Interactive comment on “Towards in-situ U–Pb dating of dolomites” by Bar Elisha et al.

Jon Woodhead (Referee)
jdwood@unimelb.edu.au

Received and published: 23 July 2020

This manuscript builds on the recent surge in interest surrounding LA-ICPMS dating of carbonates and explores application of these methodologies to dolomitic limestones. This is a welcome development and one with potentially widespread application, given the fact that many ancient limestones are in fact dolomites. The authors have produced a nice dataset and, although some of the specific implications of the results remain elusive, I think this serves as a useful starting point for studies of this kind. Nevertheless, I think that a number of improvements to the introduction and discussion could be made.

I think that the manuscript, as it stands, suffers from a somewhat selective referencing of the literature. In particular, non-specialist readers may be forgiven for thinking that dolomite has previously proved impervious to geochronological study when, of course, this is far from the case. There are many examples in the literature of successful bulk
U-Pb (e.g. Winter & Johnson, EPSL 1995), Hoff et al., J. Sediment. Res. 1995, Polyak et al. Int. J. Speleology, 2016) and Pb-Pb (e.g., Ovchinnikova et al., Stratigraphy and Geological correlation, 2007) analyses, all of which suggest that in situ dating should be feasible. Furthermore, there are also now a number of examples appearing of successful in situ determinations of dolomite using the LA-ICPMS methodology (e.g. Mueller et al, Sedimentology, 2019; Hu et al., Oil and Gas Geology, 2020 etc.). While the present manuscript certainly provides a more detailed analysis of relevant analytical issues I think it is important not to lose sight of the fact that previous work has been conducted in this area and, in fact, many of these literature studies provide highly pertinent data e.g. the Hoff et al. study looks at issues of U-mobility during dolomitization, while the Mueller et al. work provides a number of quite well constrained isochrons which could be compared with the current work, extending the reach of the current dataset.

It is of course disappointing, but nevertheless important, that a number of the samples used in this study provide ages which are seemingly inconsistent with known stratigraphic relationships. I think that this part of the manuscript in particular would benefit from some further thought/exploration of potential mechanisms.

The discussion of crater morphology is perhaps least convincing. This seems to follow the Guillong study (this volume) which predicts that matrix-related differences in drill rates (higher in dolomite cf. the calcite reference material) may potentially result in an older age bias in dolomites. Unfortunately, this is not a consistent observation in this study and many of the determined ages are in fact younger than anticipated, not older (with the exception of the two syngenetic Cretaceous samples). Furthermore, I do not think that the evidence, as presented in this study, reveals that the micritic dolomites ablate ‘much faster’ than the other carbonates. One of the SEM images suggests that the micritic dolomite crater is \( \sim 1 \) micron deeper than the others but, given its bottom morphology there must surely be large uncertainties on that determination? Even if this measurement is correct, this is nowhere near the 160% greater ablation rate suggested
by Guillong et al. and yet some of the ages show much greater than 4-8% departures from expected ages.

Speaking more generally, these are ablation craters with very large aspect ratio (85 micron wide, 15 micron deep) and so it is hard to imagine how downhole effects can dominate the isotopic signatures observed – and in fact I see that craters of this aspect ratio produce very minor effects in the Guillong et al study. Similarly, I can see how crater roughness might equate to ablation inefficiency but how does this translate into an age bias rather than simply larger age uncertainties? It would be very useful to have more discussion here and perhaps even more useful to have some further experimentation. For example, what happens if the fluence is raised in an attempt to provide better coupling with the sample? What happens if the aspect ratio of the ablation pit is changed – do the age offsets (compared to stratigraphic estimate) increase?

It is also argued that mineralogical/textural controls may results in mixed ages but, once again, the evidence provided does not seem to back up these assertions. The inclusion of remnant (pre-dolomitisation) calcite grains (section 3.3) in the analysis would surely bias the ages towards the existing stratigraphic constraints, not make them younger than expected? To my mind many of the arguments presented re. complexities in mineral textures would be similarly applicable to limestones and yet these seem to be, for the most part, amenable to dating.

I can’t help but wonder in all of this if many of these younger ages are in fact analytically just fine – and simply reflect the time of closure during late-stage dolomitization ie. it is the existing interpretation of the timing of dolomitization (not stratigraphic age) that is incorrect? Perhaps it would be worth exploring that avenue some more as some of this concern may just ‘go away’... Also, it is worth mentioning (even trying) the Drost et al (G-cubed 2018) methodology in which variation in U-Pb systematics can be directly linked to the trace element geochemistry. This would be a great asset in the interpretation of complex relationships such as those depicted in Fig. 9.

C3
A few more minor comments:

Line 40. It is not the upper intercept with Concordia that determines the common Pb value since the Concordia curve is only relevant to radiogenic Pb – actually it is the intercept with the y-axis at U/Pb = 0. I’m sure the authors know this but it should be fixed, nevertheless.

Lines 39, 40, 149, 185, 295, 297, 301, 305, 310: ‘isochrone’ should be ‘isochron’

Line 55 ‘unites’ should be ‘units’

Line 100. What does pre-ablated ‘4 times’ mean? Is this 4 pulses, or 4 groups of X? pulses? How deep does the pre-ablation go?

Line 102 how were the Daly-Faraday detectors inter-calibrated and what is the stability of the calibration?

Line 111. Why do we need to know 204Pb concentration? This information does not seem to be used anywhere in the current manuscript?

Similarly, I am not really sure why REE analyses were conducted/included in this manuscript? With the exception of line 179/180 where three samples are noted as having ‘very similar REE profiles’, REE abundances are not used anywhere else. In fact I would argue that all of the samples have very similar REE profiles anyway.

Line 148. ‘Data point analytical uncertainties are...smaller than the scatter of the spot analysis’. Surely that must always be the case in a heterogeneous material?

Line 150. the low common Pb value. Why is 0.8 considered ‘low’ - all of the samples appear to have a similar 207/206 value?

Line 152 Are positive Gd anomalies common in dolomites? These seem very large and Gd can be compromised by oxide interferences.

Line 269. Section 3.3 is actually section 3.4
BTW- I don’t really understand what is being plotted here – what is the ‘down-hole raw 207Pb-corrected 206Pb/ 238U ratio’?

Line 215 ‘hens’ should be ‘hence’

In summary this is a potentially useful contribution to the continued development of the I situ carbonate U-Pb chronometer. It is certainly appropriate to this journal and of widespread interest but I think that the discussion and literature analysis requires some refinement, as discussed above, before publication.