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

Anonymous Referee #1

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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 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.

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".

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

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 fluids with different chemistries through uplift or burial can destroy the original carbonate prior to precipitation of a new carbonate or can alter the carbonates visibly or at a microscopic scale." difficult to read, please re-structure, e.g. split into two sentences.

Line 31-32: "Special circumstances are required to have elevated U in calcite because the Kd is less than 0.05." Note that this regards oxic conditions and incorporation of UO2, as established in laboratory (please mention this). There are much higher uptake reported for anoxic natural environments that can be mentioned, which also should be mentioned, although U speciation has not been fully characterized yet.

Line 40-41: "A missing component here is that no lab experiments have studied U(IV) incorporation in carbonates. There are several published examples of natural carbonates with reduced U (Sturchio, 1998; Cole et al., 2004) and we present one more in this contribution." The presentation of U(IV) in calcite is highly relevant and an important contribution. Also here (or only here), it would be good to connect these findings to recent findings of very high U uptake in calcite precipitated under anoxic conditions.

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 μXRF (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 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).

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 surch 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.

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?

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

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.

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

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.

Line 160: Fig 7: This figure is nice, but would to readers (such as me) who reads from left to write, 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.

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

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.

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

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

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

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

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.

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"?

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

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.

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

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.

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

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