Geochronology Discuss., author comment AC3
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Reply on RC2

Johannes Rembe et al.

Author comment on "Calcite U–Pb dating of altered ancient oceanic crust in the North Pamir, Central Asia" by Johannes Rembe et al., Geochronology Discuss., https://doi.org/10.5194/gchron-2021-27-AC3, 2022

Dear Reviewer,

We thank you for the careful revision of our manuscript. We fully agree with you and are in the process of implementing the suggested changes. Below you find the detailed responses. We kept the original review comment and added responses, marked as "Reply".

Reviewer's comments:

Although the manuscript is nicely written and I like the idea of dating Palaeo oceanic curst by U-Pb in calcite, I can't recommend a publication in its present form. I see an overinterpretation of the analytical data and therefore recommend a cautious re-evaluation of the ages and their significance. I refer mainly to the analytics used, the assessment of the precision and accuracy of the data, the presentation of the results. The data must be presented more completely in the tables (online), the standardization and error consideration must be explained more clearly and adapted to the standard procedures currently in use.

Reply: Thank you very much for these comments. We have studied them in detail and agree with these suggestions. We have realized that our original Figure 4 (whole-sample TW age plots) could be misleading. The use of large numbers of spots (up to >400 per sample) somehow is disadvantageous as it erroneously conveys a message that these ages are precise. We thank the review for pointing it out. In the revision, we will provide TW plots and age calculations (including propagated errors) based on individual areas.

Reviewer's comments:

I do not believe that the calcite ages match those of the ocean crust, but possibly within an age error/scatter range of 3-6% (which I believe is realistic for the data).

Reply: Thank you for noting this. This comment made us to realize that we should have done a better job in making our core conclusion more explicit, which was in fact consistent with the reviewer's comment here. In our original manuscript (e.g., Line 182—184, 214ff.), we interpreted the ages as minimal formation ages of these basalts. These calcites likely formed during alteration processes that affected the basalts after emplacement under sea-water coverage (stated at e.g., Lines 42—43). We agree (here and in our original submission) that these ages do not represent the timing of rock formation. We sincerely thank the Reviewer for this comment as it highlights the unclear expression in our original submission. In the revised version, we will explicitly state the difference between radiometric ages of volcanic rocks and the age of associated ocean floor alteration.

Reviewer's comments:

Be aware that it is an interpretation of the data, it could be also the result of the mixing of a complex domain consisting of multi-generation veins. I would suggest using an age range (e.g. 310-330 Ma) for each sample as the results do not suggest that they formed during one short-lived event. Alternatively use weighted average (carefully evaluate the uncertainty, see below), although it is statistically incorrect.

Reply: We will more carefully discuss the ages obtained for each single ablation area by introducing a new figure showing ablation area specific Tera-Wasserburg plots. Grouping of ablation areas for data calculation will be avoided. Following the Reviewer's suggestions, we will give an age range for each sample that better reflects the spread of the obtained single ablation area ages. However, as stated in the original text, the dated calcite filled vesicles are very close together. It seems unlikely that one vesicle crystallized millions of years after a vesicle not more than 2 cm away from the first. We will discuss this issue in a greater detail.

Reviewer's comments:

Referring to Su et al 2020 and Yang et al 2021 for a description of the method is insufficient, both papers are also application papers. You need to explain how the raw data were treated; corrections and outlier rejection, standardization, and uncertainty propagation have been done. This has to follow the recommendation of Horstwood et al. (2016, Geostandards and Analytical Research)

Data in high-rank journals should include comparable data sets, in which uncertainties were correctly propagated (see Horstwood et al. 2016): random uncertainties, from background correction, counting statistics and access of variance (drift correction using NIST614), and systematic uncertainties, ratio uncertainty of RM (>1%), long-term variance (>1% !), decay constants. It is not clear how the authors correct for matrix-related Pb/U fractionation (using one or both of the mentioned carbonates). The material they used is no international reference material and its age and uncertainty have not been evaluated by an independent method (e.g. ID-TIMS). Please explain in more detail the applied approach to re-evaluate your uncertainties and uncertainty propagation. Report data in table S2 of your reference material measured during the sessions, report data for long-term variance (reproducibility) of your method and that of access of variance of your NIST614.

Reply:

Thank you very much for this comment. We will include more technical details in the revised text and will also discuss our results. In our analysis, we used NIST614 as the primary reference material to correct for 207Pb/206Pb fractionation and for instrument drift in the 238U/206Pb ratio. 238U/206Pb ratios were calibrated with a matrix-matched reference material (our in-house reference material) and validated by using WC-1 as the monitoring standard. We will explain it better in our revised version in line with other published studies using this approach. We will also conduct uncertainty propagation following the recommendations of Horstwood et al. (2016). We do believe this will significantly improve the quality of the data.

We would like to note that our manuscript is intended to be an application paper as well. It is not our intention here to provide any methodology development because pitfalls and advantages of laser ablation calcite U-Pb dating have been thoroughly discussed in the community (Rasbury & Cole, 2009; Roberts & Walker, 2016; Roberts *et al.*, 2017; Roberts *et al.*, 2019; Kylander-Clark, 2020; Rasbury *et al.*, 2020; Nuriel *et al.*, 2021; Rasbury *et al.*, 2021; Roberts *et al.*, 2021). The message we would like to highlight here is that calcite phases yielded useful U-Pb ages that constrain (not directly date) the formation of ocean-floor basalt.

Reviewer’s comments:

The authors use WC-1 (incorrectly labeled WC01 in their text) as secondary RM to evaluate the accuracy of their data.

Reply: Thank you for pointing it out. We will correct this in the revised manuscript and will do a thorough check to make sure no such mistake is presented in the revised version.

Reviewer’s comments:

However, based on this the data is up to 5% inaccurate. The data of Roberts et al. reflects some heterogeneity of this material and is explained by sampling bright and darker domains to achieve some spread in the Pb/U (see Rasbury et al. 2021). They report a 2.5% uncertainty. Rembe et al. report a 1% younger age with a 1.5% uncertainty (no systematic uncertainties propagated), which means the data can be up 5% inaccurate! This needs to be mentioned in the paper and considered in the discussion of the data!

Reply: We accept the reviewer’s comment. We will propagate systematic errors from the results of the monitoring standard (WC-1) into the final reported ages. We are aware that the errors given in the original manuscript represent solely analytical errors that underestimate the geological spread and the uncertainty arising from calibration to heterogenous reference material.

Reviewer’s comments:

Based on the data it is not possible to evaluate the precision and accuracy of the ages. However, the authors report ages in the text of the manuscript with a precision of better than 1%. This is misleading and gives the impression they can date their sample and events with precision and accuracy of better than 1%. For the majority of carbonate ages so far published, uncertainties range from 3-5% or worse (Roberst et al. 2021, Geochronology) and only very few labs demonstrated a long-term variance of 2% (e.g., Guillong et al. 2021, Geochronology). The authors need to access their precision/long-term variance/accuracy and should not quote any uncertainties in the text with the figure behind the dot (300 +/- 4, instead of 300.5 +/- 3.6 Ma) and with no or maximal one figure (!!) after the dot in the figures.

U-Pb ages: Fig.4: First of all, I can’t reproduce exactly the ages using the data presented in table S2.

Reply: We respectfully disagree with the reviewer’s comment that our data “it is not possible to evaluate the precision and accuracy of the ages”. Our analytical session included the measurement of WC-1, one of the widely used reference material for calcite U-Pb dating, as the validation of accuracy. We do admit that we should have done a better job in presenting the data and therefore we will thoroughly follow the reviewer’s suggestion in propagating errors, openly stating the size of errors of calculated ages, and avoiding quoting too many digits after the decimal point. We also seriously examined the reviewers observations of not being able to exactly reproduce the ages and re-calculated all of our ages. Our ages were calculated with the IsoplotR program (Vermeesch, 2018) version 3.5 running in R version 3.6.0. We found that our original ages remained unchanged and suspected that the possible discrepancies between our and reviewer’s results might have arisen from rounding errors when using e.g. Ludwigs Isoplot in Excel.

Reviewer’s comments:

Secondly, an MSWD of around 2 or higher means the data forms, not a uniform population/event or uncertainties were not probably propagated.

Reply: In the original submission, we grouped all ablation area ages out of the same sample together and produced the following MSWDs: 2.0 (Sample 17NP436a), 1.4 (Sample 17NP436b), 3.0 (15NP233), 2.1 (15NP236). We noted that single ablation area ages overlap within 2 sigma errors and they are statistically indistinguishable. We did not provide clear visual presentations (e.g., TW plots in the main manuscript) and therefore made it difficult for readers to access this information. In the revision, we will follow the reviewer’s suggestion and present TW plots/calculation out of each area. In the revised version, the MSWDs out of the area ages are:

Basalt breccia samples

17NP436a_A, MSWD = 0.9	17NP436b_A, MSWD = 0.4
17NP436a_B, MSWD = 1.1	17NP436b_B, MSWD = 2.4
17NP436a_C, MSWD = 1.4	17NP436b_C, MSWD = 0.7
17NP436a_D, MSWD = 2.0	17NP436b_D, MSWD = 1.1
17NP436a_E, MSWD = 2.6	
17NP436a_F, MSWD = 2.6	

Vesicular basalt samples

15NP233_A, MSWD = 2.4	15NP236_A, MSWD = 1.3
15NP233_B, MSWD = 1.6	15NP236_B, MSWD = 1.1
15NP233_C, MSWD = 5.6	15NP236_C, MSWD = 1.8
	15NP236_D, MSWD = 0.8
	15NP236_E, MSWD = 3.7

We show that 11 out of total 18 area ages yielded MSWD < 2.0 (16 areas < 3.0), suggesting single-phase calcite for most areas. Compared with recently published geochronological results on carbonates, our MSWDs seem to be generally small. We believe this reflect the complex nature of dated calcite (e.g., multiple generations) as stated by the Reviewer. We have developed our manuscript to include clear notes on the areas that have large MSWD and make it explicit that such ages should be treated with caution.

Reviewer's comments:

In the first case, it would mean the different areas are not formed at the same time. In figure 2 it is shown that data was acquired from different domains, so you can't group them together and calculate a common age as you have done. This is a mixed-age with misleading incorrect precision and accuracy. You should report the ages of individual areas and compare these ages with each other as you have done in figure 3. So change Fig 4, only use some representative examples for the Tera-Wasserburg diagram.

Reply: We agree with this comment and will add a reworked figure, as stated above.

Reviewer's comments:

If you want to use a weighted average, do not forget that they likely represent mean ages, representing more an age range. But still, you have to add systematic/expanded uncertainties to the final age on the weighted average ages when comparing it with other data. So for Fig3 weighted average use 316 ± 8 / 12 Ma (internal/expanded uncertainty).

Reply: Thank you for this comment. We will consider this for the revised version.

Reviewer’s comments:

As it is visible from scans B3, B4 the investigated domains do not form by a single process of calcite vein-forming but show a more complex pattern with different generations of cross-cutting fractures.

Reply: We are very happy with reviewer’s comment here as it is consistent with what we stated in the original manuscript in line 140ff. Those fissures with low Sr content formed obviously under differential stress causing pressure solution and reprecipitation. This was also pointed out in the figure caption of Fig. 2. We avoided fissures which occasionally crosscut the coarser calcite cement, resedimented cement fragments and matrix in basaltic breccia samples 17NP436a and b.

Reviewer’s comments:

And still, the authors what to interpret the U-Pb ages as representing a single calcite precipitation event at the time of basalt-crystallization? Please be more cautious in the interpretation of your data. The obtained ages of the different areas of one sample scatter and reducing the uncertainties by statistical tricks using all data in one single Tera-Wasserburg, is not the way to go.

Reply: As discussed before, we have completely taken this comment on board and revised the ablation area ages. In the revised manuscript we will present Tera-Wasserburg plots for each ablation area (similar to Appendix C in the original manuscript) along with lower intercept ages with correctly propagated errors. In the original manuscript we already pointed out that the age of alteration of the basaltic rocks was the scope of our dating. This might be similar or younger than the crystallization age of the basalt (as stated in the original manuscript line 178-180) Therefore, we are aware that this process may last for up to 25 Ma (as it was found out for (sub)-recent oceanic crust e.g. by Coogan & Gillis, 2018). This was discussed in the original manuscript (e.g. 38ff., 63ff.). Thank you for giving us the opportunity to underline this fact.

Reviewer’s comments:

I also have to comment that the geochemical data is not presented very convincing, I would like to see plots showing that the spots of the different domains show similar trace element composition e.g. using elemental ratio plots, incompatible/compatible.

Reply: Thank you for this comment. We will follow your suggestion and present more geochemistry plots. We used different minor and trace elements to find indicators for the influence of sea water. We see the complexity of this issue.

Reviewer’s comments:

Figure caption of D1 does not explain the greyish field (whole rock data??).

Reply: Thank you for this comment. The grey area should be labelled as the range of all presented REE analysis.

Reviewer’s comments:

Having insitu Sr isotope data would support the interpretation.

Reply: We thank the reviewer for this suggestion but investigating in situ Sr isotopes is beyond the scope of our study. Therefore we would like to respectfully take this comment on board for future studies.

Reviewer’s comments:

Line 181-184: A rough overlap of U-Pb carbonate ages with metamorphic (meta-andesites)

Reply: We should stress those Ar-Hbl ages are interpreted as igneous ages with minor argon isotope disturbance indicating a younger thermal event. (see data and interpretation by Schwab *et al.*, 2004).

Reviewer’s comments:

and felsic magmatism in the range of 350-314 Ma, does not prove that the obtained ages reflect calcite precipitation related to oceanic crust formation.

Reply: Thank you for this comment. We should discuss other possibilities of calcite formation in the revision. However, as we have stressed, the geochemistry indicates the influence of relatively cold, oxidating sea water.

Reviewer’s comments:

The U-Pb data tables and metatables have to be prepared accordingly to Horstwood et al., to enable readers to understand the data quality and the method. Data tables should include U and Pb content calculated, the signal strength of 206 and/or 238 in cps, the Th/U ratio, and the rho value (even it is close to 0!).

Reply: Thank you for this comment. We will improve our data tables, as suggested.

Samples should be clearly separated in Table S2. Sample coordinates should be included.

Reply: We agree with the reviewer and will do as suggested. We believe this will improve the readability of the data tables.

Reviewer’s comments:

From the existing data table S2, I get similar ages and similar uncertainties but not the same numbers as reported!

Reply: Thank you for informing us. As stated above: All ages were calculated using IsoplotR (Vermeesch, 2018) version 3.5 running in R version 3.6.0. Possible discrepancies might arise from rounding errors when using e.g. Ludwigs Isoplot in excel. We will revaluate table S2 and make sure that it is consistent with the presented ages. We will also clarify which programmes and versions we used to calculate the ages.

Reviewer’s comments:

Figure C1, please include MSWD of each age, add the information that you used 2sigma uncertainties

Reply: We agree with the reviewer and will do as suggested.

Reviewer’s comments:

Line 149: ‘they overlap within 2s-error for each sample'. Please explain this better

Reply: We will better explain this in the revised manuscript.

Reviewer's comments:

Line 169: … 'overlap mostly within 2s-error per sample' – I don't agree with using this as evidence they formed during one event. No, they differ in age, and looking at the scans in B4-B4, it is not compatible with the idea of one single event of vein formation.

Reply: Thank you for your comment. In the original manuscript in line 140ff, we emphasised that these fissures with low Sr content formed under differential stress causing pressure solution and reprecipitation. They formed much later than the resedimented sparry calcite cement in samples 17NP436a and b. They must have formed at a time when the basalt breccia was already lithified. Therefore, dating of those cross-cutting fissures was avoided in the original manuscript. Note that they were not present in the vesicular basalt samples.

Overlap in 2s-error suggests to us that the ages are statistically identical. As noted in the replies above, we will stress that calcite precipitation happened during a long time span. We will more carefully discuss ablation area age MSWD values. We will also be more careful and will not present overly exact sample ages. We will present, as you suggested, age ranges for each sample. Calcite ages must be seen as a constraint on ocean floor formation. They clearly do not date the crystallization of the basalt, nor have we stated this.

Reviewer's comments:

Fig. 3: Quote the MSWD for each sample, they do not form a homogenous population, be careful to interpret this as one age. Use in addition the expanded uncertainty (see below/above). The intial Pb of the different domains scatter also quite a bit…

Reply: As stated previously, we will underline this fact in the revised manuscript. Thank you for the comment.

Fig.4. figure caption, explain better, .e.g all data obtained from the different areas of the 4 samples. However, I do not agree that you can plot (U-Pb) them in this way together (see above).

These REE plots are for me not very convincing to support that the veins form during a single event…

Reply: We agree with the reviewer and will clarify that we use the geochemistry solely to interpret and discuss the process responsible for calcite precipitation. We are convinced that ocean floor alteration is a reasonable interpretation (process wise). We will make clear that this process happened during a longer time span and does not reflect one single, precisely dateable event. Indeed, alteration is unlikely to occur as an event (in the sense of an igneous eruptive/intrusive event).

Fig.5. Report all the ages with reasonable accuracy (including Ar-Ar ages, LA zircon ages, and the LA carb ages), so without figure behind the dot (only ID-TIMS data should be presented with sub-% accuracy!). It also makes ages not better accessible if more figures are reported.

Reply: We agree with the reviewer and will do as suggested.

Thank you for your constructive comments. We are sure that this will improve the quality of our manuscript.

Sincerely,

Johannes Rembe, on behalf of all co-authors

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