April 16, 2024

To the Editors and Associate Editors:

On behalf of me and my co-authors, I send you the revised manuscript titled "Navigating the complexity of detrital rutile provenance: Methodological insights from the Neotethys Orogen in Anatolia."

The manuscript investigates U-Pb and trace element data reduction, processing, and common Pb correction workflows using new detrital rutile U-Pb geochronology and trace element geochemistry results from the Late Cretaceous to Eocene Central Sakarya and Sarıcakaya Basins in Anatolia. We use our dataset to demonstrate how to navigate the complexities of natural datasets. We provide recommendations for common Pb correction, discordance calculation and data filtering that are applicable to detrital rutile and other common Pb-bearing detrital minerals. Additionally, to facilitate the standardization of data reporting approaches, we provide open access code as Jupyter Notebooks for data processing and analysis steps, including common Pb corrections, uncertainty filters, discordance calculations, and trace element analysis.

The second round of reviews of this manuscript (manuscript number egusphere-2023-1293) indicated minor revisions were needed before acceptance. One referee and the Associate Editor provided constructive comments that enabled us to clarify and strengthen the manuscript. The reviewer critiqued the number of U-Pb analyses discarded during data reduction and interpretations of the trace element data. The reviewer's comments are addressed below. The revised manuscript includes all of the changes and revisions indicated in our responses.

We thank the Associate Editor for comments, which mainly highlighted the reviewer's points, so we address them here. (1) We use the daily instrument tuning data of NIST612 glass and U-Pb precision to demonstrate that there are no analytical issues. The first-round revision manuscript was edited to emphasize that the rejection of analyses during data reduction is not a unique limitation of this study, but typical of many detrital rutile studies (see Discussion section). We reiterate that the number of discarded analyses is surprising, but is the result of a natural dataset and rather common in the literature. Our reply to Reviewer #4 provides further evidence that the number of rejected analyses is not due to analytical or data reduction errors. (2) Cumulative KDE distributions are commonly used and the difference between CKDEs and CDFs are not the focus of the manuscript. We updated the figures to CDFs. (3) To shorten the manuscript, we moved a significant portion of the discussion on discordance to the supplemental material, including the log-ratio method. Additionally, Reviewers 1, 2, and 4 commented on whether PCA is adding anything "new or interesting." In the manuscript text and reply to reviewers, we tried to demonstrate the many ways in which we have looked at the trace element data. In the end, the most insights are gained from Cr, Nb, and Zr values. In light of this assessment and the recommendation to shorten the manuscript, we moved the PCA text and figure to the supplemental material. (4) Regarding manuscript length, we shortened the manuscript by moving several sections of text and 3 figures to the supplemental material.

Thank you again for consideration of the revised manuscript.

Sincerely,
Megan Mueller

Response to the Reviewer #4's comments on manuscript egusphere-2023-1293

This paper from Mueller et al. details complexities around the dating of detrital rutile in rocks from Anatolia. It provides some information that are commonly not provided in geochronological datasets, to provoke discussion about how we can best treat these kinds of data and materials (i.e. detrital Pbc–bearing minerals that contain provenance-diagnostic trace elements and that can be dated by the U–Pb method). As this paper has already been reviewed, I have few comments about the abstract, introduction and "synopsis" (section 2), which have been altered quite heavily from the initial submitted manuscript and which appear to me to be a useful and concise discussion of relevant topics. The Geological context (section 3) is also perfectly followable in its current format, and the methodology (section 4) can also be easily parsed and appears robust to me. And, overall, the paper provides several interesting diagrams and discussion on topics related to dating of Pbc bearing phases.

Section 5.1 has my first comment. Here you state that 665 of your 1,277 analyses have been rejected (line 395). I am familiar with detrital rutile dating, and this seems to be uncommonly high. In general, however, I think that anyone would agree that methodologies that screen data must be applied lightly and applied only to improve the accuracy of the resulting dataset, and also that any screen that is too onerous can run counter to that purpose. As this is the most significant screen in your data processing workflow, it thus needs to be rigorously and extensively justified. Figure 3 attempts to do this, but it is a blunt tool for this task. Qualitative descriptions of unsuitable raw ICPMS signals are given, but reproducible thresholds to include or not to include a grain aren't provided. You identify three problems that are cause for you to discard grains. These are "spikiness", inclusions, and low-signals. Firstly, which of these three reasons is most significant, and in what proportion do these three categories occur? Secondly, a 'spiky' raw ICPMS signal can be a sign of poor gas flow in the analytical set-up, cones that need to changed, or other build-up in the system's cells and tubing. For completeness, you should consider and discuss this. Thirdly, and most seriously – screening grains on the basis of low raw counts on U and Pb is philosophically just as incorrect as screening grains on the basis of low U in ppm, similar to the authors whose methodology you disagree with (i.e. Okay et al., 2011). The only difference is that, instead of discarding grains on the processed signal, you now reject grains on the basis of the raw signal. On those grounds, I fundamentally disagree with this approach. Why not use the Chew et al. power-law filter for all grains, regardless of a screen for raw background corrected counts on 238, 206, 207 etc.? Such an approach would at least treat all grains in the same way.

We reiterate that the number of discarded analyses is surprising, but is the result of a natural dataset and not analytical or data reduction error.

Rejecting/filtering data is common practice, whether due to high uncertainty or discordance, etc. However, using a filter based on element abundance (i.e., 4-5 ppm U threshold) is only valid for a certain abundance sensitivity (cps/ppm), which depends on instrument (laser and ICP-MS type) and instrument settings (see also Section 7.2 text). A threshold/filter based on the raw data (basically on cps) on the other hand is directly linked to counting statistics, which is a fundamental statistical limitation and not instrument or setting specific. This is not at all the same as the reviewer claims. Basing it on the U ppm makes the most sense for our dataset of mostly Phanerozoic rutiles, because we are mostly interested in the grains with high U/Pb, not the ones with high Pb counts and low U/Pb. For datasets with largely Precambrian rutile another approach may be needed.

The U (ppm) versus 206Pb/238U uncertainty plot (Figure R1) shows that the main issue is the very low U and therefore Pb concentrations, followed by inclusions. We demonstrate that the very, very low concentration grains have corresponding low counts therefore have high uncertainty. We reiterate that the rutile material we are working with has significantly lower U concentrations than many other studies. There is a good reason to reject data with high uncertainty, because they do not allow geologically significant dates to be calculated. At some point a threshold has to be set. We include grains down to 10^{-3} ppm U, which is three orders of magnitude below the 4-5 ppm threshold in the literature, therefore we argue that excluding low U and low Pb signals is not the same as screening low U grains at 4-5 ppm. Further, the U filter used here is based on the CPS and therefore the limits posed by pure counting statistics, whereas a "ppm filter" is instrument and setting dependent.

The “spiky” signals are mainly a result of very low count rates due to the exceptionally low U concentrations encountered in many of the analyzed rutile grains (Fig. R1). We provide a few comments on instrument set-up by addressing instrument tuning and the precision of results. A summary of daily tuning results is given in Table R1. QA/QC for tuning is aimed at stable signal, high count rates and low oxide production monitored by measuring NIST 612 glass. U238 for 50 micron spot size and 3.3 J/cm2 fluence is at 2.4- 4 million cps. Oxide rate is below 0.2% 254UO as percentage of 238U. The cps yield per ppm U was 64,000-107,000 cps/ppm for NIST612 for 50 micron spots, and 63,000-75,000 cps/ppm for 50 micron spots on rutile with 3.0 J/cm2 fluence (Table R1; now added to method table S2 in supplement). The NIST 612 cps/ppm values are in the high range of what is typically achieved on our Element2 ICP-MS since 2009 (This is monitored every day). We do not have data from other laboratories since this is data that is rarely published, but we contend that this is more than adequate in comparison to any other laboratory with a single collector ICP-MS and similar detector setup. We are not aware that other labs with a similar setup (Element2 without xcones setup) can achieve significantly higher cps yield unless they are using much higher rep rates or laser energy, which produces deeper pits and can have a detrimental effect on downhole fractionation. It is noted that some publications report much higher fluence values, but from discussion with other colleagues and laser company engineers, many of these are not properly calibrated and are overestimates.

Further, we compare the precision of our U-Pb results (single collector HR-ICP-MS) to those of two published studies using an HR-ICP-MS (Odlum et al., 2024), MC-ICP-MS (Bracciali et al., 2015) and Q-ICP-MS (Jenkins et al., 2023) (Figure R1). We achieve lower uncertainties on rutile with U concentrations in the parts per million range (> 1 ppm U) compared with the unknowns analyzed on a multi-collector. Compared with the reference materials analyzed on a Q-ICP-MS, we achieve similar precision on our unknowns in the parts per million U range (> 1 ppm U). Our rutile range extends to 100x or less U than the rutile analyzed by quadrupole and multi-collector instruments, and the rutile we had high uncertainty on is in the lower U range (less than 1 ppm U).

Table R1: Summary of daily instrument tuning results.

NIST612 ppm U:	37.38	NIST 612				Th/U	R10 ppm U	44.1			GSD		
	cps/ppm	238U	206Pb	spot (µm circle)	J/cm2		cps/ppm	238U	spot (µm circle)	J/cm2	Ti49	spot (µm circle)	J/cm2
7/12/2021	107009	4.00E+06	750,000	50	3.3	0.7	40816	1.80E+06	35	3.0			
7/13/2021	101659	3.80E+06	800,000	50	3.3	0.78	74830	3.30E+06	50	3.0			
7/13/21 trace	101659	3.80E+06	730,000	50	3.3	0.7			35	3.0			
7/14/2021	66881	2.50E+06	500,000	50	3.3	0.75	68027	3.00E+06	50	3.0			
7/14/2021 trace	66881	2.50E+06	500,000	50	3.3	0.75	68027	3.00E+06	50		1.80E+06	25	3
7/15/2021	66881	2.50E+06	500,000	50	3.3	0.7	63492	2.80E+06	50	3.0			
7/16/2021	64205	2.40E+06	480,000	50	3.3	0.75	68027	3.00E+06	50	3.0	1.70E+06	25	3
7/19/2021 trace	66881	2.50E+06	520,000	50	3.3	0.8					1.80E+06	25	3

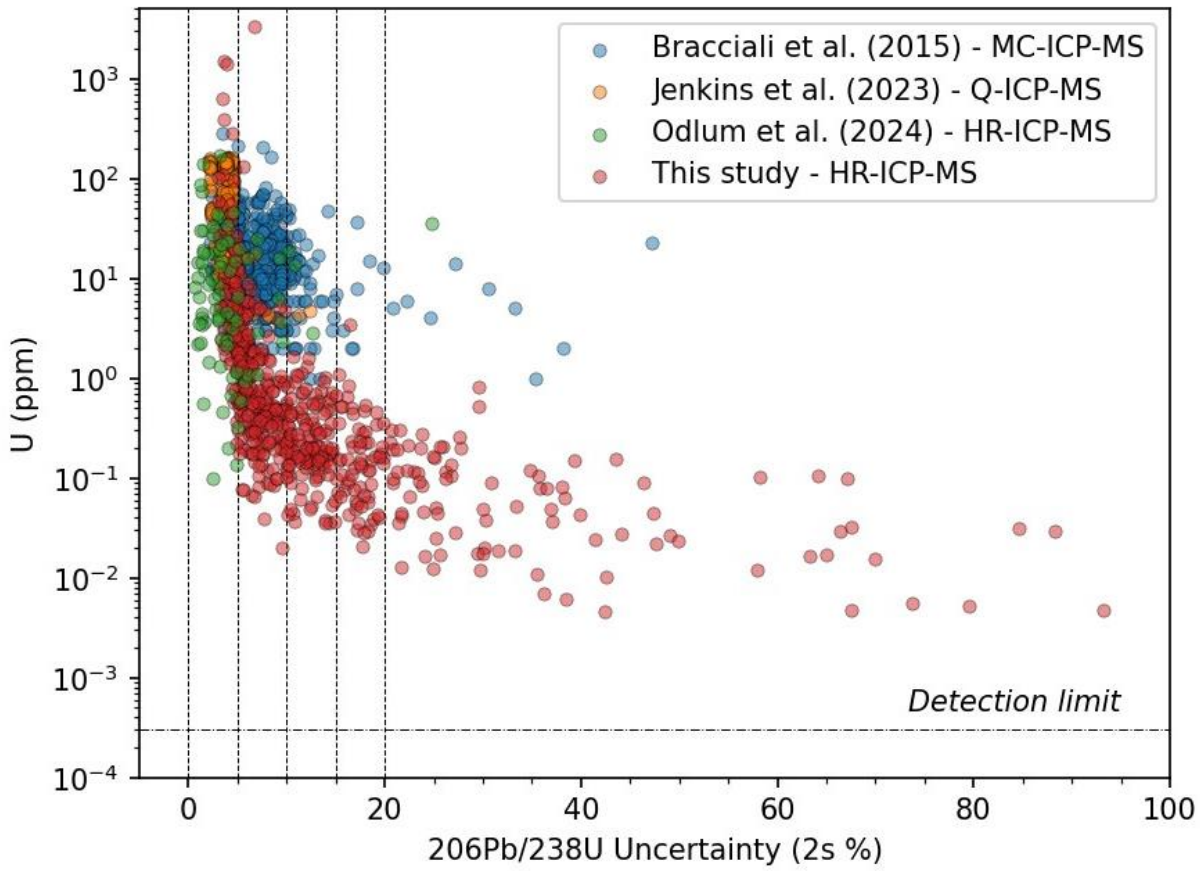

Figure R1: Comparison of 206Pb/238U uncertainty (2s %) versus uranium concentration from this study (detrital rutile unknowns; analyzed on single collector HR-ICP-MS), Odlum et al. (2024) (detrital rutile unknowns; single collector HR-ICP-MS) Bracciali et al. (2015) (detrital rutile unknowns and rutile secondary standard; MC-ICP-MS), and Jenkins et al. (2023) (rutile reference materials; Q-ICP-MS).

My second comment relates to interpretations of the trace elements.

- *Firstly, point 4) in the abstract could be due to an artefact in your detrital dataset. In particular, figure 10 does not convince me that you have sufficient data to determine whether metapelitic or metamafic rutile in general contains proportionally more U. It could be that the metamafic rutile have lower average U due to random chance due to low numbers of analysed grains. Additionally, your finding only holds within the confines of your dataset, which is not globally representative.*

We show that "mafic classified grains are dominantly low U (95%, n=106/112 below 4 ppm). The majority of rutile with U contents above 4 ppm are classified as pelitic (85%, n=34/40)" (Section 6.2). Figure 10 does not show all of the rutile grains with measured U ppm, but rather shows the smaller subset of grains with both U-Pb and trace element data, as noted in the figure caption. In any case, we agree that our dataset is not a universal representation of detrital rutile, however, it is documented that "uranium concentration in rutile varies among metamorphic protoliths: for example, rutile from mafic

eclogites tend to have, 134 on average, 75% less U than those from metapelites (i.e., 5 ppm vs. 21 ppm; Meinhold, 2010)" (Section 2.2). Our dataset affirms this trend.

- *Secondly, exploration of the trace element data is underdeveloped. PCA is an extremely useful tool for exploratory geochemical data analysis, but it inherently results in loss of information, as all geochemical variation is condensed into a 2-dimensional space – it is possible that scatterplots etc. may reveal useful information not shown on PCA diagram. In section 6.3, you make the interpretation that the trace element data derives from protolith (Cr, Nb etc.) and temperature (Zr, Hf) factors. However, the vectors on figure 12 demonstrate that PC1 is dominated by Tungsten (W). Why is this? What is the significance of that finding? And why is it not discussed? Additionally, why not colour the points by their metapelitic/metamafic categorisation, and/or Zr-in-rutile T? This would indicate whether PC2 really is discriminating on the basis of protolith, or PC1 on the basis of T.*

The main trace elements discussed in the rutile literature are Cr, Nb and Zr (citations), with additional attention given to the combination of Cr, Nb, Zr, V and Fe for discriminating TiO2 polymorphs (i.e., rutile, anatase, brookite see our supplemental Figure S2) (Triebold et al., 2012) and to Nb and Ta as tracers of subduction zone fluids and continental crust formation (Figure R2; Rudnick et al., 2000; Xiao et al., 2006). We include the commonly used scatterplots of these elements in the main text (e.g., Figure 9). Additionally, we display the results on Tera-Wasserburg diagrams to show the distribution of scatter plot discrimination fields by age (e.g., Figures 9, 11), which is not commonly done.

There is little literature on W in rutile and how it can be used in detrital rutile datasets. The elements W, Sb and Sn can be used in mineral exploration (Plavsa et al., 2018; Agangi et al., 2019). We show our trace element results with rutile from orogenic gold deposits, which were used to roughly define ore (Au mineralized), metamorphic and granitoid fields (Agangi et al., 2019). Most of our data plot within the metamorphic field and there is no correlation by rutile age (Figure R3) or by protolith.

Reviewers 1, 2, and 4 have commented on whether the PCA is adding anything "new or interesting." In the manuscript text and reply to reviewers, we have tried to demonstrate the many ways we have looked at the trace element data. In the end, the most insights are gained from Cr, Nb, and Zr. In light of this and the Associate Editor's recommendation to shorten the manuscript, we removed the PCA text and figure from the revised manuscript.

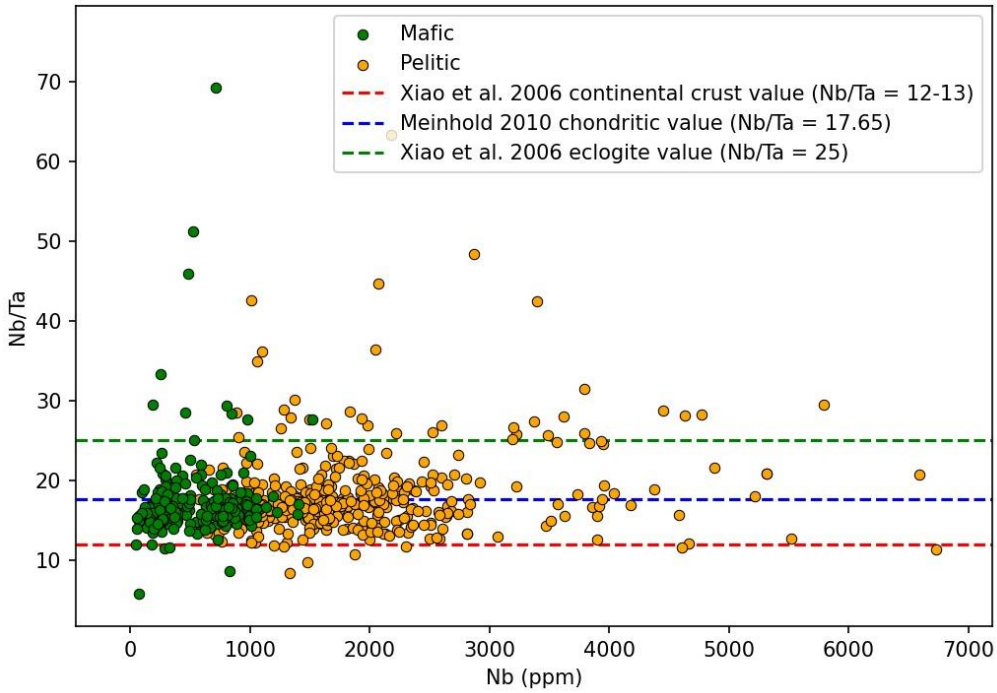

Figure R2: Nb/Ta versus Nb diagram after Xiao et al. (2006). The rutile grains are colored by their mafic-peitic classification (Cr vs Nb; see main text). The mafic and pelitic grains group together, which is expected as protolith is classified by Nb contents. The grains are scattered between continental crust, chondritic or eclogite values and there is no clustering by grain date.

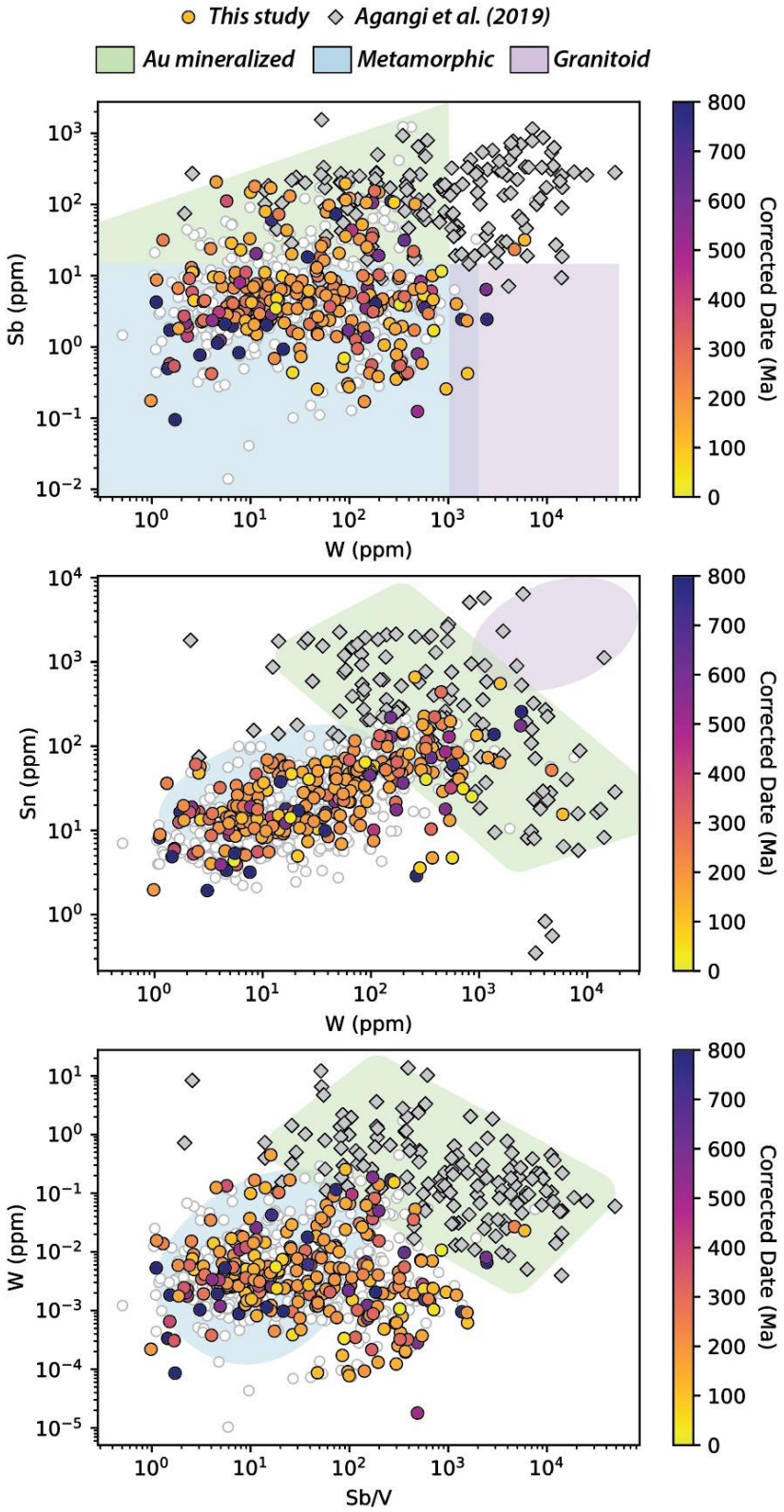

Figure R3: Trace element data plots of Sb, Sn, W and V used to delimit ore-related (Au mineralized) rutile (after Agangi et al., 2019). Rutile from this study are shown with the dataset of orogenic gold deposit rutile from Agangi et al. (2019). White circles are rutile grains without U-Pb dates.

- *Thirdly, plots of PCA loadings are discussed in section 6.3, but not such plots are shown.*

We moved the PCA from the main text to supplement, and briefly address this comment. The loadings are shown in the PCA figure as lines with arrows. PCA scores represent the transformed data points in the new coordinate system defined by the principal components, where each data point in the original dataset is projected onto the principal component axes, resulting in a set of scores that describe the position of the data points in the new coordinate system. Loadings represent the correlations between the original variables and the principal components, thus describing the relationships between the original variables and the principal components. The loadings vectors indicate the direction and magnitude of the contribution of each original variable to the principal components.

- *Fourthly, and lastly, consideration is not given to the fact that some rutile derive from igneous rocks. It is possible that some rutile labelled as metamafic or metapelitic using the scheme of Triebold et al. (2012) may derive from a plutonic rocks (e.g. Huang et al., 2024 – igneous rutile dated from an Archean pluton; Pe-Piper et al., 2019 – igneous rutile dated from a syenite; Janousek and Gerdes, 2003 – igneous rutile dated from a granitoid pluton). Indeed, on line 76 it is stated that rutile is a common accessory mineral in metamorphic *and igneous* rocks. How might this affect interpretations on the basis of a metamorphic/igneous division, especially WRT high-T concordant "metapelitic" grains on figure 11. Might these be igneous?*

Distinguishing igneous versus metamorphic rutile is not straightforward in detrital samples, and is reviewed in Pereira and Storey (2023). The composition of heavy mineral assemblage (e.g., counting the total number of rutile and zircon grains in a sample) can be used as an index for igneous or metamorphic sources (Morton and Hallsworth, 1994). Another proposed method is using the ore discrimination diagrams discussed above (Figure R3). In those diagrams, the majority of grains plot in the metamorphic field rather than granitoid. Additionally, we suggested that igneous rutile could potentially be identified if their date overlaps with detrital zircon populations. For example, “we interpret the 90 Ma rutile population as either igneous or metamorphic rutile derived from Late Cretaceous magmatism and associated contact metamorphism on the Pontides” (Section 8). This is because the “rutile grains that (poorly) define the ca. 90 Ma population [...] include some of the highest Zr-in-rutile temperatures” and because the “zircon record has abundant Late Cretaceous and Eocene populations [...] associated with magmatic flare-ups” (Section 8). We suspect that the 90 Ma rutiles are either igneous or formed during syn-magmatic, high-T metamorphism.

My third and last comment relates to the discussion. From line 599 several examples are given of papers where a significant proportion of rutile ages were rejected from published studies (Caracciolo et al., 2021; Govin et al., 2021; Shannan et al., 2020). Firstly, it is not clear from this section whether these rates of rejection are typical of detrital rutile studies, or whether perhaps they are instead related to the specific source regions of these rutile. And secondly, it is noted that the study of Shannan et al. (2020) uses a discordance filter, which is a method that is discounted by the present study and thus not particularly useful for comparative purposes. Consequently, I don’t find this section convincing as an argument to support the interpretation from line 607: “Together these studies illustrate Together these

studies illustrate that there is a formidable methodological hurdle in trying to scale up detrital rutile U-Pb to large-n provenance applications".

We are uncertain how representative these 4 studies are for the rates of U-Pb data rejection in detrital rutile. It is rarely reported and these 3 published studies plus this manuscript are what we found available. We are unaware of large-n detrital rutile datasets (> 300 analyses / sample), which is likely limited by rutile fertility and data rejection. As far as we are aware, this is the first manuscript to discuss the rejection of data, criteria for rejection, and potential bias. These 4 datasets evidence that data rejection does occur. It is hard to speculate how prevalent it is without more data reporting on data inclusion/rejection. For this reason, "more rigorous data reporting and standardizing metrics used for evaluating 'acceptable' U-Pb analyses. We recommend that the criteria for data rejection be explicitly discussed in all detrital rutile studies."

Figure comments
Figures 5, 8 – a cumulative age distribution plot would be more useful than a cumulative KDE plot, which is simply a repetition of the data below it in a more awkward form.
We changed the figures, thank you.

Figure 11 – near-concordant grains are often very high T grains. Is it possible that these are primary igneous rutile?
Yes, it is possible. Please see above discussion.

Figure 12 – colour by protolith according to the scheme of Triebold et al., 2012.
We removed this figure. See above discussion.

References Cited

Agangi, A., Reddy, S. M., Plavsa, D., Fougerouse, D., Clark, C., Roberts, M., and Johnson, T. E.: Antimony in rutile as a pathfinder for orogenic gold deposits, Ore Geol. Rev., 106, 1–11, https://doi.org/10.1016/j.oregeorev.2019.01.018, 2019.

Bracciali, L., Najman, Y., Parrish, R. R., Akhter, S. H., and Millar, I.: The Brahmaputra tale of tectonics and erosion: Early Miocene river capture in the Eastern Himalaya, Earth Planet. Sci. Lett., 415, 25–37, https://doi.org/10.1016/j.epsl.2015.01.022, 2015.

Jenkins, K., Goemann, K., Belousov, I., Morissette, M., and Danyushevsky, L.: Investigation of the Ablation Behaviour of Andradite-Grossular Garnets and Rutile with Implications for U-Pb Geochronology, Geostand. Geoanalytical Res., 47, 267–295, https://doi.org/10.1111/ggr.12478, 2023.

Odlum, M. L., Capaldi, T. N., Thomson, K. D., and Stockli, D. F.: Tracking cycles of Phanerozoic opening and closing of ocean basins using detrital rutile and zircon geochronology and geochemistry, Geology, https://doi.org/10.1130/G51826.1, 2024.

Pereira, I. and Storey, C. D.: Detrital rutile: Records of the deep crust, ores and fluids, Lithos, 107010, https://doi.org/10.1016/j.lithos.2022.107010, 2023.

Plavsa, D., Reddy, S. M., Agangi, A., Clark, C., Kylander-Clark, A., and Tiddy, C. J.: Microstructural, trace element and geochronological characterization of TiO2 polymorphs and implications for mineral exploration, Chem. Geol., 476, 130–149, https://doi.org/10.1016/j.chemgeo.2017.11.011, 2018.

Rudnick, R., Barth, M., Horn, I., and McDonough, W. F.: Rutile-Bearing Refractory Eclogites: Missing Link Between Continents and Depleted Mantle, Science, 287, 278–281, https://doi.org/10.1126/science.287.5451.278, 2000.

Triebold, S., von Eynatten, H., and Zack, T.: A recipe for the use of rutile in sedimentary provenance analysis, Sediment. Geol., 282, 268–275, https://doi.org/10.1016/j.sedgeo.2012.09.008, 2012.

Xiao, Y., Sun, W., Hoefs, J., Simon, K., Zhang, Z., Li, S., and Hofmann, A. W.: Making continental crust through slab melting: Constraints from niobium–tantalum fractionation in UHP metamorphic rutile, Geochim. Cosmochim. Acta, 70, 4770–4782, https://doi.org/10.1016/j.gca.2006.07.010, 2006.