EGUsphere, referee comment RC1
https://doi.org/10.5194/egusphere-2022-72-RC1, 2022

Comment on egusphere-2022-72

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Referee 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-RC1, 2022

This is an interesting study that shows that some (but maybe not many?) evaporites have the potential of dating by U-Pb LA-ICP-MS dating. It is not a ground breaking study, and it is a shame that the samples were so young as to yield relatively poor analytical uncertainties, but nevertheless it is significant for those who might want to understand evaporite formation, and it is an appropriate contribution for this journal. It needs some organizational improvements and additional discussion before final publication; the main issue (matrix effects discussion) is discussed below, but also the methods section is somewhat incomplete, and it isn't until later in the data reporting and discussion that the reader understands what experiments were run, how they were configured and why they were changed. The figures and tables are mostly complete and legible but the Tera-Wasserburg diagrams could be simplified and thus easier to understand.

The main issue apparent in this paper: Why did the authors decided to use calcite as the reference material as opposed to some other material? This should be stated in the introduction. As it stands the introduction only states that new minerals are rapidly being introduced for U-Pb, non matrix-matched standards aren't reliable, and the authors decided to use calcite. But there is no mention of why calcite was chosen. Did the authors reach into a bag of RMs and pull out calcite or did they suspect that calcite should behave more like gypsum when ablated and ionized in a plasma? Calcite reference materials are not nearly as well characterized as zircon, and require a two-step process that also requires the accurate measurement of NIST glass.

If this manuscript is about using non matrix-matched reference materials, there needs to be more discussion within on the differences between glass and calcite, and zircon and glass etc. In fact, there is data in the paper that can be explored: for some reason (which should be discussed) the instrument conditions produced considerably different U/Pb fractionation factors between NIST and WC-1. Sometimes there was little to no offset, and other times there was 8% offset. This is interesting (albeit also a bit troubling), that two different matrices produce varying U/Pb fractionation depending on instrument parameters. It is important because the same could be true for gypsum vs. calcite - one

day the offset could be negligible, the next day, the offset could be 8%. Not surprising, as mentioned in the introduction, zircon can be used to normalize garnet under some operating conditions, and other times it can't (just like the different sessions of NIST and calcite in this study).
There is considerable time spent regarding pit depths of the gypsum and calcite. No pit depths were mentioned for the NIST glass, and neither was there any discussion about the other factors that yield discrepancy in U/Pb ratios in different matrices. Why does pit depth have to be the most important? Certainly, if the matrix is similar, then we might care most about pit depth, but when one is introducing ablated hydrated calcium sulfate vs. calcium carbonate into an Ar plasma, how are the U and Pb ionized differently in such environments? This may be much more important than the pit depth.

Finally, unfortunately, in this study only young sample with relatively low U/Pb ratios were measured (the best 238U/206¬Pb ratios are only 1/4 of concordant values). This limits the ability for the authors to test their hypotheses; if the analyses do not yield better than 10% uncertainty, how do we know that calcite is a better reference material than anything else? In fact, for all but one of the sessions, the NIST glass would have worked just as well. This is worth a comment, though I do not expect the authors to find older, high-U/Pb gypsum at this point.

Several notes on specific line items:
86: here it should be stated clearly that the data was collected over 4 XX-long sessions, from XX date to XY date, and which sessions used the SC and which used the MC. It should also be mentioned that the MC was used in the latter sessions because it was deemed necessary because of poor results in the first session. As pointed out in a few cases below, this section could stand some better organization and clarification to better set up the results and discussion.
98: what was the spot size and depth drill rate to get these sensitivities? Is the XR more sensitive than the Neptune Plus? This would imply so. But it looks like in tables 1 and 2 that different spot sizes were used. Either this should be normalized (and with the same units so the reader can compare them) to a specific volume ablation rate or the spot size and rep rate should be given herein for clarity.
104. I believe the authors mean mV, not V.
107: These tables should be referenced earlier.
110: This is confusing because both instruments are sector-field instruments.
111: Wow - big difference between sequence 1 and 3. Why? And if there is no difference in sequence 3 between NIST and calcite, why bother using calcite at all?
112: So you did a matrix correction and a down-hole correction? Does this mean the difference between the surface and the bottom of the hole was 3%? Did you made a data point by data point correction? This section is confusing and it sounds like there was a double correction made on the sulfate data.
119. Might be worth noting that the Pagel paper only reports LA data for B-6.
119. What was the in-house RM? Calcite? How old? Has it been analysed by TIMS?
121: This is worse than the 1.5% added in quadrature. So maybe 2% should be the minimum expanded uncertainty.
125. It looks like there was only one secondary RM in the SC experiments. This should be stated in the methods text.
Table 2 Spot shape and size:

Why use a different spot size for 614? In every session? Maybe this explains some of the

variability in corrections between NIST and WC-1 in the different sessions.

Is this why the "sensitivity" was lower for the Neptune?

T2 QC. Generally, people use the term session, not sequence. There are only 3 mentioned in the text, but there are 4 here.

133. were not are

Table 3. Maybe good to highlight the samples that actually worked. This table probably belongs in a repository.
Figure 3: 3 significant figures is overkill (harder to read). Please reduce to 2 significant figures.

Figs 3 and 4: Why not have 1 figure for each sample, and plot the data from the different sessions in different colors (and a legend somewhere to indicate sessions)? It would be much easier to compare them. That way, one could even calculate an age and MSWD for all sessions, as the data should be equivalent. The text is difficult to read at this resolution.

213: what does "low salinity" here mean? Relative to sea water? Relative to other evaporites? Salinity increases during evaporation, no?

217: The header of this section is "high common-Pb content." This paragraph doesn't reflect that header.

219: maybe poor, but not meaningless.

224: This is misleading: n = 34 and 17 in the SC session, whereas n = 66, 75 and 35, 43 in the MC session (twice as much data in latter sessions). Still better with the MC, but not as much better as this sentence would suggest.

234: sulfate not sulfates

234: specifically calcite - not just carbonate.

236: what does hardness have to do with light absorption and ablation? Did you measure the zircon pits? How deep are they? Does ablation depth relate to hardness in other materials?

238: But fluorite isn't very hard compared to zircon. I suggest removing the hardness argument unless there is some scientific evidence that indicates it is important.

239: What is the point here? Fluorite is similar to calcite or different? What does this have to do with gypsum ablation? Clarify or remove.

264: are these single crystals or multi-grain conglomerations? Is their texture described anywhere?

280: It would be nice to mention this in the methods (along with mentioning the specifics of each session).

282: Four of them were indistinguishable, not lied.