

Interactive comment on “Stepwise chemical abrasion ID-TIMS-TEA of microfractured Hadean zircon” by C. Brenhin Keller et al.

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We appreciate the thorough and positive review by both reviewers, and respond here to any comments from Reviewer 2 that required changes to the text. Quotes from the review are italicized.

This is an interesting, well planned and well executed study. While its contribution to understanding the geological history of Jack Hills detrital zircons, the world's oldest known minerals, is relatively modest, the paper is valuable for exploring the new ways of extracting most information from zircon. I believe the paper can be published after moderate revision.

C1

Comments linked to the text:

p.3 lines 14-15. “frequently presumed” by whom? There are several studies after Mattinson 2005 and Mundil et al. 2004 where the effects and conditions of chemical abrasion are explored in greater detail: Mattinson 2011 Canadian Journal of Earth Sciences, 48, 95–105; Huyskens et al. 2016 Chemical Geology 438, 25–35; Widmann et al. 2019 Chemical Geology 511, 1–10.

There is indeed more literature here. The “frequently presumed” comment is pointed at the fact that in practice, many of us in the zircon TIMS community routinely chemically abrade for 12 hours (at either 180 or 210) and hope for the best unless obvious signs of Pb-loss are observed in the resulting data; we ourselves are as guilty of this as any.

p.3 line 16. A more appropriate study to compare to is the paper by Amelin 1998 Chemical Geology 146, 25-38, where multiple fragments of 14 Jack Hills grains were dated by U-Pb ID-TIMS using air abrasion and some HF leaching. That study was indeed done before the advent of chemical abrasion, but it has substantial similarity in concept to this one, and I think it would be wrong to ignore it.

You’re right; we originally cited Amelin 1999 Nature, but we have added a citation of this earlier paper as well.

p.4 lines 16-17. Are you using both 3M HCl and 3.1M HCl? I doubt it. Please correct the wrong number.

We have standardized on 3 M; this imprecision in terminology comes from the fact that while 3.0 M HCl is applied by dropper bottle, the columns at this point have been previously conditioned with 6.0 M HCl, so the first eluent is slightly stronger than the

C2

3.0 M HCl added; this is phenomenon is sometimes acknowledged (in lab chemistry manuals, etc.) by referring to the resulting eluent "3.1 M".

*p.5 line 12. You can also consider the second study of $^{238}\text{U}/^{235}\text{U}$ in zircon by Livermore et al. 2018 *Geochimica et Cosmochimica Acta* 237, 171–183.*

Yes, the Livermore et al. value of 137.817 ± 0.031 is quite consistent with the Hiess et al. value of 137.818 ± 0.045 .

p.5 line 14. Strictly speaking, the Zr concentration in zircon depends on the Zr/Hf ratio, but this is a small change in normalisation (not really necessary to change).

p.5 lines 14-17. This way of getting Th/U ratios does not make much sense to me. You can get these ratios independently from measured concentrations of both elements (by either ICPMS or ID-TIMS), and from Pb-isotopic systematics, and compare the value. This gives useful information about the open system behaviour in the U-Th-Pb system.

Yes indeed, though this will be below analytical uncertainty for the Zr/Hf. To avoid this approach for Th/U, one would need (at minimum) a Th isotope dilution spike: all U is consumed by the TIMS analysis, so there is no U in the TEA solutions by which Th/U could be determined by ICPMS.

p.11 lines 21-22. Please take a look at the paper by Widmann et al. 2019 mentioned above where partially dissolved zircons produced by sequential leaching steps of chemical abrasion were studied by Raman spectrometry. This could help you to refine this speculation.

Thanks! This paper came to our attention only after submission, but is indeed quite relevant.

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p.11 lines 27-31. I cannot remember the exact paper(s), but I am sure that ancient natural annealing of zircons during metamorphism and its effect of temporary suppressing the loss of radiogenic Pb, until the radiation damage builds up again, have been discussed before.

Seems likely, if perhaps not in this exact context.

p.12 line 3. I doubt that it is correct to speak of "complete absence of water on the moon". "Low abundance of water" is more accurate.

Fair enough – "near absence"

p.12 line 4. Do you mean "in crystalline zircon"?

Yes, we will add this clarification.

p.212 lines 9-14. About sphene (btw you should use its proper name "titanite") and e.g. apatite I would agree. But monazite? AFAIK its content of Pbc is as low as in zircon and baddeleyite. So I think there should be another explanation.

While monazite certainly has lower Pbc than sphene or apatite, there seems to be some evidence (e.g. Catlos and Miller 2008, doi.org/10.2475/05.2016.03) that monazite Pbc can be quite variable and in any case higher than zircon. Nonetheless, we have tried to reduce the speculativeness of this section.

p.12 line 15 on. The temperature of decomposition of metamict zircon clearly depends on the degree of metamictisation. How metamict is the zircon that decomposes at 800 C?

C4

Fully metamict, generally. However, as Vaczi et al (2009) note, the details can be complicated, especially for partially metamict zircon: "it is far from uncommon to observe that zircon breaks down at temperatures well below the thermodynamically predicted decomposition temperature. There appears to be no well-defined temperature for the onset of decomposition."

p. 12 line 20. Baddeleyite is more easily soluble than zircon in HF. Direct extrapolation of this difference to response of these minerals to natural processes is unfounded (at least without additional tests) because the composition of the fluids, temperature and duration of exposure are quite different.

We have reduced the speculation here, but the solubility in HCl (not HF) is more likely applicable to natural solutions; here the difference between zircon and baddeleyite is fairly stark.

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