nature portfolio

Peer Review File

Sources of lead in a Tibetan glacier since the Stone Age

Corresponding Author: Dr Roxana Sierra-Hernandez

Attachments originally supplied by the reviewers can be found at the end of this file, in order by reviewer number and revision.

Version 0:

Decision Letter:

** Please ensure you delete the link to your author home page in this e-mail if you wish to forward it to your coauthors **

Dear Dr Sierra-Hernandez,

Your manuscript titled "Tracing lead (Pb) sources to remote high-altitude glacier since the Stone Age" has now been seen by 3 reviewers, whose comments are appended below. You will see that they find your work of some potential interest. However, they have raised quite substantial concerns that must be addressed. In light of these comments, we cannot accept the manuscript for publication, but would be interested in considering a revised version that fully addresses these serious concerns.

In particular, we would need to see that the revised manuscript meets the following editorial thresholds:

* Fully justify that the presented data significantly advance our understanding of Pb sources in the pre and post-industrial periods on this site*

* Explain clearly the methods, in particular, the method used to calculate the Enrichment factors*

We hope you will find the reviewers' comments useful as you decide how to proceed. Should additional work allow you to address these criticisms, we would be happy to look at a substantially revised manuscript. If you choose to take up this option, please either highlight all changes in the manuscript text file, or provide a list of the changes to the manuscript with your responses to the reviewers.

Please bear in mind that we will be reluctant to approach the reviewers again in the absence of substantial revisions.

If the revision process takes significantly longer than three months, we will 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.

We are committed to providing a fair and constructive peer-review process. Please do not 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 reviewers' comments with a list of your changes to the manuscript text (which should be in a separate document to any cover letter), a tracked-changes version of the manuscript (as a PDF file) and any completed checklist:

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Please do not hesitate to contact us if you have any questions or would like to discuss the required revisions further. Thank you for the opportunity to review your work.

Best regards,

Yama Dixit
Editorial Board Member
Communications Earth & Environment

Carolina Ortiz Guerrero, PhD
Associate Editor
Communications Earth & Environment

EDITORIAL POLICIES AND FORMAT

If you decide to resubmit your paper, please ensure that your manuscript complies with our editorial policies and complete and upload the checklist below as a Related Manuscript file type with the revised article:

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An updated and completed version of our Reporting Summary must be uploaded with the revised manuscript
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For your information, you can find some guidance regarding format requirements summarized on the following checklist: (https://www.nature.com/documents/commsj-phys-style-formatting-checklist-article.pdf) and formatting guide (https://www.nature.com/documents/commsj-phys-style-formatting-guide-accept.pdf).

REVIEWER COMMENTS:

Reviewer #1 (Remarks to the Author):

The paper by Sierra-Hernández et al., entitled “Tracing lead (Pb) sources to remote high-altitude glacier since the Stone age,” uses Pb isotopes to consider the contribution of different dust sources, and how their Pb composition and potential contamination sources have changed over time. Samples for this study came from the Guliya ice cap, a remote and pristine environment in Tibet. They evaluated samples from local likely dust sources to identify non-anthropogenic dust Pb isotope ratios, considered pre-industrial revolution samples to establish any early human impact, and then focused on recent ice core samples. Results show a clear onset of pollution from leaded gasoline, along with the transition to dominantly coal-sourced Pb. These relationships were improved from previous records by the measurement of the rare Pb isotope, 204Pb, providing more isotope ratios to better constrain source regions. Overall, this paper highlights the global extent of Pb pollution and the utility of Pb isotopes as pollution tracers.

This is a well-constructed study that builds off of two previously published papers using trace metals to identify anthropogenic pollution at this site. While the trace metal results in Sierra-Hernández et al. (2018) support fossil fuel sources based on enriched concentrations of Pb, Cd, Zn, and Sb, the Pb isotope records provide the clearest link to fossil fuels.

My only real challenge with this paper is if the results are more incremental and better suited for a more focused journal. It is well-written and contains an interesting data set, once that I do think has broad appeal. It provides a clear example of both the utility of Pb isotopes in source characterization, the application of mixing model tools to establish those relationships, and highlights how pervasive Pb pollution is. However, this paper does not provide a new conclusion or true new application. I agree that the inclusion of the 204Pb isotope does aid in refining source descriptions, but it’s unclear to me that, in this instance, it has improved predictions enough to establish this as a required measurement for all new investigations. I could see if this paper took a more holistic view, incorporating the trace metal data, in particular, the larger conclusions would be of interest to the more diverse readership of this journal.

Minor Edits:

Line 49; rephrase, this makes it sound like there’s a 20 year gap with no anthropogenic emissions.

Extended figure 1: could you do a stack of the three ratios, (206/204, 207/204, 208/204) and possibly

Extended Figure 3: Add the core site to this map

Reviewer #2 (Remarks to the Author):

This manuscript presents new Pb isotope data from the Guliya ice core and interprets it in terms of potential natural and anthropogenic sources through time. The data appear to be of high quality and the methods generally sufficient to support the main interpretations. However, I have a few suggestions and/or concerns that need to be addressed before I would consider the paper ready to publish. In addition, the writing needs some revision throughout to improve grammar and readability (e.g. the title contains typos).

Regarding enrichment factors, there are several important variables that are not addressed but which can have a large influence on the calculated Efc. First, were the trace element samples used to calculate Efc subjected to a weak acid leach (e.g., 1% HNO3) or were they fully digested? If a weak acid leach, how long was the acidification time prior to analysis? Also, what are the estimated recovery rates if a full HF digestion was not done? These factors can be significant and may influence different elements differently depending on their bonding and structure. Also, why is Fe the only element used for this calculation? It is more standard to use several different elements to obtain a range of Efc values, as different dust-related elements may yield different enrichment factors. I'd like to see clear answers to all these questions and a more thoughtful treatment of the Efc calculation overall, as this is essentially the basis for discriminating between the two main clusters of data. Moreover, an Efc value of 1.5 is not very enriched. Samples from other locations that show a high degree of Pb pollution may have values in the 4-15 range, depending on the normalization element used. So while I agree that the post-1974 samples are likely showing an influence of pollution, the degree of pollution is still an open question.

My second major critique regards the interpretation of PSAs. The paper needs to include a clear figure that plots all the ice core data along with both dust and pollution PSAs (supplementary figure would be fine). At present, the pre-1974 samples are plotted with dust end-members and the post-1974 samples are plotted with pollution end-members (figures 3 and 4). However, given the low Efc of 1.5 and the substantial overlap in Pb isotope space of the natural dust sources and Chinese coal, for instance, the post-1974 samples likely contain significant locally-sourced dust. I understand that the MixSIAR modelling was an effort to quantify these different contributions; but might there be additional approaches that could help constrain the dust vs pollution input (e.g. ice core sulfur or additional trace elements)?

Related to the second point, I would disagree with the statement in line 100 that the Efc of 1.5 "strongly suggests" an anthropogenic source for Cluster 2 samples. Rather, there is clearly a strong contribution from anthropogenic sources, but they cannot be the exclusive sources. More nuance here is needed. Also related, figure 1 needs to include sampling locations of the PSA samples presented in the study and a clear depiction of which sample locations (both new and literature data) are included in each of the different dust regions (TP, eastern TP, southwest TP, northeastern TP, NMY3, etc.). These are not indicated anywhere yet are clustered as if they are meaningfully different in figures 3 and 4. What is the rationale for these different regional signatures? Are they statistically or geologically distinct?

My third point is that this dataset is presented in seeming isolation from much of the literature. I think the findings here would be more interesting when placed in context with similar snow and ice core records (and corals, etc) from other Asian and Pacific sites. For instance, how do the timing and magnitude of changes at Guliya compare with those measured in other ice cores (e.g. Greenland)? Such a detailed analysis could lead to interesting conclusions about, for instance, atmospheric transport patterns and the influence of natural dust at different locations. As written, the paper seems to exist in a bit of a vacuum, with the exception of the Mt Everest record, to which it is compared.

Finally, the paper ends with a paragraph that sounds rather methodological and passive: "A binomial filter was also applied…". I would suggest reorganizing and including a clear conclusion paragraph stating the key findings and contributions of the study.

Figures:
Figure 1: Add PSA locations and color-code by the regions shown/labeled in figures 3 and 4

Figure 2: Connect the dots, and consider blowing up the 20th century to clearly show the recent changes. Inserting an axis break as in other figures, or including a separate panel, would be appropriate here.

Figure 3: If error bars are smaller than symbols, state that in the caption. Otherwise, plot them. The caption needs to give acronyms and define them (e.g.NMY, TP). Again, there needs to be a clear relationship to Fig. 1 and a rationale for separating the TP samples into these 4+ different regions.

Figure 4: At least a version of this figure in the supplement needs to include dust PSAs alongside the pollution PSAs.

Figure 5: This is pretty clear and easy to read.

Figure 6: The range of the bars is hard to see. I would suggest expanding the ranges vertically and compressing horizontally to show the values more clearly. This could be moved to the supplement.

Extended fig. 1: Define GS in the caption.

Extended fig. 2: The Lee et al citation needs formatting. Suggest breaking the axis here to show the 20th century more

clearly, or adding a separate panel for more recent data.

Extended fig. 3: This would be more useful if the regions designated in Fig.3 were clearly marked here.

Data tables: It's great these are provided here, but supplements are notoriously challenging/obscure places to archive data. I would strongly suggest including the data and metadata in a public database and including a data availability statement at the end of the manuscript. This will make the data much more likely to be used by others in the future.

Minor comment: The introduction could benefit from reworking, especially the final paragraph.

Reviewer #3 (Remarks to the Author):

The authors based their findings on ice core samples from different time periods, measured data on lead isotopes especially on 204Pb, and comparisons with various sources, they found the following:
The Pb isotope ratios of the samples covering the pre-Industrial period 1500-~1950 are very similar to the Pb isotope ratios for those samples that are pre-Bronze age, the Pb isotope ratios show a slight decrease in values starting in ~1950 following the establishment of China as a Republic and when the Pb emissions from gasoline began to rise in China。
The decrease in Pb isotope ratios are more pronounced after 1980 when the Pb emissions from leaded gasoline rise exponentially likely due to the demands of energy in China after it adopted a policy of openness and reform in 1978.
In the province of Xinjiang, north of Guliya, coal combustion has also been increasing since the 1950s but in ~2007 it increased exponentially.
For the Stone Age ice core samples，the mixing model MixSIAR estimates of mean contributions of ~12%, 2%, and > 1% from fuels, Pb/Zn ores, and coal, respectively.
Overall, all these found are novel, the work is compelling, the conclusions are original. They provided sufficient methodological detail that the experiments could be reproduced. The statistical analysis of the data is sound. On a more subjective note, i feel that the paper will influence thinking in the field in terms of either lead isotopes understanding or technological capability.

Three questions are the following:
1. Line 197 ：The sentence in the following begins with the use of "And". Is that correct ? “And even though leaded gasoline was phased out in 2000, it remained the primary source of anthropogenic Pb at Guliya until ~2007 when coal combustion took over as its primary source. ”
2. Line 162-164：“The Pb isotope ratios of aerosols collected in Eastern China cities (except Xin Shao, whose Pb isotope ratios are comparable to those from Guliya) are less radiogenic than the ratios at Guliya but still closer to Guliya's Pb isotope ratios.” Does this mean that aerosols from these eastern cities travel to the Guliya Glacier in the west? If so, how are these aerosols transported to Guliya.
3. Line 50-52： In Supplementary Information Text S1: Sample Selection “Samples were acidified to a final concentration of HNO3 2% (v/v) to dissolve TEs in microparticles and to keep in solution those already dissolved. The acidified samples were kept in a class 100 clean room for 30 days to allow the acid to leach the TEs” The acidification time is one month and the content of acid is 2%. Obviously，the samples preparation method are different from those in reference, where pb isotopes data have been compared. Will different pretreatment methods also lead to changes in the isotopic composition of lead? even for the same sample.

Author Rebuttal letter: The author's response to these comments can be found at the end of this file.

Version 1:

Decision Letter:

** Please ensure you delete the link to your author home page in this e-mail if you wish to forward it to your coauthors **

Dear Dr Sierra-Hernandez,

Your revised manuscript titled "Tracing lead (Pb) sources to remote high-altitude glacier since the Stone Age" has now been seen by our original reviewers, 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. In specific, please address Reviewer's #2 discussion points and improve the figures' presentation. 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.

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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

Yama Dixit
Editorial Board Member

Communications Earth & Environment

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

In reviewing the responses to my comments, along with those of the other reviewers, I feel that the authors adequately responded to the comments and have improved the manuscript. My comments had focused mostly on the presentation of the data and if the results would be relevant to the larger author-base of this journal. The inclusion of data from other regions greatly improves the reach of this manuscript. Additionally, the writing is improved, particularly the inclusion of a true concluding paragraph. I am happy with this version and recommend publication.

Reviewer #2 (Remarks to the Author):

Overall, I find the manuscript to be improved compared to its previous iteration, and I appreciate the authors' careful consideration of prior reviews. However, there are still some areas that need to be strengthened both in the scientific interpretation (see main points below) and in the writing, to make the paper publication-ready. I would recommend hiring an English language editor to help with grammar and sentence structure.

The paper has been improved by the comparison to other Northern Hemisphere ice core records. The new figure 2 is helpful, and the new figure 3 provides needed context for the observations at Guliya. However, with all the records plotted on the same y-axis, the records obscure each other and the timing of changes is hard to determine visually. I suggest separating each record (e.g. with y-axes alternating left-right-left-right) so that the changes within each record can be seen more clearly. I would suggest adding the Gross et al 2012 Pb isotope record from the Eclipse Icefield to Fig. 3 and the discussion, as this record relates specifically to Asian industrialization. Likewise, the Osterberg et al 2008 Pb concentration record would offer a second regional perspective on North Pacific pollution that could be helpful for comparison. To strengthen this part of the discussion, a statistical analysis of the timing of changes among the different Pb records (e.g. breakpoint analysis) would provide a more robust framework for the discussion. Currently the paragraph beginning Line 143 uses approximate ages for the analysis; this discussion would be strengthened by the determination of breakpoints within each record, as the relative timing could be explored in a more meaningful way. Also, line 154 needs to be clarified as to the timing of anthropogenic pollution signals arriving in the TP.

Figures 4 and 5 are much clearer now. I would advocate for adding into the captions the general characterization of Cluster 1 and Cluster 2 (e.g. main sources and/or age ranges for each cluster) so readers have this information readily available when looking at the figures.

As stated in my first review, I would strongly suggest including the data and metadata in a public database and including a data availability statement at the end of the manuscript. This will make the data much more likely to be used by others in the future, rather than just including a table in the manuscript.

I don't understand the logic in lines 240-242. If leaded gasoline was phased out in 2000, how could it remain the major source of anthropogenic Pb until 2007? This needs to be reasoned through more explicitly.

The paragraph beginning Line 288 is highly speculative and could use clearly described evidence to support the interpretations about atmospheric circulation. Similarly, the concluding paragraph refers to changes in atmospheric circulation but this interpretation is not well developed or supported in the paper as currently written. Please explain this somewhere and make the steps of the interpretation more clear to the reader.

Line 267: refer to Fig 7 here and label the changepoints on the figure.

Line 277: Where is this shown?

Line 568: what is the source of the Xinjiang coal data? Please add to the caption here.

Figure 7 and throughout: if there is space available in a figure label to write out the full name of a location, e.g. "Tibetan Plateau" instead of "TP," then please do so to make the reader's job easier.

References

Gross, B. H., Kreutz, K. J., Osterberg, E. C., McConnell, J. R., Handley, M., Wake, C., & Yalcin, K. (2012). Constraining recent lead pollution sources in the North Pacific using ice core stable lead isotopes. Journal of Geophysical Research, 117(D16307). doi:10.1029/2011JD017270

Osterberg, E. C., Mayewski, P., Kreutz, K., Fisher, D., Handley, M., Sneed, S. B., . . . Bourgeois, J. (2008). Ice core record of rising lead pollution in the North Pacific atmosphere. Geophysical Research Letters, 35(L05810). doi:10.1029/2007GL032680

Reviewer #3 (Remarks to the Author):

Dear editor,
It is found that the author has made changes to the parts of the manuscript that need to be modified, and has reached the level of publication.I agree to publish in your journal.

** Visit Nature Research's author and referees' website at www.nature.com/authors for information about policies, services and author benefits**

Author Rebuttal letter: The author's response to these comments can be found at the end of this file.

Comments:

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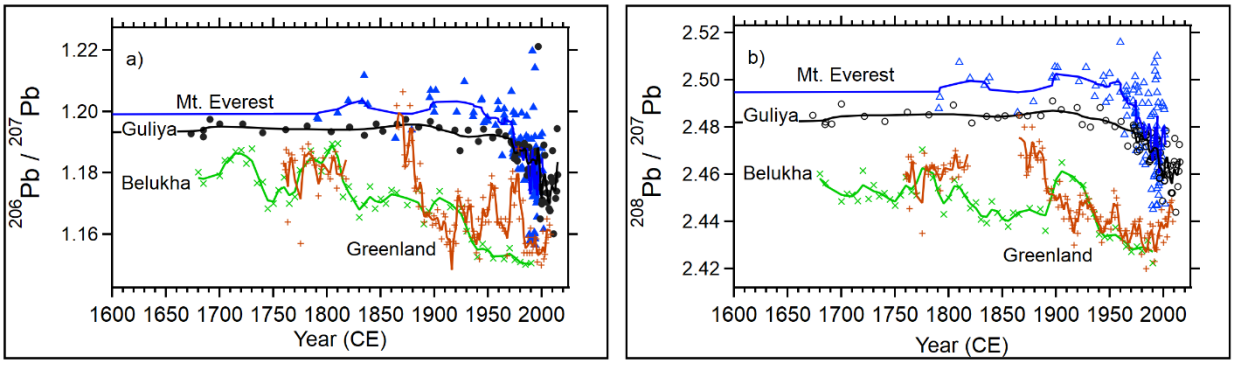
- We thank the reviewer for their constructive feedback. A new figure (Figure 2 in the main text) has been created using three ratios, (206/204, 207/204, 208/204) and the EFs of Pb, Sn, Cd, Zn, and Sb. A more holistic approach was taken in the revised version. Additionally, the conclusion was revised in the last paragraph: "In conclusion, the Guliya Pb isotope record reveals two significant changes in Pb sources over the last 500 years. First, changes in atmospheric circulation between ~1800 and 1950 led to incursions of mineral dust containing more radiogenic Pb, likely originating from southern Tibet. Second, local emissions, mostly from Chinese gasoline combustion, introduced an anthropogenic signal in the Guliya Pb record starting in 1974, followed by contributions primarily from local Chinese coal combustion in 2007." Furthermore, records from Belukha in the Altai and from Summit, Greenland are shown for comparison in the new

Figure 3. We think these changes will appeal to a more diverse readership of this journal.



- Regarding the novelty of 204Pb, Longman et al (Scientific Reports 2018, 8:6154) used the MixSIAR Bayesian model to quantify the contributions of Pb sources in natural archives, archaeological artifacts. The authors found that using the three 204Pb isotope ratios to run the MixSIAR Bayesian model provides maximum variability in the isotopic signature during the modelling. Additionally, the authors indicate that having the three 204Pb isotope ratios provides some independence among the three ratios as each Pb isotope originate from a different decay chain. Thus, having the 204Pb isotope in this study was important to determine the contribution of Pb sources using MixSIAR. This has been noted in the Methods Section under the MixSIAR subsection. It is also important to note that the Bayesian model MixSIAR is mostly applied in fields including Archaeology and Biology. It has not been widely used in the ice core field, thus, we think our study can be of interest to researchers in different fields.

Minor Edits:
Line 49; rephrase, this makes it sound like there's a 20 year gap with no anthropogenic emissions.

- This is indeed the case for the Guliya ice core. There is a gap of 20 years where no anthropogenic signals were detected in the ice core. This does not mean there was no emissions at the time. That is why we use "detected" in the sentence.

Extended figure 1: could you do a stack of the three ratios, (206/204, 207/204, 208/204) and Possibly

- It was difficult to stack the three ratios in this plot. But considering the comments above about including the trace metals used in our previous studies and this comment here, we decided to replace the 'Extended Figure 1' with a figure that includes the three ratios and the trace metals Pb, Sn, Cd, Zn, and Sb and this is now one of the main figures in the main text (new Figure 2).

Extended Figure 3: Add the core site to this map.

- We originally attempted to do this, the problem is that several Guliya PSAs overlap with the Guliya ice core drilling site marker since the corresponding sites are in extreme proximity. We have added a sentence in the caption of the corresponding figure (Figure S4) to note this.

Reviewer #2 (Remarks to the Author):

This manuscript presents new Pb isotope data from the Guliya ice core and interprets it in terms of potential natural and anthropogenic sources through time. The data appear to be of high quality and the methods generally sufficient to support the main interpretations. However, I have a few suggestions and/or concerns that need to be addressed before I would consider the paper ready to publish. In addition, the writing needs some revision throughout to improve grammar and readability (e.g. the title contains typos).

We thank the reviewer for their detailed comments and suggestions.

- The typo in the title was corrected.

Regarding enrichment factors, there are several important variables that are not addressed but which can have a large influence on the calculated Efc. First, were the trace element samples used to calculate Efc subjected to a weak acid leach (e.g., 1% HNO3) or were they fully digested? If a weak acid leach, how long was the acidification time prior to analysis?

- First of all, **the results, discussion, and interpretation of this study are driven by the Pb isotope ratios.** In fact, the fact that EFs were low (as mentioned by the reviewer) and had limited resolution in discerning source changes, was the motivating factor for using Pb isotopes (including the additional 204 Pb isotope), as noted in the Introduction of this manuscript. This was the "problem" in our previous publications that relied solely on EFs. However, and importantly, the Pb isotopes show that there is clear onset of pollution, as pointed out by the other reviewers, despite the "low" EFs. The discussion about the particularly low EF values was largely explained in the previous publications Sierra-Hernandez et al., 2018 and 2019, and does not bear repeating here, as these values are **not** an essential part of this new study (see below concerning the cluster analysis). Hence, we included only a brief description of the EFs in the Methodology. In the revised version, we added an explanation about the particular low EF values at Guliya. The details about the acidification have been added in the Methods section. We used a 2% v/v acidification using Optima HNO_3 for 30 days.

Also, what are the estimated recovery rates if a full HF digestion was not done? These factors can be significant and may influence different elements differently depending on their bonding and structure.

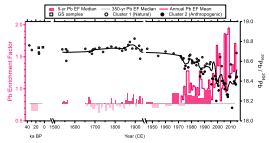
- The recovery rate for Pb is 20-50% in ice cores (Uglietti C et al Applied Geochemistry 47 (2014) 109–121). The reviewer brings up a good point in that the leaching method can influence different elements differently and affect EF. In fact, this is why calculating EF relative to local dust Potential Source Area (PSA) samples, which were prepared and analyzed exactly like the ice core samples, gives small values compared with those obtained using the most common Upper Continental Crust (UCC) background. However, in this new study we focus on Pb isotopes only. In the revised version we do present TEs to take a more holistic view as suggested by another reviewer. However, as mentioned in our second bullet point above, since the EF of these samples were already fully

documented in Sierra-Hernandez et al., 2018 and 2019, we only briefly discuss them in the revised version.

Also, why is Fe the only element used for this calculation? It is more standard to use several different elements to obtain a range of Efc values, as different dust-related elements may yield different enrichment factors. I'd like to see clear answers to all these questions and a more thoughtful treatment of the Efc calculation overall, as this is essentially the basis for discriminating between the two main clusters of data. Moreover, an Efc value of 1.5 is not very enriched. Samples from other locations that show a high degree of Pb pollution may have values in the 4-15 range, depending on the normalization element used. So while I agree that the post-1974 samples are likely showing an influence of pollution, the degree of pollution is still an open question.

- why is Fe the only element used for this calculation? The answer to this question was also fully documented in previous publications (Sierra-Hernandez et al. 2018 and 2019). However, we noted on the revised versions that other crustal TEs (Al, Mg and Ba) were used as reference crustal elements. Enrichment factors calculated with those crustal TEs showed no significant difference to those obtained with Fe (see Sierra-Hernandez et al. 2018 and 2019).

  Regarding the Clustering: The reviewer mentions that the EFs are "the basis for discriminating between the two main clusters of data…" In a simple way, looking at the Figure below, one can see that all samples with EFs above the 350-yr median and before 1974 were grouped in the "Natural" cluster. Also, several samples with high EF in the post-1974 period were grouped in the "Natural" cluster (see for instance the 1980-1985 and the1990-1995 periods). This indicates that EF is **not** relevant for the cluster classification.



In addition, in a more rigorous fashion:
We performed two independent k-means cluster analysis:

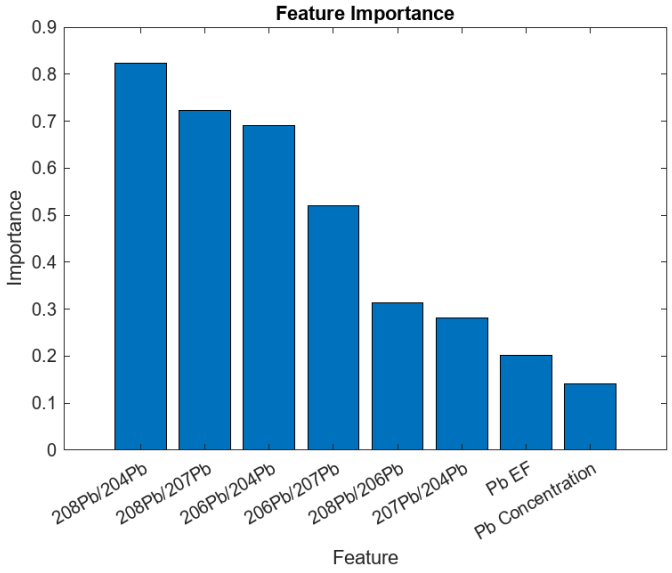
1) using all 6 Pb isotope ratios, Pb concentrations, and Pb EFs
2) using only the 6 Pb isotope ratios
Since the original text was not clear, in the revised version we clearly explain that we did two different cluster analyses and that both analyses produced the same results.

Additionally, for this revised version a chi square test for feature selection was performed after performing the first cluster analysis. This test allows us to select the features or variables that are more relevant, or that are associated with a target variable (the cluster index in our case).

In this revised version we performed the following steps:
1) k-means analysis using all 6 Pb isotope ratios, Pb concentrations, and Pb EF
2) chi square test for feature selection
3) k-means analysis using the most relevant features from step 2 (i.e., five Pb isotope ratios).

Again, both cluster analyses produced the same set of clusters which indicates that only the Pb isotope ratios determine the classification of samples into the different clusters. Therefore, the values of EFs are not relevant for the interpretation of Pb origin in the current study.

Furthermore, to confirm that EF is **not** relevant in the cluster analysis, a Random Forest model was performed to determine relative feature importance as shown in the figure below.



My second major critique regards the interpretation of PSAs. The paper needs to include a clear figure that plots all the ice core data along with both dust and pollution PSAs (supplementary figure would be fine). At present, the pre-1974 samples are plotted with dust end-members and the post-1974 samples are plotted with pollution end-members (figures 3 and 4). However, given the low Efc of 1.5 and the substantial overlap in Pb isotope space of the natural dust sources and

Chinese coal, for instance, the post-1974 samples likely contain significant locally-sourced dust. I understand that the MixSIAR modelling was an effort to quantify these different contributions; but might there be additional approaches that could help constrain the dust vs pollution input (e.g. ice core sulfur or additional trace elements)? Related to the second point, I would disagree with the statement in line 100 that the Efc of 1.5 "strongly suggests" an anthropogenic source for Cluster 2 samples. Rather, there is clearly a strong contribution from anthropogenic sources, but they cannot be the exclusive sources. More nuance here is needed. Also related, figure 1 needs to include sampling locations of the PSA samples presented in the study and a clear depiction of which sample locations (both new and literature data) are included in each of the different dust regions (TP, eastern TP, southwest TP, northeastern TP, NMY3, etc.). These are not indicated anywhere yet are clustered as if they are meaningfully different in figures 3 and 4. What is the rationale for these different regional signatures? Are they statistically or geologically distinct?

- The reviewer makes a good point indicating that there is some overlap. We decided to present two separate figures, one with dust sources and the other with anthropogenic sources. Otherwise, it is very hard to see all the end-members as pointed out by the reviewer. A new figure has been created with both dust- and pollution-end members and it is shown in the SI as suggested.
- Although we think that in the case of Guliya, an EF of 1.5 'strongly' suggests anthropogenic contributions, we recognize that the community is not used to these "low" values, so the word "strongly" has been removed as it is a subjective adverb.
- The explanation on how the different regional PSAs were assigned was explained in the SI. This section has been moved to the Methodology in the main text along with the respective tables. This should now be clearer for the reader.

My third point is that this dataset is presented in seeming isolation from much of the literature. I think the findings here would be more interesting when placed in context with similar snow and ice core records (and corals, etc) from other Asian and Pacific sites. For instance, how do the timing and magnitude of changes at Guliya compare with those measured in other ice cores (e.g. Greenland)? Such a detailed analysis could lead to interesting conclusions about, for instance, atmospheric transport patterns and the influence of natural dust at different locations. As written, the paper seems to exist in a bit of a vacuum, with the exception of the Mt Everest record, to which it is compared.

- Thank you for this suggestion. The ice core records from Belukha and Greenland of Pb isotopes have been added to Figure 3 and discussed in the text along with other natural archives.

Finally, the paper ends with a paragraph that sounds rather methodological and passive: "A binomial filter was also applied…". I would suggest reorganizing and including a clear conclusion paragraph stating the key findings and contributions of the study.

- The paragraph: "A binomial filter was also applied…" was not meant as a Concluding paragraph. We have added a concluding paragraph in the revised version.

Figures:

Figure 1: Add PSA locations and color-code by the regions shown/labeled in figures 3 and 4.

- Figure 1 has been modified. A map of the world with other ice cores discussed in the text has been added. The right panel of the figure corresponds to the original Figure 1. Adding the PSA locations in the right map is not clear as several PSA markers overlap with the Guliya drilling site marker. Figure S4 is a map showing the location, grouping and radiogenic gradient of all the PSAs.

Figure 2: Connect the dots and consider blowing up the 20th century to clearly show the recent changes. Inserting an axis break as in other figures, or including a separate panel, would be appropriate here.

- There is a new Figure 2 which includes other TEs (see response to Reviewer #1). A separate panel was added with a blow up of the 20th century. The markers cannot be connected as they represent discrete samples, not continuous. To facilitate visualization, a smoothing line was added.

Figure 3: If error bars are smaller than symbols, state that in the caption. Otherwise, plot them. The caption needs to give acronyms and define them (e.g., NMY, TP). Again, there needs to be a clear relationship to Fig. 1 and a rationale for separating the TP samples into these 4+ different regions.

- The acronyms NMY and TP have been defined in the figures and tables as suggested. The original Figure 3 contained no error bars therefore it was not mentioned in the caption. Error bars (2σ) and the corresponding caption have been added to what it is now Figure 4.

Figure 4: At least a version of this figure in the supplement needs to include dust PSAs alongside the pollution PSAs.

- A new figure was created as suggested and it is now Figure S5.

Figure 5: This is pretty clear and easy to read.

- Thank you.

Figure 6: The range of the bars is hard to see. I would suggest expanding the ranges vertically and compressing horizontally to show the values more clearly. This could be moved to the supplement.

- This is Figure 7 in the revised version, and has now been modified to make the bars clearer. The y axis remains 0-100% for all subplots to make them all easily comparable.

Extended fig. 1: Define GS in the caption.

- GS has been defined in the new Figure which is now Figure S3.

Extended fig. 2: The Lee et al citation needs formatting. Suggest breaking the axis here to show the 20th century more clearly, or adding a separate panel for more recent data.

- This is now Figure 3 and the Lee citation has been formatted.

Extended fig. 3: This would be more useful if the regions designated in Fig.3 were clearly marked here.

- This is now Figure S4. The new figure has different markers for the PSAs analyzed in this study and for the published ones. In the map the PSAs are encircled according to the PSA group assigned.

Data tables: It's great these are provided here, but supplements are notoriously challenging/ obscure places to archive data. I would strongly suggest including the data and metadata in a public database and including a data availability statement at the end of the manuscript. This will make the data much more likely to be used by others in the future.

- They have been moved to the main text.

Minor comment: The introduction could benefit from reworking, especially the final paragraph.

- We revised the last paragraph as suggested.

Reviewer #3 (Remarks to the Author):

The authors based their findings on ice core samples from different time periods, measured data on lead isotopes especially on 204Pb, and comparisons with various sources, they found the following:

The Pb isotope ratios of the samples covering the pre-Industrial period 1500-~1950 are very similar to the Pb isotope ratios for those samples that are pre-Bronze age, the Pb isotope ratios show a slight decrease in values starting in ~1950 following the establishment of China as a Republic and when the Pb emissions from gasoline began to rise in China。

The decrease in Pb isotope ratios are more pronounced after 1980 when the Pb emissions from leaded gasoline rise exponentially likely due to the demands of energy in China after it adopted a policy of openness and reform in 1978. In the province of Xinjiang, north of Guliya, coal combustion has also been increasing since the 1950s but in ~2007 it increased exponentially. For the Stone Age ice core samples the mixing model MixSIAR estimates of mean contributions of

~12%, 2%, and > 1% from fuels, Pb/Zn ores, and coal, respectively. Overall, all these found are novel, the work is compelling, the conclusions are original. They provided sufficient methodological detail that the experiments could be reproduced. The statistical analysis of the data is sound. On a more subjective note, i feel that the paper will influence thinking in the field in terms of either lead isotopes understanding or technological capability.

- We appreciate the reviewer's useful comments and questions.

Three questions are the following:

1. Line 197: The sentence in the following begins with the use of "And". Is that correct？"And even though leaded gasoline was phased out in 2000, it remained the primary source of anthropogenic Pb at Guliya until ~2007 when coal combustion took over as its primary source. "

- The sentence has been modified for the revised version.

2. Line 162-164：*"*The Pb isotope ratios of aerosols collected in Eastern China cities (except Xin Shao, whose Pb isotope ratios are comparable to those from Guliya) are less radiogenic than the ratios at Guliya but still closer to Guliya's Pb isotope ratios." Does this mean that aerosols from these eastern cities travel to the Guliya Glacier in the west? If so, how are these aerosols transported to Guliya.

- This is an important point. Here, we wanted to compare Guliya with aerosols in China which probably have similar anthropogenic sources (e.g. Chinese gasoline, Chinese coal). Since the Pb isotope ratios are comparable, it is likely that they have similar sources. This does not mean that they both are influenced by emission from the same geographical origin. In our case, Pb at Guliya is probably influenced by emissions from Chinese fossil fuels burned in western Tibet, while the aerosols collected in eastern China were also influenced by Chinese fossil fuels but emitted in Eastern China. The sentences have been

modified highlighting that we are talking about Chinese anthropogenic source comparisons.

3. Line 50-52： In Supplementary Information Text S1: Sample Selection “Samples were acidified to a final concentration of HNO3 2% (v/v) to dissolve TEs in microparticles and to keep in solution those already dissolved. The acidified samples were kept in a class 100 clean room for 30 days to allow the acid to leach the TEs” The acidification time is one month and the content of acid is 2%. Obviously, the samples preparation method are different from those in reference, where pb isotopes data have been compared. Will different pretreatment methods also lead to changes in the isotopic composition of lead? even for the same sample.

- While acidification method affects how much Pb is recovered, it does not affect the Pb isotope ratios as they are not by fractioned by physical or chemical processes. Therefore, they can be used independently of the acidification method used.

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

In reviewing the responses to my comments, along with those of the other reviewers, I feel that the authors adequately responded to the comments and have improved the manuscript. My comments had focused mostly on the presentation of the data and if the results would be relevant to the larger author-base of this journal. The inclusion of data from other regions greatly improves the reach of this manuscript. Additionally, the writing is improved, particularly the inclusion of a true concluding paragraph. I am happy with this version and recommend publication.

Reviewer #2 (Remarks to the Author):

Overall, I find the manuscript to be improved compared to its previous iteration, and I appreciate the authors' careful consideration of prior reviews. However, there are still some areas that need to be strengthened both in the scientific interpretation (see main points below) and in the writing, to make the paper publication-ready. I would recommend hiring an English language editor to help with grammar and sentence structure.

- The manuscript has been reviewed by all co-authors whose first language is English, in addition Prof Ellen Mosley-Thompson has helped improve the English of the manuscript while maintaining the style of the first author. We think the English grammar and structure is correct.

The paper has been improved by the comparison to other Northern Hemisphere ice core records. The new figure 2 is helpful, and the new figure 3 provides needed context for the observations at Guliya. However, with all the records plotted on the same y-axis, the records obscure each other, and the timing of changes is hard to determine visually. I suggest separating each record (e.g. with y-axes alternating left-right-left-right) so that the changes within each record can be seen more clearly. I would suggest adding the Gross et al 2012 Pb isotope record from the Eclipse Icefield to Fig. 3 and the discussion, as this record relates specifically to Asian industrialization. Likewise, the Osterberg et al 2008 Pb concentration record would offer a second regional perspective on North Pacific pollution that could be helpful for comparison.

- Figure 3 has been modified accordingly. We considered adding the Gross et al 2012 Pb isotope record and the Osterberg et al 2008 Pb concentration record. We agree with the reviewer that these records offer a second perspective of the North Pacific pollution. However, the Gross 2012 record is only 30 years long and does not offer a longer perspective like the other records, also since it is strongly influence by North America we think it is not as relevant as the other records. Therefore, we only added the Pb concentration of the Mt. Logan record (Osterberg 2008) to Figure 3.

To strengthen this part of the discussion, a statistical analysis of the timing of changes among the different Pb records (e.g. breakpoint analysis) would provide a more robust framework for the discussion. Currently the paragraph beginning Line 143 uses approximate ages for the analysis; this discussion would be strengthened by the determination of breakpoints within each

record, as the relative timing could be explored in a more meaningful way. Also, line 154 needs to be clarified as to the timing of anthropogenic pollution signals arriving in the TP.

- We have performed a changepoint detection analyses and added in the discussion the exact years.

Figures 4 and 5 are much clearer now. I would advocate for adding into the captions the general characterization of Cluster 1 and Cluster 2 (e.g. main sources and/or age ranges for each cluster) so readers have this information readily available when looking at the figures.

- Done

As stated in my first review, I would strongly suggest including the data and metadata in a public database and including a data availability statement at the end of the manuscript. This will make the data much more likely to be used by others in the future, rather than just including a table in the manuscript.

- The data has been archived in the NOAA repository and this has been stated at the end of the manuscript with the corresponding link. The data will be available as soon as the paper is accepted.

I don't understand the logic in lines 240-242. If leaded gasoline was phased out in 2000, how could it remain the major source of anthropogenic Pb until 2007? This needs to be reasoned through more explicitly.

- This was changed and now it reads as:
  Hence, gasoline remained the primary source of anthropogenic Pb at Guliya until 2007 even though leaded gasoline was phased out in 2000, probably as the result of the continuous use of leaded gasoline and/or the remobilization of legacy Pb [20]. After 2007, coal combustion emerged as the primary Pb source

The paragraph beginning Line 288 is highly speculative and could use clearly described evidence to support the interpretations about atmospheric circulation. Similarly, the concluding paragraph refers to changes in atmospheric circulation, but this interpretation is not well developed or supported in the paper as currently written. Please explain this somewhere and make the steps of the interpretation clearer to the reader.

- We agree that this is speculative but important to mention as a possible explanation. After performing the changepoint analyses suggested by the reviewer, the results show that the increase in Pb isotope ratios coincide with an increase in contribution from southwest Tibetan mineral sources. Thus, we added the word "possible" and now the conclusion reads:
  "In conclusion, the Guliya Pb isotope ice core record reveals two significant changes in Pb sources over the last 500 years. First, possible changes in atmospheric circulation between 1750 and 1935 led to incursions of mineral dust containing Pb, likely originating from southwestern Tibet."

Line 267: refer to Fig 7 here and label the changepoints on the figure.

- Done. Additionally, a new figure was added to the Supplement showing the Changepoints detected in Pb isotope ratio records.

Line 277: Where is this shown?

- Fig. 7 and S1. This has been added in the corresponding line.

Line 568: what is the source of the Xinjiang coal data? Please add to the caption here.

- The reference has been added

Figure 7 and throughout: if there is space available in a figure label to write out the full name of a location, e.g. “Tibetan Plateau” instead of “TP,” then please do so to make the reader’s job easier.

- Thank you for the suggestion, this has been added.

References

Gross, B. H., Kreutz, K. J., Osterberg, E. C., McConnell, J. R., Handley, M., Wake, C., & Yalcin, K. (2012). Constraining recent lead pollution sources in the North Pacific using ice core stable lead isotopes. Journal of Geophysical Research, 117(D16307). doi:10.1029/2011JD017270

Osterberg, E. C., Mayewski, P., Kreutz, K., Fisher, D., Handley, M., Sneed, S. B., . . . Bourgeois, J. (2008). Ice core record of rising lead pollution in the North Pacific atmosphere. Geophysical Research Letters, 35(L05810). doi:10.1029/2007GL032680

Reviewer #3 (Remarks to the Author):

Dear editor,
It is found that the author has made changes to the parts of the manuscript that need to be modified, and has reached the level of publication. I agree to publish in your journal.