

## List of final responses to reviewer comments and associated changes

The responses/modifications listed below correspond to the reviewers' comments relating to the specified line number in the original submission.

### Final response to comments made by Bob Cliff

**Original line 158.** We have now clarified that  $^{207}\text{Pb}$  is measured entirely dynamically, and that the Faraday collectors are not used in the Pb measurement steps (c. revised line 209)

**Original line 203.** The citation for the published spike composition has now been added (new line 148) and the potential impacts of sample  $^{204}\text{Pb}$  mentioned (revised lines 246-250 and 346-350)

**Original line 221.** We have attempted to clarify that we try to sample for  $^{234}\text{U}/^{238}\text{U}$  measurements as close to the same sample material used for the corresponding U/Pb as possible (revised lines 260-262). We have also introduced the idea that initial  $^{234}\text{U}/^{238}\text{U}$  variation will produce variation in the  $^{238}\text{U}/^{206}\text{Pb}_{\text{rad}}$  ratio in section 3.5

**Original line 280.** We have clarified that a normal distribution is used for the assumed initial  $^{234}\text{U}/^{238}\text{U}$  in the relevant footnotes to Table 2. We have also clarified that where we are assuming initial  $^{234}\text{U}/^{238}\text{U}$  ratios in the present work that these are chosen arbitrarily for illustrative purposes only (revised lines 326-327).

**Original line 350.** The figure caption has been revised to include the sample name (revised figure 2).

**Original line 440.** As suggested, the figure has been re-plotted with error ellipses (revised figure 6).

**c. original line 495.** There is little correlation of the uncertainty arising from  $^{207}\text{Pb}$  with that of other measured isotopes owing to  $^{207}\text{Pb}$  being measured dynamically, hence the correlation coefficients between the  $^{238}\text{U}$ - $^{206}\text{Pb}$  and  $^{235}\text{U}$ - $^{207}\text{Pb}$  systems are rather different.

**Original line 564.** As suggested, we have added a paragraph in to the discussion (revised lines 676-683) dealing with recent hardware advances and how the method could be refined in light of these.

### Final response to comments made by Ryan Ickert

**General comment 1:** As suggested, the discussion section has been expanded (revised lines 649-674) to better pull together the advantaged and disadvantages of the new method in a single location.

Also, as suggested section 3 has been somewhat rewritten, with the two subsections dealing with the analytical methodology (section 3.2 dealing with the U-Pb measurements and section 3.4 dealing with the  $^{234}\text{U}/^{238}\text{U}$  measurements), focussed more on what was done, limiting method justification etc. to that which we feel is necessary for the reader to understand the logic for the approach. These subsections have also been restructured so that they each progress more linearly from sample preparation to mass spectrometry. Section 3.1 also has an introductory paragraph added setting out that there are two distinct procedures, one for the U-Pb measurements and one for the  $^{234}\text{U}/^{238}\text{U}$  measurements, so the logic for describing these in separate subsections should be more apparent to the reader.

**General comment 2:** As suggested we have included additional detail regarding previous blanks in the introductory section and clarified that the blank-related aspect of the new method is more focussed on side-stepping potential blank problems by omitting steps where problems can arise (revised lines 57-63). To the extent that it is practical, we have also attempted to be more quantitative in describing blanks, precision, interferences etc. in the main text. There are, however, some practical limitation here. The Pb blanks of the new procedure cannot be directly quantified because of instrumental detection limits (which we have made clearer). However, we have attempted to put a numerical limit on the blank based on the typically observed detection limit for Pb to allow some comparison with other techniques. Similarly, the Sr<sub>2</sub>O<sub>2</sub> interference cannot be quantified in a simple way because its effect depends substantially on the <sup>208</sup>Pb signal intensity and the radiogenicity of the sample, both of which show large variations. However, we have tried to give some indication of this in section 3.1, and made it clear that the method is reliant on the effective elimination of this interference, either by minimising it to the point that its effect on the common Pb correction is irrelevant (for material with little common Pb) or the interference is effectively resolved by measuring on the high mass side of the Pb peak side-stepping the problem. Any further specific quantification would require knowledge of the <sup>208</sup>Pb/<sup>208</sup>Pb ratio for each measurement, which is not analytically feasible to routinely measure.

Original Fig 1 and 2 have been removed as suggested.

**Original lines 17, 47, 47, 49, 92.** There are typos/minor inconsistencies in hyphenation etc., and have been corrected.

**Original line 57.** We have attempted to clarify why we consider the traditional ID approach to involve considerable effort for carbonates, primarily the fact that our initial setup involved using 2 ml resin bed columns, not microcolumns where blank control is relatively easy because the reagent volumes used are tiny, so our reagents required additional purification. We also now include that we experienced problems with resin purity (revised lined 57-61).

We have also clarified the point about why reconnaissance analyses were required using the traditional approach (revised lines 61-63).

**Original lines 75-78.** We have attempted to clarify this slightly. However, given that we have presented solution-based <sup>238</sup>U-<sup>234</sup>U-<sup>206</sup>Pb ages and <sup>235</sup>U-<sup>207</sup>Pb ages, the former of which utilise relatively high precision <sup>234</sup>U/<sup>238</sup>U measurements, the original basis for the reviewer to consider this as speculation and not really used in the present work is unclear.

**Original line 84, and throughout the manuscript.** As suggested, a neater notation for radiogenic <sup>20x</sup>Pb has been used.

**Original line 85.** We have attempted to clarify this section (revised lines 86-98) as it appears the reviewer had not fully understood what we were attempting to communicate. What we meant by 'an arguably better' approach was that using two separate 2-D isochrons based on <sup>204</sup>Pb as the unradiogenic isotope allows separate correction of common <sup>206</sup>Pb and common <sup>207</sup>Pb allowing the <sup>238</sup>U-<sup>206</sup>Pb and <sup>235</sup>U-<sup>207</sup>Pb systems to both be used (as Rasbury and Cole had done), but that <sup>204</sup>Pb has practical limitations because of <sup>204</sup>Hg and its low abundance.

**Original line 103-106.** We have added additional detail in regard to the distilled reagents etc. used (revised lines 129-131).

**Original line 107.** The mesh size information has been added (revised line 119).

**Original line 124.** We have added a line to section 7.1 of the discussion in regard to partial dissolution effects (revised line 604-607).

**Original line 118-127.** We have attempted to more clearly define a subsample as a small part cut from a larger collected sample that represents part of a specific stratigraphic horizon or growth interval. We have also attempted to clarify that cut subsamples range from c. 50 mg to several hundred mg depending on how much material is available (with the larger masses being for convenience handling), and that a few mg is finally dissolved by the spike for analysis (revised lines 135-153).

**Original line 141.** We have attempted to clarify that the estimated sample U concentration is based on the amount of sample expected to dissolve in the HNO<sub>3</sub> in the spike (revised lines 150-155).

**Original line 147-155.** It is now clearly stated that no correction is made for the Sr<sub>2</sub>O<sub>2</sub><sup>+</sup> interference, and the method is based on its effective elimination. It is now noted that the magnitude of this interference varies substantially with gas settings, but that it can be largely eliminated by optimising the gas flows. As far as is practical, an indication of the worst case magnitude of any residual interference after optimising the gas flows is now given, and this leads in to the steps taken to decide whether or not to measure on the high mass side of the Pb peaks where the residual interference is effectively resolved (revised lines 181-199). No further quantification of the magnitude of this interference is realistically possible based on the existing data.

It was always clearly stated (original lines 162-163) that <sup>202</sup>Hg was monitored to correct for the <sup>204</sup>Hg interference on <sup>204</sup>Pb. Quantification of the typical magnitude of the <sup>204</sup>Pb interference has been added (revised lines 210-211).

**Table 1.** The 'DVM' notation is retained as it is referenced directly in the main text.

**Original Line 160 and line 161-162.** It is now clearly stated that no beam interpolation is made and the dynamic measurements are made on the assumption of a steady-state measurement (revised lines 209-210). We regard further consideration of beam interpolation to be out of scope for the present work. For most analyses signal variation will be dominated by random noise rather than systematic drift (bear in mind we are not measuring by TIMS, where signal decay is common, relatively smooth and predictable, and with relatively little random signal noise), such that implementing/assessing beam interpolation would be non-trivial because of the need to disentangle systematic and random signal intensity variations. There is also a clear potential downside to beam interpolation in the form of assigning false significance in terms of systematic drift to random signal variations, thereby introducing rather than eliminating biases on dynamic ratios. However, in the absence of suitable carbonate CRMs during the present work, it is not really possible to separately evaluate biases associated with utilising or not utilising beam interpolation based on the existing data. This would either have to be done as a new analytical exercise assuming a suitable reference material was now available, or as a separate modelling exercise with synthetic data, neither of which are realistic additions to the present work.

**Original line 167 and line 214.** A paragraph has been added to section 3.5 setting out the limit at which we consider <sup>232</sup>Th to be negligible (revised lines 310-320).

**Original line 169.** As suggested, the original studies are now also cited (revised lines 217-218).

**Original line 171.** It is now explicitly stated that Pb fractionation is also based on the <sup>238</sup>U/<sup>235</sup>U ratio. It has also been added that based on previous tests we consider the 2 permil/AMU offset to still be applicable with the matrix heavy samples (revised lines 218-220). There is also a line added to

section 7.1 of the discussion in regard to the passing of the method validation tests being an implicit test of the mass fractionation correction.

**Original line 171.** We did initially experiment with Tl for correcting instrumental biases, however the signal intensity from the samples themselves tended to be too small to reliably utilise, and Tl doping had associated Pb blank issues. Moreover, we found that transmission of Tl through the sample introduction system while running in H<sub>2</sub>O was poor. The sample <sup>238</sup>U/<sup>235</sup>U proved the better option.

**Original line 184.** This has been re-worded (revised line 179).

**Original line 185.** All aspects of the Sr<sub>2</sub>O<sub>2</sub> interference and the associated tuning etc. to suppress it are now dealt with together in the same paragraph in section 3.2 (revised lines 181-199).

**Original line 191.** As already noted, this is not entirely feasible, but the information that is available regarding the Sr<sub>2</sub>O<sub>2</sub> interference is now included (revised lines 181-199).

**Original line 210.** As suggested it is now noted that <sup>205</sup>Pb may be a better choice of spike isotope for other instrument hardware configurations (revised line 244).

**Original lines 210-213.** As suggested this has been reworded to indicate all <sup>204</sup>Pb not originating from the spike (revised lines 245-246). The subsequent wording (specifically the use of 'mitigate') has also been changed to be clearer that adding more spike <sup>204</sup>Pb does not eliminate sample <sup>204</sup>Pb, only dilutes its presence (revised line 244).

**Original line 237.** This has been reworded and a typical U blank amount included (revised lines 276-283).

**Original line 241.** This has been reworded and clarified to indicate that we mean an approximation of the mixing trend between the radiogenic and common Pb end member. We also include an example of the form such approximation could take (revised lines 303-305).

**c. Original line 260.** It appears that we were unclear here as based on the reviewer's reference to using the 'total' U-Pb isochron but substituting <sup>208</sup>Pb for <sup>204</sup>Pb, and their comment in regard to only being able to independently evaluate <sup>235</sup>U/<sup>207</sup>Pb and <sup>238</sup>U/<sup>206</sup>Pb if separate common Pb corrections are applied... that they had not fully understood what we were trying to communicate. Section 3.5 has been significantly re-written in an attempt to clarify the common Pb correction, particularly why we prefer using 2-D isochrons in <sup>208</sup>Pb/<sup>206</sup>Pb – <sup>235</sup>U/<sup>207</sup>Pb space so that common <sup>206</sup>Pb and <sup>207</sup>Pb can be independently corrected, why we prefer to use the isochron-type approach to derive the common Pb composition, model ages calculated from paired U/Pb and <sup>234</sup>U/<sup>238</sup>U measurements etc. This should now also be clearer based on the revision to section 2 where some of the different isochron approaches used previously are introduced, and the limitations of using approaches that rely on intersections with concordia made more explicit.

**Original Fig. 6 and line 418.** We now give a short explanation that we consider the common Pb compositions themselves to be somewhat radiogenic owing to ingrowth of <sup>206</sup>Pb in the source of the common Pb (presumably the cave/vein host rock) prior to the formation of the samples (revised captions to re-numbered figs 4 & 5).