

Interactive comment on “High-precision ID-TIMS Cassiterite U-Pb systematics using a low-contamination hydrothermal decomposition: implications for LA-ICP-MS and ore deposit geochronology” by Simon Richard Tapster and Joshua William George Bright

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Summary and general comments: Tapster and Bright present a novel, low-blank laboratory procedure for U-Pb ID TIMS measurements. The authors successfully apply their method to produce U-Pb dates for three cassiterite samples that have previously been dated by LA ICP-MS (Neymark, et al., 2018; Moscati, et al., 2019), and thus provide a comparison between their method and levels of precision reported in the

C1

most recent studies using micro-beam measurements. They also utilize the increased levels of analytical precision provided by their method to assess the reproducibility of cassiterite U-Pb dates on both a single-grain and multi-grain population.

In this manuscript, Tapster and Bright provide U-Pb ages for 2 potential cassiterite micro-beam reference standards. Their datasets, while having a considerably smaller sample size than previous LA ICP-MS datasets, benefit from much lower uncertainties on each single data point and therefore provide more tightly constrained ages than those previously published. They measure U-Pb cassiterite ages for the Cligga Head W-Sn greisen deposit and show that cassiterite mineralization was coeval with magma emplacement in the area. Results Cligga Head samples also show that the initial Pb composition of cassiterite can be heterogenous on a single grain scale, which can result in biased U-Pb micro-beam ages.

Overall, I think the data provided in this paper are of high quality, the experiments, results and conclusions are sound, and the authors successfully show the promise of their new method. The authors do a nice job of identifying challenges to U-Pb cassiterite geochronology that should be considered in future studies. This contribution is particularly timely, as there is growing global interest in high-precision analyses of ore-bearing mineral deposits, with many recent publications utilizing U-Pb cassiterite dating. It is my opinion that this paper fits well within the scope of Geochronology and I recommend it for publication following minor revisions.

My one general critique of the manuscript is that the text, while well structured, could benefit from revision to present the main points more clearly, and to fix several instances of typos and run-on sentences. I also suggest that the authors make sure that they call out all of their figures in the text.

Specific Comments: Methods: 1) To justify that they achieved full decomposition they use SEM and EDS scans of post HBr dissolution solids and show that there are no Sn-oxides left. Why don't they include these data? Given that full decomposition is of

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fundamental importance to this paper, I suggest that you include these data if not in the main text, in the supplement.

2) I have several questions regarding the HF leaching procedure: How long do you leach in HF (you might say this on line 242 but it's not clear that you mean that you refluxed samples in HF overnight)? How much HF do you use? Do you rinse after HF leaching? Do they lose any material after leaching? I think the paper could benefit from a clearer description of the HF leaching process.

3) You mention that the HF procedure effectively removes Pbc from inclusions that are exposed during powdering with mortar and pestle. Do you feel that this is 100% affective? Although it appears to be on C1.1, could micro-inclusions or variable levels of leaching be responsible for the differing Pbc composition in C1.1-4?

4) It is likely that variation in initial Pb composition in a single grain of cassiterite would be unavoidable, but could you decrease the risk of sub-grain scale heterogeneity (like that in C1) by imaging (SEM or CL) the grains before ID TIMS analyses? I acknowledge that most inclusions would be much smaller than the ID TIMS sampling size, but large-scale features like secondary growth zones, imbedded grains, or secondary mineral growth may be large enough to avoid.

Following up on two of Corey Wall's comments: 5) I also suggest that the optimal methods for the total procedure should be more clearly laid out in the text. What do the authors suggest is the optimal sample size, leaching reagents and duration, mortar and pestle powder size, etc.

6) I had a similar though that HBr chemistry could be a useful column method that would eliminate the need for acid conversion. The procedure introduced by Amelin in 2008 has been used for U-Pb dating of trace phases (rutile, apatite). One potential issue is that I don't believe its efficacy for Sn separation has been tested.

Results: 7) This comment is not meant as a suggestion for this paper, but just a thought

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for future work: I find it a compelling argument that the heterogenous Pbc composition found in C2 is likely not from inclusions of local igneous detritus, based on the $\sim 0.8-0.9$ values of 207/206 measured in Cornubian Batholith. However, this could be tested by measuring the Pb composition of the HF after one or more cassiterite leaches.

Discussion: 8) In the beginning of the paper you describe SPG and Jian-1 as possible reference materials. I think it would be useful to come back to these samples in the conclusions, and to mention that in light of your new data these possible standards are now better characterized.

9) I think that the results of this manuscript show that both ID TIMS and LA ICP-MS have their advantages and disadvantages when it comes to cassiterite U-Pb dating. The data presented here clearly show the power of better single data point precision for resolving potentially large source of bias resulting from Pb isotope heterogeneity. However, the coarse sampling for ID TIMS incorporated more variable Pbc domains and hinders the ability to carefully screen domains within a single cassiterite grain. I suggest including a sentence or two in the discussion or conclusions that acknowledges this and suggests careful consideration to both the pros and cons of ID TIMS and LA ICP-MS analyses that were outlined in this paper.

Technical comments: Line 26: This sentence, while important, can be stated more clearly. Line 28: Should be more specific in regard to what "analyses" you are referring to. The x-axis in figure 7 is wrong. Line 32: While pedantic, I think you can be a little more specific than "properly characterize" to more clearly state the main conclusion. Line 68: There are two periods at the end of this sentence. Line 95: "Terra" should be spelled Tera. Line 148: "have been" is written twice. Line 242: I think it would be useful to mention here will touch more upon HF leaching below. Line 243: This sentence is unclear and should be reworded. Line 260: Consider rewording this sentence for readability Line 277: Run-on sentence. Line 287: Erroneously placed parenthesis after survey Line 415: The sentence starting here is broken. Generally, this paragraph can be reworked for readability. Line 439: The age for C1.1 here is 285.13, but in figure

C4

Line 440: Is 0.8760 the upper intercept of the Tera-Wasserburg or the y-intercept? The same question applies to the upper intercepts reported in figure 7. Line 609: I think there should be a "to" in between "attributed variable" Line 623: I don't see a figure 9 in Moscati and Neymark 2019. Do you mean figure 5? Line 696: "cam" should be can Figure 5: On the second line you refer to Z1 and 2 instead of Z1 and Z2. On the fourth line of the caption add (Z2) after rhyolite porphyry dykes. Figure 7: Ratio on the x-axis is flipped

I hope these suggestions are helpful, Sincerely, Gavin Piccione

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