

## ***Interactive comment on “A Sample Characterization Toolkit for Carbonate U-Pb Geochronology” by E. Troy Rasbury et al.***

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The replies are also uploaded as a supplement pdf with the reviewers questions/ comments in black and the replies and changes in red text.

The manuscript of Rasbury et al describes a toolkit for U-Pb geochronology and specifically presents characterization of a couple of used or potentially applicable reference materials. The methods are up to date, although some commonly used characterization methods for natural samples are missing. The discussion about U speciation is interesting but requires some more connection to published findings of high U incorporation of U into calcite. I think this manuscript can be published after some minor revisions. Specifically important is the measurements of U(IV) in the calcites, but some

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more discussion on how the U speciation affect geochronology considerations and results could be suitable. A minor setback is that discussions of processes of U speciation and incorporation and suitability of and heterogeneity of different reference materials are mixed and make the paper a bit un-distinct in its focus.

reply To our knowledge, the manuscript has referred to all of the published work on the oxidation state of U in carbonates. There is really no evidence that it matters for dating if the U is reduced or oxidized. Rather, the question is how is uranium available to be incorporated. For the three examples we present, we suggested how the uranium was available. To address this concern though, we state up front now that there is no evidence that the oxidation state of uranium matters to the reliability for U-Pb dating. We added: 'Understanding U incorporation in carbonates is important for a holistic approach to U-Pb dating, but there is no evidence that the oxidation state of U in carbonates has any control on the reliability of the dating. However, it could indicate something about when during diagenesis the U was incorporated, and therefore affect the interpretation of the U/Pb date'

Specific comments: Title: It would be good if the title specifies that it is calcite and dolomite that is in focus of this manuscript as there are many other minerals under the "carbonate" umbrella. Title and throughout the MS: consider changing "standards" to "reference materials".

reply While it is true that we only discussed calcite and dolomite in this contribution, we would argue that the tools are also relevant to other carbonates, and would rather the title be broader so that researchers that are analyzing any carbonate, particularly ones that they would like to date, would find our paper.

We agree that the use of reference materials is more accurate than standards and this has been globally replaced.

Abstract: It would be helpful if it was stated whether the "split stream" analysis of  $^{87}\text{Sr}/^{86}\text{Sr}$  together with U/Pb, is done with LA-ICP in the same spot, in nearby spots,

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or if the  $^{87}\text{Sr}/^{86}\text{Sr}$  is done on dissolved samples and U/Pb with spot analysis. And, if it is the latter, the later discussion should discuss how the difference in scale of larger dissolved aliquotes match spots, when taking heterogeneity of the material into account.

reply We have not done split stream analyses. The beauty of split stream though, is that it can be done on the same spots. Our  $^{87}\text{Sr}/^{86}\text{Sr}$  results are from Thermal Ionization Mass Spectroscopy and the range of values obtained is included to make these possible reference materials available for split stream for those labs that are set up for it. We added 'While not part of the current contribution, this combination could streamline split stream analyses of  $^{87}\text{Sr}/^{86}\text{Sr}$  and U/Pb geochronology'. to clarify this to the reader.

Line 20-21: "Mixing of fluids can be particularly corrosive or can be responsible for mineral precipitation." please give more details. Lines 21 and onwards: "Introduction of C2 fluids with different chemistries through uplift or burial can destroy the original carbonate prior to precipitation of a new carbonate

reply These two comments are coupled and are addressed together here. We added to this statement to clarify, and we added important references for papers that are foundational to this statement. Mixing of fluids can be particularly corrosive such as seen where seawater and fresh water mix in a carbonate platform, or can be responsible for mineral precipitation depending on the saturation state of the combined fluids \citep{runnells\_diagenesis\_1969, wigley\_mixing\_1976}.

Lines 55-58: "Laser ablation mapping (Woodhead et al., 2010, 2007; Piccione et al., 2019; Drost et al., 2018; Roberts et al., 2020), synchrotron XRF mapping (Cole et al., 2004; Piccione et al., 2019; Frisia et al., 2008; Vanghi et al., 2019), PIXE (Ortega et al., 2005, 2003) and  $\mu\text{XRF}$  (de Winter et al., 2017) are all ways to take the physical observations of different phases to a new level with in situ chemistry, that maps U in particular, along with other elements that provide details of the fluid chemistry." It

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would also be good to add the FE-EMPA for spatial characterization of presence of U nano-particles in calcite (see Suzuki et al., 2016 SciRep).

reply Thanks. We added this reference in the context suggested here.

Because the uranium in this contribution is not in the calcite lattice, but rather U mineral nano-inclusions we added this as well: 'In some cases, uranium minerals are encapsulated in calcite which can protect them from alteration \citep{suzuki\_formation\_2016,ludwig\_uranium-daughter\_1978}.' Lines 61-65: "Given that the major element composition of seawater has changed appreciably through time (Hardie, 1996; Horita et al., 2002), that meteoric fluid compositions are controlled by water rock interaction (Chung and Swart, 1990) and that deep brines have evolved since deposition in basins (Musgrove and Banner, 1993), we can imagine that there is no such thing as a typical fluid. A holistic approach to dating carbonates should involve an effort to see back to the fluid or fluids that have been responsible for its formation and how they might have changed through the diagenetic history." At some point in the introduction or in the other text, that search for growth zonations using SEM, CL, and SIMS C- and O-isotope analyses prior to dating. see Milodowski et al APGEO <https://www.sciencedirect.com/science/article/pii/S0883292718301938>, and Drake et al NatComm 2019 <https://www.nature.com/articles/s41467-019-12728-y>. What also could be included in a toolbox for complex samples are fluid inclusion studies that can tell about mixing at particular events and about different fluid flow events by giving T and salinity estimates. Another tool is in situ Sr isotope values of different growth zones of calcite crystals. see Drake et al., 2019 for the latter.

reply We agree that all of these tools are important for a full characterization of carbonates and clumped isotopes are useful as well. Many techniques are applicable to characterize the cement stratigraphy of samples. We rephrased our introductory paragraph on techniques to read as follows: "Often, combining microanalytical tools that characterize carbonates at the micron to centimeter scale of growth zones is required to understand the origin and timing of various textures in complex samples.

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Chemical imaging techniques, carbonate staining, and polarized light, fluorescence, electron, and cathodoluminescence microscopy provide spatial context for quantitative microscale analyses of fluid inclusion, ion microprobe, electron microprobe, and laser ablation measurements. Integrated data from such a toolkit enables collection of LA-U/Pb isochrons that reliably date a single paragenetic event and permits geologically meaningful interpretation of U/Pb ages."

Line 129-130: "The cements have mostly been altered to calcite, though Chafetz et al.(2008) found original aragonite in similar cements. Calcite with the greatest alteration is light brown..." This is a bit unclear, is the light brown calcite the most altered of the calcites, or is it replacing aragonite to a larger degree than other calcite types does?

reply It is almost all calcite as stated : The Walnut Canyon sample has incredible preservation of the original fibrous aragonite texture even though it is almost entirely converted to calcite. We added: "While optical orientation is preserved and fluid inclusions and aragonite relict mineral inclusions delineate the original acicular growth habit, the carbonate is almost entirely replaced by cloudy brown calcite (Mazzullo 1980)." Mazzullo, S. J. "Calcite Pseudospinel Replacement of Marine Acicular Aragonite, and Implications for Aragonite Cement Diagenesis." *Journal of Sedimentary Research* 50, no. 2 (June 1, 1980): 409–22. <https://doi.org/10.1306/212f7a18-2b24-11d7-8648000102c1865d>.

Line 131: "WC-1", mention "Walnut Canyon" at first mention of this material.

reply Done

Line 135: Fig 3: quality of figure is not publishable. Maybe this has to do with compression for pdf conversion. The veins are difficult to see.

reply Rescanned and grouped with former Fig. 4

Lines 139-140: "Cathodoluminescence (CL) has been a go-to test for diagenesis, and when an activator such as Mn is present, this often gives phenomenal images that illu-

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minate alteration." and is also very good for veins and single crystals in open fractures, to track different events of precipitation and/or reactivation and fluid flow fluctuations.

reply Agreed, and added. Thank you.

Line 144: Fig. 4, 5, 6: These are nice figures, some suggestions; 1. however, what is the difference between Fig 4a, and 5a Since fig 4b and "5-Sr" are the same, maybe 4 can be deleted and 4a inserted (if it is not the same as 5-"photo" but in B&W, the caption does not say.) 2. What is roughly the range of Sr concentrations in these figures (4-5)? It would be very interesting to know as there is also clear drop in Ca in the Sr-rich parts, so I assume Sr concentrations are quite high.

reply Figure 4a (top) is a CL image of the slab shown in Figure 3. The only overlap in images is that 5Sr is indeed the same as the one we paired with the CL in figure 4. We think it is nice to have it in both places because it is easier to see how it relates to other elements when they are side by side as in Fig 5, but a major point is that the Sr map does a better job of showing alteration than the CL so having them paired together in 4 and blown up to make it easier to convey that seems justified. We are suggesting that as a reference material, we think that maps of each slab and only using areas that are the least altered (which is still more than half of the slab) would result in better reproducibility of measurements of this reference material.

Line 160: Fig 7: This figure is nice, but would to readers (such as me) who reads from left to right, be more logic if starting at left (old) towards right (young). How were the aliquots for Sr prepared, micro-drill, or are they in situ analyses using LA-MC-ICP-MS?details can be given here.

reply It is certainly reasonable to reflect this graph so that older is on the left- so we changed it as suggested. We added 'The aliquots were microsampled, dissolved and purified using Sr spec resin, and run by Thermal Ionization Mass Spectrometry' to the figure caption. We also changed the scales to zoom in a bit and added a line that is the average of 1, 3, 4, 5 and for the 2SD of that average. While 2 isn't included in the

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average it plots on the lower line. We left out the tiny slabs of the rock because it isn't possible to make them easy to see and they are described.

Line 160: "...with an average of 0.706930(69)", what is "(69)"? a reference with wrong formatting?

reply We changed this throughout the text to (0.000069). It is a somewhat normal convention to leave the zeros off but since it was confusing to the reviewer it makes sense to be as clear as possible.

Line 165: "...in seawater through the growth of the cements." Here, fluid inclusions may be useful to give more information on the history of fluids and alteration.

reply We agree with this and this reviewer is right on target with these comments. However, we start the sentence that without more work it isn't possible to know, and it seems off target to put too much more emphases on this point.

Line 169: TES: define, both in terms of settings and acronym

reply We do define this in the early section on synchrotron measurements starting on line 94. However, we had not done a good job of talking about the settings so we added a section about the energy range this represents. It now reads: 'These brighter sources offer micron sized resolution for low ppm levels of the elements of interest. Emerging tender energy spectroscopy (TES), using the energy range between soft and hard Xray techniques allows mapping of elements such as Mg and S that are important in carbonates \citep{northrup\_tes\_2019}.'

Line 173: fig 8, add to caption which sample it is

reply Done- it is Walnut Canyon and we state that it is the same slab shown in Fig. 3-6.

Line 179-180: "Through neomorphism to calcite, U was left behind because active functional groups such as carboxyl have a high affinity for uranyl." So was uranyl complexed to carboxyl in the primary fluid and incorporated into aragonite as carboxyl-

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complexes. Or did this complexation occur after recrystallization? if the former, could the aragonites have had exceptional U/Sr already at the aragonite stage?

reply This is a good question. Aragonite doesn't exclude U, but we don't know the U concentration or U/Ca ratio of Permian seawater so we can't know this. There is certainly abundant organic matter and whether the active functional groups represent the degradation products of the original organisms that produced them, or if these were organic molecules that were structurally incorporated is not possible to know. As written, we imply that the U was incorporated in the aragonite and then retained because of this affinity for the organic acid functional groups. We didn't change anything, but if we missed the point of the question we will be happy to revisit it.

Line 189-191; this sentence is not comprehensive, something is missing. and full reference should not be within ().

reply We fixed the parenthesis and we reworded the sentences relevant to this comment to make it clear we are characterizing a new sample that is large enough to share with the community. 'The sample that we are using to illustrate these tools for characterization is large enough to be suitable for distribution as a secondary reference material for LA carbonate dating (Fig. \ref{fig:BarstowTufa}). Most of the samples used in the \citep{cole\_using\_2005} study were small slabs from Vicki Pedone (Cal State Northridge) and are too limited in quantity to distribute to the community. Here, we are characterizing a new sample that is large enough to distribute widely.'

Lines 192-193: "Isotope dilution on this sample is under way and will be completed when Covid quarantine is lifted." Such a phrase makes me question if this something that will be included in this MS at revision, otherwise this level of details is probably not adding anything.

reply AGREE WE WILL EITHER FINISH THIS DATA OR DELETE THE STATEMENT AT SUBMISSION OF THE MANUSCRIPT.

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Lines 198-199: "there are mm to cm scale layers of higher and lower U concentrations (Cole et al., 2004)." what are these concentrations: "higher" and "lower"?

reply We added approximate concentrations in parentheses. 'citet{becker\_cyclic\_2001} showed that layers in the Barstow tufa deposits have a pattern of low (~10ppm) to high (several hundred ppm) U concentrations across laminae revealed by fission track mapping.'

Line 207: "The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios are similar throughout the sample..." this is a bit unspecific. maybe say "show relatively small variability" because there is indeed some variability

reply This is true and we have changed the wording to be more accurate. 'The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios of 3 aliquots ranged from 0.719877 to 0.721038 (Table \ref{tab:BT\_Sr})'. Line 209; "...making it a good Sr isotope standard..." I am not certain that the three analyses presented here are enough to state it is a suitable standard for Sr isotope analysis. It is stated that zones with high Sr would narrow the range (also for Sr isotope variability?), I cannot see how this is justified with the data presented, especially since there is no information on Sr-concentrations for table 1.

reply We agree. This was poorly worded and not well justified. This now reads: 'More work will be needed to determine if this sample can be a Sr isotope reference material as well as a secondary U/Pb carbonate reference material.'

Lines 214-215: "We hypothesize that U(IV) is complexed with some oxyanion in the lake water (phosphate, bicarbonate, etc) that keeps it in solution and perhaps is also incorporated into the calcite lattice." here it would be good to show some thermodynamic modelling or properties of U(IV)-bearing solutions from the laboratory, there are some of those available in the literature. and perhaps also compare to measurement of U-speciation in highly reducing waters at Forsmark, Sweden (Tullborg et al., 2017, <https://www.sciencedirect.com/science/article/pii/S187852201630145X>) that show that U is indeed complexed with carbonate in these solution, but is still U(VI) dominated

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uranyl-complexes. So the explanation presented here may be a bit oversimplified without further evidence.

reply The question of U complexation in a fluid and how it becomes part of the carbonate are unquestionably important and remain to be answered. We added a reference to Langmuir because that is foundational work on the fluid side of things and we included this Tullborg ref as an example of a field situation with highly reduced waters and U is still in solution as U(VI). The question then becomes how that is incorporated into the carbonate as U(IV) and this remains to be answered. Thus we scaled back on our interpretations and offered some suggestions for the way forward. 'While it is easy to conceive of a stratified lake with reducing bottom waters, reduced U is insoluble in most solutions, begging the question of how it is available to go into the calcite \citep{langmuir\_uranium\_1978}. Elevated actinide concentrations are found in the Great Basin lakes, and it is thought that the carbonate alkalinity is responsible for this elevation \citep{anderson\_elevated\_1982, simpson\_radionuclides\_1982}. Similarly, \citep{tullborg\_occurrences\_2017} demonstrates U(VI) complexes in extremely reducing fluids of deep groundwaters in Sweden. It seems clear that there is a kinetic barrier to U reduction even in the most reducing fluids, and yet some carbonates have entirely reduced U in their structures \citep{sturchio\_tetravalent\_1998}. More work is needed to understand the incorporation mechanism and use of synchrotron facilities to image the distribution of U with respect to other elements, and XAS measurements of U and other redox sensitive elements are important tools for advancing this research. Additionally lab directed studies that can produce U(IV) in carbonates would be a huge leap forward.'

Line 267; "...this sample could be a standard U/Pb dating, Sr isotopes, and synchrotron U spectroscopy" this sample looks promising as Sr isotope standard. But a few more samples than 2 (although with two aliquots each?) would be needed to confirm this further.

reply There are three aliquots, but we agree, we are presenting it as a possibility to

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be worked on by a number of labs before it could possibly be put out there as a reference material. This now reads:  $^{87}\text{Sr}/^{86}\text{Sr}$  of three aliquots of the Turkana dolomite from the outside (oldest) to the inside (youngest) are indistinguishable from each other at 0.703306 (Table \ref{tab:TBW\_Sr}). With the well behaved U/Pb systematics, high concentrations of reduced U and homogeneous  $^{87}\text{Sr}/^{86}\text{Sr}$ , and further work in collaboration with other labs, this sample could be a reference material for U/Pb dating, Sr isotopes, and synchrotron U spectroscopy.

Summary: line 272: "Details such as the U oxidation state..." Here, and elsewhere, much emphasis is put on the importance of knowing the U oxidation state of the carbonate for U/Pb dating. How exactly is this affecting the geochronology considerations and outcome? I may have missed it in the MS. please add some discussion about this particular matter

reply We addressed this in the first instance by saying that there is no indication that the oxidation state of U matters for the reliability of dating.

Please also note the supplement to this comment:

<https://gchron.copernicus.org/preprints/gchron-2020-20/gchron-2020-20-AC2-supplement.pdf>

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Interactive comment on Geochronology Discuss., <https://doi.org/10.5194/gchron-2020-20, 2020>.