EGUsphere, author comment AC2
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Reply on RC2

Aratz Beranoaguirre et al.

Author comment on "In situ LA-ICPMS U–Pb dating of sulfates: applicability of carbonate reference materials as matrix-matched standards" by Aratz Beranoaguirre et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-72-AC2, 2022

We thank both referees, Dr. Mottram and Dr. Kylander-Clark, for their insightful and useful comments, which will improve the manuscript. We have implemented the changes that were needed and below, we reply to their comments.

Summary of paper

This paper builds on the approach of in-situ U-Pb carbonate geochronology to develop a methodological approach to dating sulfates. The authors explore the feasibility of using carbonate reference materials to date sulfates. The same approach as U-Pb carbonate dating is utilised where data are initially corrected for mass bias and drift using NIST614 followed by a secondary correction using the WC-1 carbonate reference material (Roberts et al., 2017). ASH-15D (Nuriel et al., 2021), B-6 (Pagel et al., 2018) and an in-house reference material were analysed as secondary reference materials (~1.5-2% reproducibility). Sulfates contained variable U which meant hat the majority of samples were undateable. Supfate was found to ablate faster than carbonates but the relatively offset was thought to be not significant and accounted for by the uncertainties. The five analysed samples reasonable dates were yielded given previous geochronological constraints.

Review

Overall, I think this is useful contribution to the growing literature analysing new and unconventional geochronometers. The authors use up to date geochronological methods to yield a robust dataset, following established methods for carbonate geochronology. The methods are thoroughly presented following the recommendations of Horstwood et al., (2016) and the results are well presented in both tables and concordia plots. The authors present some useful discussion about the use of carbonate reference materials for analysing other geological materials. The paper is within the scope of the journal and will be of interest to a range of geochronologists. I therefore think that this paper should be published subject to the corrections below.

Suggestions for edits

Applicability and flaws in the approach: The discussion should be expanded to discuss the flaws with U-Pb sulfate dating- what is the potential wider scale applicability considering the relatively low success rate (5/32) for this study?

Beranoaguirre et al.: *According to experimental studies (Astilleros et al., 2010; Morales et al., 2014; Kameda et al., 2017), a large amount of common-Pb in gypsum and anhydrite can be expected. This fact makes the young samples more difficult to date, as their success strongly depends on the spread in the X-axis ($^{238}U/^{206}Pb$). The success in older samples (for example, Cretaceous) is more influenced by the spread in the Y-axis ($^{207}Pb/^{206}Pb$). The experience in our laboratory confirms this statement, as the success rate increases with the age of the sample. However, the goal of this study was to check the applicability of the carbonates as reference materials, it was necessary to analyse samples with known age. Unfortunately, the samples from the Messinian Salinity Crisis were the only available sulfates with known age.*

In any case, the discussion has been extended regarding this idea.

Are there any potential gypsum reference materials? Can you include discussion of work being done to develop matrix matched reference materials?

Beranoaguirre et al.: *So far, we did not find any sulfate that matches the requirements for becoming a reference material, i.e. reproducible age, isotopically homogeneous, etc. Indeed, one of the ideas of publishing the manuscript is to bring the attention of the community towards sulfate dating, with the hope that further research on them will develop matrix-matched standards in the near future. Although meanwhile, working with carbonate RMs is an alternative.*

Can you include some background to the astrochronology method- how does this work and how do results compare with absolute radiometric dating methods?

Beranoaguirre et al.: *Astrochronology is the dating of sedimentary units by calibration with astronomically tuned timescales, such as Milankovic cycles. A short sentence and a reference are added to the text.*

Suggestions for additions to the supplementary materials:

Grid references of samples

Beranoaguirre et al.: *Some of the samples are drill cores collected in the 60's and 70's that were stored in different institutions. We were able to reuse the samples, but we have no information about the exact positions where the samples were collected.*

More thorough information about each sample include hand specimen, thinsection/puck, any sample characterisation- SEM images? CL? Image showing spot locations on the analysed material.

Beranoaguirre et al.: *No SEM or CL study was carried out before the analysis. The samples are massive sulfates and we observed/followed no specific systematic or criteria*

to set the spots. The spots were located after pre-screening (see answer below). In our opinion, the images do not add any information on this issue.

Include laser conditions written out in the main merthods

Beranoaguirre et al.: *Following the suggestions of both reviewers, the methodology section has been expanded.*

Th-Pb data- did you analyse Th? If so, then please present this data and you could also use the 208-approach of Parrish et al., 2018

Beranoaguirre et al.: *We have analysed Th, but not the ^{208}Pb. The Th is monitored to check for possible outliers, i.e. extremely different Th/U ratios, although almost none of the analyses has been rejected due to it. The ^{208}Pb is not measured because of different reasons. The peak width of the MICs (multiple ion counter) that should be used for ^{208}Pb is narrower and less sensitive than the SEMs (secondary electron multiplier) used for ^{206}Pb and ^{207}Pb. In theory, this should not be a problem, although it requires more carefulness when tuning. But given the fact that the ^{208}Pb can saturate easier (we do also measure other materials with higher U content), and ages can be calculated using only the ^{206}Pb and ^{207}Pb, we do not use the ^{208}Pb on a regular basis.*

Data table- expand to include more columns as per suggestions of Horstwood et al., 2016 and include comments on analysis location on materials.

Beranoaguirre et al.: *We have followed the suggestions of Horstwood et al. (2016), and all the representative data from our analyses is shown. Horstwood et al. (2016) data table was mainly thought for zircon analysis, and in our case some of the columns, like the ones referring to the single spot ages, are useless. Regarding the comments on spot locations, there is no information to add about it. The samples are massive sulfates, and the spots were set all over the thin section/slab after pre-screening (see below).*

Can you plot data from the MC and SF on the same concordia for comparison?

Beranoaguirre et al.: *The changes are performed as suggested.*

Line comments

Line 30 – add Rasbury, E. T., & Cole, J. M. (2009). Directly dating geologic events: U-Pb dating of carbonates. Reviews of Geophysics, 47(3).

Beranoaguirre et al.: *The suggested reference is now added.*

Line 31- Skarn garnet reference missing

Beranoaguirre et al.: *The references Burisch et al. (2019) and Yan et al. (2020) at the end of the sentence are already examples of Skarn garnet.*

Line 46- Can you outline best practice for evaluating suiyability of non-matrix matched reference materials?

Beranoaguirre et al.: *We realized that the use of the term non-matrix matched reference material is a bit misleading, and we should better used almost matrix-matched standardization. According to our experience the match between RM and sample should be as close as possible. Sulfates show very similar ablation behaviour (e.g. drill speed) as calcite and similar behaviour of the U/Pb fractionation, with only a very weak dependence on ablation conditions (e.g. when doubling laser frequency and fluence)*

Line 46- Can you outline why one might want to date sulfates (or move lines 55-56 up)

Beranoaguirre et al.: *Following the suggestion, the third paragraph of the introduction has been reformulated.*

Line 48- outline what astrochronology is.

Beranoaguirre et al.: *A short sentence and a reference have been added to the text.*

Line 66- Where in the world is this?

Beranoaguirre et al.: *The Tripoli Formation is located in Sicily (Italy). Now it is specified in the text.*

Line 68- What is Astronomical tuning?

Beranoaguirre et al.: *The astronomical tuning is the most accurate dating technique for sediment records spanning the time interval of the last 35 m.y. for which astronomers provide a valid and precise orbital solution for variations in Earth's orbital parameters (Laskar, 1999)*

Line 73- 'mention' seems vague- make more specific

Beranoaguirre et al.: *now "describe" is used instead of "mention", and a reference is added (Hsü et al., 1973).*

Line 91- How were samples pre-screened?

Beranoaguirre et al.: *We do a brief ablation, ca. 1 second, while checking the live U and Pb signal. Based on that, we decide where to set the spots.*

Line 97- average sensitivity based on what ablation conditions?

Beranoaguirre et al.: *This is now specified in the extended Methods section.*

Line 106- state the carbonate reference material here and reference needed for NIST?

Beranoaguirre et al.: *The changes are performed.*

Line 112- how was downhole fractionation corrected?

Beranoaguirre et al.: *The downhole correction is calculated for the common-Pb corrected WC-1 and then, the fixed calculated value is applied to all the unknowns. Usually, the WC-1 gives a downhole fractionation of ca. 3%.*

Line 119- What is the in house reference material? Name and age?

Beranoaguirre et al.: *This is a calcite that has been measured several times in our lab. The data is highly reproducible (ca. 36 Ma) and it is under consideration for becoming a potential calcite RM. TIMS analyses are still to be performed.*

Table 3- add unit to average U and Pb concentrations. Add column for whether successful or not.

Beranoaguirre et al.: *The changes are performed as suggested and the successful samples are now highlighted. However, following the suggestions of the other reviewer,*

this table will be now attached as supplementary material.

Line 264- How does crater compare to NIST?

Beranoaguirre et al.: *The NIST pit is usually ca. 10-12 µm deep, slightly shallower than the carbonate and sulfate. This is now explained in the text.*