxidation of OC_{petro} with the same parent materials, weathering intensity and weathering rate. In other words, all the soil data from different rock-soil profiles were fitted with single $TOC_{bedrock}$ and f_{ox}. The approach might be applicable to sedimentary terranes but appears to be unrealistic for active orogens with heterogeneous lithology, steep topography, and dynamic climate. As being revealed in this and previous studies[47], bedrock composition alone can even exhibit a wide variation. Furthermore, f_{ox} is susceptible to localized characteristics of soil, plant, landscape, bedrock and climate, thereby varying over a considerable range. The f_{ox} should be fitted for individual samples using their corresponding $TOC_{bedrock}$ and categorized in accordance with lithology as raised in response 3-01. We have added this argument to Discussion.

Comment 3-09: Line 524: what is the calculated catchment average TOCbedrock and fox? Also could you give here the average fox value for each rock type? (or after Line 520)

Response 3-09: The values of $TOC_{bedrock}$ and f_{ox} were 0.28 ± 0.23% and 0.65 ± 0.12 for slate, and 0.53 ± 0.39% and 0.49 ± 0.29 for schist, respectively. We have added the

value of each variable and detailed calculation to Supplementary Note 4. Thank you for the reminder.

Comment 3-10: Line 527: why such a large range of value (and uncertainty)? I suggest to give the details of the calculation in the supplementary materials (add one section). Maybe you could report two values, i.e. one calculated with 10Be erosion rate and one calculated with sediment gauging data?

Also, this calculation is based on soil data (weathered materials), but you show that this material is a "negligible" contribution to the suspended sediment load where intermediate and medium grade graphite dominates (indicating low OCpetro oxidation intensity). Is that not a bias in the calculation of total CO2 emission to extrapolate the f ox values from highly weathered soil to the rest of the catchment area? You use the most highly weathered setting to calculate CO2 emission, but these settings do not contribute much actually.

Response 3-10: The large uncertainty of carbon flux is primarily related to a large range of $TOC_{bedrock}$, f_{ox} and erosion/denudation rate for the investigated catchment. For detailed explanation and the assigned erosion rate for flux calculation, please refer to response 3-01. We have added calculation details to Supplementary Note 4. Thank you for the suggestion.

As suggested by the modeling, the oxidation fraction of OC_{petron} varies over a considerable range with an average of 0.65 ± 0.12 for slate and 0.49 ± 0.29 for schist, leaving a large fraction of residual weathered materials eroded and transported rapidly in the catchment. As the riparian zone is limited, the temporary storage and even degradation of OC_{petro} are minimized along the river channel. Therefore, disordered OC_{petro} in river sediments is essentially absent. Instead, the majority of weathered materials is probably drained and deposited in the estuary as evidenced by the high fraction of the disordered OC_{petro} to total OC_{petro} at NOR3-1 (66%). What still remains unknown is how the progress and pathway of OC_{petro} oxidation can be quantitively traced with the combination of spectroscopic and isotopic approaches. We have added this part and further details to Discussion.

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Review #1
Comment:
I appreciate the efforts that the authors have made to address the review comments. The clarifications and additional information provided, in both the text and figures, is sufficient.

Response:
Thank you for the positive feedback and for taking the time to review our revisions. We greatly appreciate your thoughtful comments, which have helped us improve the manuscript.

Editors
Comment:
At the same time we ask that you edit your manuscript to comply with our format requirements and to maximise the accessibility and therefore the impact of your work. Specifically, please clarify the technical parts of the figure captions for Figs 2 and 3, for which things like "bands" and "positions" are not easy to interpret for someone unfamiliar with the topic area.

Response:
Thank you for the feedback and suggestions which help us improve the readability and accessibility for a broader audience. The manuscript and supplementary files have been formatted in accordance with the requirements, as outlined in the Editorial Request Table. Additionally, the terms "positions" and "bands" in the figure captions have been clarified as "the center wavenumbers for specific Raman peaks" and "the ranges of wavenumbers for specific Raman peaks", respectively.