Reviewers' comments:

Manuscript ID: egusphere-2025-4801

Title: " U-Pb dating of chrysocolla from supergene copper deposits in the Coastal Cordillera of northern Chile, Atacama Desert"

We sincerely thank the reviewers for their thoughtful and constructive comments. Below, we provide a detailed, line-by-line response to each point raised. For clarity:

- Reviewer comments are shown in italics.
- Our responses follow immediately after each comment in grey colour.
- All corresponding changes have been incorporated into the revised manuscript, where modifications are marked for easy reference.

<u>Reviewer Comment 1: Donald Davies 23.10.2025</u>

This manuscript presents interesting data on the ages of copper-bearing minerals from hypogene ore deposits in the Atacama Desert in Chile. The results have important implications for regional climate history and so should be of interest to environmentalists as well as economic geologists. The writing is not bad considering that English is not the primary language of the authors. I have made minor suggestions for improvement on an annotated copy of the text.

Comment 1.1: *The analytical work is extensive but important documentation is lacking, and error propagation is questionable. Since all the Pb and U measurements were made together, the 207Pb/206Pb and 238U/206Pb data must be correlated, but correlation coefficients for all the U-Pb data are set to zero in the tables. Errors are reported on only 207Pb/206Pb and 238U/206Pb ratios, making it impossible to calculate the correlation values, which could be calculated from the formula: rho = (%SigX^2 + %SigY^2 - %Sig(X/Y)^2) / (2 * %SigX * %SigY) although it is better to calculate them in the data reduction program from the variance in X*Y. This will have the effect of rotating the error ellipses.*

Response 1.1: Thank you very much for the comment. Error propagation has been done following the guidelines set by Hosrtwood et al. (2016). The correlation coefficients have been calculated, and they consistently equal to zero or greatly approximate to zero. We find that this is the common situation for the correlation coefficient, rho, of Tera-Wasserburg ratios, with laser ablation and high sensitivity mass spectrometers data. We agree that rho is calculated with the mentioned formula by the reviewer, which we consider that is eq. 122 from Schmidt & Schone (2007), with the particularity that the third term of the denominator (i.e. "%Sig(X/Y)^2") is the relative uncertainty of ^{207}Pb/^{235}U ratio (instead of ^{238}U/^{207}Pb ratio as stated in Schmidt & Schone 2007). As ^{235}U is calculated as ^{238}U/137.818, "%Sig(X/Y)^2" can be easily calculated from the uncertainties reported in our data tables ("%Sig(X/Y)^2 = (%Sig (^{238}U/^{206}Pb)^2 + %Sig (^{207}Pb/^{206}Pb)^2)^0.5. Therefore, rho can be easily calculated from the data provided. Furthermore, we also calculate this rho value with the formula A13 of Noda 2017, which yields the same results. As the reviewer points out, the graphical effect of rho is ellipse rotation. As rho is ~ 0, ellipses are not rotated. We also consider that the reported ratios and uncertainties are appropriate and common practice. If the reviewer or editors consider that other ratios should be reported, please indicate us which, and we will report them.

Comment 1.2: *The data sets are presented on Tera-Wasserburg concordia plots blown up to the scale of the data spread. This does not give a very good feel for the reliability of the results. Most data sets have a limited spread near the Y axis, meaning that Pb is weakly radiogenic and the scope of each diagram is different. The ages are very young meaning that the intersections with the concordia curve, which define the ages, are well beyond the scope of the figures (the intersection would be at infinite 238U/206Pb for age zero). I suggest that the authors include at least one large-scale composite plot so the reader can get a better idea of the distance between the data and the concordia intersections.*

Response 1.2: The scale is blown up to the ellipses themselves so that the readers can assess how well the ellipses are aligned, to see if only a few ellipses greatly influence the regression line or not, and to assess the relative concentration of Uranium on each analysis. This indication of relative U concentration is given by colour coding. Plots have been updated accordingly. U-Pb analysis on materials with very low amount of radiogenic Pb relative to its total Pb (e.g. carbonate, sulfate), usually show the same particularity, a low spread near the Y axis. We assume that the readers are familiar with this type of plots and that they are able to assess the reliability of the results. Nevertheless, we agree with the reviewer that adding a large-scale plot would be beneficial, and therefore we have added it. See Figure 11.

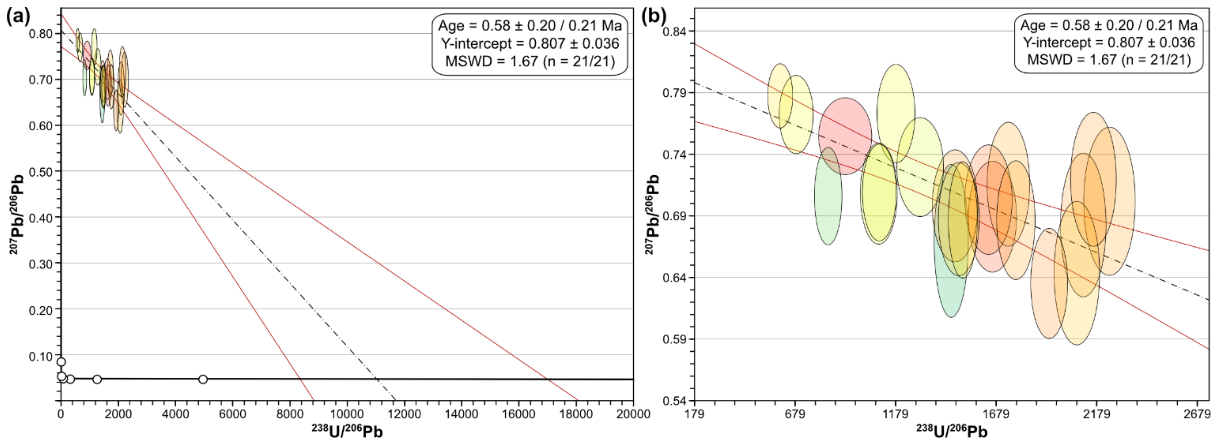

Figure 11. (a) Large-scale plot of sample MA22-01-04b showing the distance between the data and the concordia intersections. (b) Zoomed view of the data. Note the variations of the scale on the x axis. Ellipse colour denotes relative U abundance (red = highest; green = lowest).

Comment 1.3: *Significance of the Y-axis intercepts is worthy of discussion in the manuscript. Regression on the T-W plot defines an initial 207Pb/206Pb ratio as well as an age. The initial ratio is more constrained than the age. Many, if not most, initial ratios from carbonates and phosphates accord with the simple crustal Pb growth model of Stacey and Kramers, which was defined using Pb from large ore deposits with diverse ages. This model predicts a 207Pb/206Pb ratio of about 0.84 for the late Cenozoic, which accords within error with most of the data sets. Significant deviations are almost always toward lower 207Pb/206Pb values as seen here for 3 of the samples. These could be due to mixing with radiogenic Pb released from the breakdown of other minerals during formation of the dated minerals. Are there any coeval high-Pb minerals in the assemblages that could be used to measure a more precise initial Pb ratio that could anchor the isochrons? The ratios that agree within error could be averaged and used to anchor individual isochrons giving more precise ages. Even using an artificial number with no error should result in ages that are accurate relative to each other, provided one can assume the same initial ratio.*

Response 1.3: This is a great point. Coeval high-Pb minerals were not found, or their cogenetic nature was doubtful. We agree that averaging these initial Pb/Pb ratios and anchoring the regression lines to them would greatly improve our results. The variability of these ratios shows, as the reviewer points out, that fluids with high radiogenic Pb were involved in the precipitation of at least some of the samples, and therefore, using the ratios provided by Stacey and Kramers model to anchor our linear regressions did not seem appropriate. Furthermore, the number of samples per site, which we could have calculated an average, is low, and therefore we decided that averaging these ratios and using them as anchors could hinder our accuracy.

Comment 1.4: *I do not understand the rationale of expanding the data errors so as to get MSWD values near 1 (lines 167-169). Errors on the individual ratios should be determined based on the numbers of counts. MSWD values serve to check whether scatter can be accounted for by measurement errors alone or whether it may be affected by other factors such as late disturbance. A moderately high MSWD does not invalidate data, it just serves as a warning of possible complications.*

Response 1.4: The uncertainty budget on the individual isotopic ratios comes from 5 sources (see Horstwood et al., 2016):

1) Internal uncertainty (standard error of the individually collected ratios)
2) Excess of scatter derived from the primary reference material calculated after drift-over-time correction
3) Uncertainty from background correction
4) Uncertainty from counting statistics
5) Excess of variance calculated from our offset reference material.

One of the main difficulties of this article is that we lack a matrix matched reference material (RM), i.e. a Chrysocolla RM. To overcome this, we used not only one offset RM, but three. We assume that the real isotopic bias that comes from the fact that our primary RM is a Nist glass and what we are dating is Chrysocolla, i.e. our "matrix offset", is enclosed within the biases or offsets of the 3 chosen RM, which are Zircon, Monazite and Titanite, plus the Nist glass. Therefore, we applied the full offset (U/Pb bias) from the three RM (and Nist Glass) as a systematic uncertainty (see lines 168-170).

As we have used three offset RM we must apply the excess of variance correction technique (abovementioned source of uncertainty 5) from all three offset RM. This so-called "excess of variance" consists of increasing the uncertainties so that the MSWD of all ratios or linear fittings (depending on how the age is calculated) of all three RM have an MSWD <= 1 (see Horstwood et al., 2016).

Comment 1.5: *It is not logical to add the dispersion of results on the standards to each other or to the sample.*

Response 1.5: We do not agree, and we do think it is logical. As explained previously we assume that the real "Chrysocolla offset" is enclosed in the combined offsets shown by Nist glass, Zircon, Monazite and Titanite.

Comment 1.6: *Adding in quadrature assumes that deviations are random, whereas biases are systematic.*

Response 1.6: We do not agree. It is true, that all random uncertainties are added by quadratic addition (to our knowledge), but it is also true that some systematic uncertainties can be also added by quadratic addition, e.g. long-term variance. In other words, the mathematical instrument used to add uncertainties is independent from the nature of the uncertainty itself.

Comment 1.7: *The sample data should be corrected linearly for the Pb/U bias determined using a matrix-matched standard. The ablation biases on monazite, titanite and zircon chosen as standards* *should be quite different from each other as well as the samples. Although there are no chrysocolla standards there are many carbonates that qualify (although there are also differences between carbonates like calcite and dolomite).*

Response 1.7: To our knowledge a chrysocolla standard or reference material (RM) does not exist. This is one of the main difficulties that this article wants to overcome. The sample data has been corrected for the Pb/U bias by polynomial regressions following instrumental drifts corrected with Nist. It has also been corrected linearly based on the Monazite RM. This was not stated in the text and has been added in line 186: “Monazite was used as the matrix offset RM”. As the reviewer points out, this would have been the correct way, if we had a matrix matched RM, but we haven´t. Therefore, our strategy has been to calculate the entire dispersion of Pb/U biases from all RM and feed it into the systematic uncertainty budget. We have chosen monazite, titanite and zircon precisely because their biases should be very different from each other. This way, we have a good chance that the real and unknown Chrysocolla Pb/U bias is accounted for. We also considered carbonate as a candidate for offset RM but it was discarded because Chrysocolla has no carbon nor carbonate ion in their composition. Despite this, we agree with the reviewer that it would have been a good decision to add a carbonate, in an attempt to enlarge the abovementioned Pb/U bias dispersion. It is obviously too late now, as the analysis have been concluded, but we will consider it for future analysis. Thank you.

Comment 1.8: *The normal procedure is to use NIST only for correcting 207Pb/206Pb mass bias. A primary matrix matched standard is then used to correct 206Pb/238U, which is affected by both mass and ablation bias. A different secondary matrix matched standard is then run to confirm the correction of the first. This is especially important for spot analyses where ablation biases can be tens of percent and vary with pit depth. Ablation bias should be minimized (although not eliminated) by performing scans rather than spot analyses (Dix et al. 2021 doi.org/10.1016/j.chemgeo.2021.120582). I suggest that the authors analyze some carbonate standards, such as WC1, under the same conditions as their samples. Since the ages are so young, they can tolerate relatively large errors and still be useful, but it is a shame to degrade such extensive results by poor calibration. In any case, the results on standards should be explicitly reported (e.g. give the measured 238U/206Pb ablation bias found for them).*

Response 1.8: We thank the reviewer for the suggestion of using scans to minimize laser induced elemental fractionation. We agree that the U/Pb bias for each of the reference materials should be reported. We have updated the metadata files and added this information (see Supplement File 2).

Comment 1.9: *Raw data files (usually CSV files) should be reported as Supplementary Data so results can be recalculated in future when we might have a better understanding of bias correction.*

Response 1.9: Please consider that we have recorded 10 channels of detection on both analogue and counting detection modes for each of the 6 masses considered for 300 runs per analysis. The size of the raw files is quite big (this is probably why raw files are never reported). We are happy to provide these files per request but reporting them as supplementary material is most probably not convenient due to file size.

Minor comments (from PDF file):

We changed and corrected all minor grammatical errors marked in the attached pdf file accordingly.

We thank Don Davis for the very detailed review of our manuscript and highly appreciate the valuable input. We corrected and modified the manuscript and dataset to meet the reviewers’ comments and questions.