Review Preprint Gchron-2023-15
Title: “Constraints on average alpha recoil distance during 238U decay in baddeleyite (ZrO2) from atom probe tomography”
Authors: Davis et al.

General Comments

This work highlights the use of Atom Probe Tomography (APT) to answer specific questions in geochronology and geochemistry, which are unattainable by more conventional techniques (e.g., SIMS, LA-ICP-MS, etc.). In this work, the authors focus on baddeleyite crystals, sourced from two localities dated previously using the high-precision U-Pb technique ID-TIMS. In both cases, the baddeleyite grains were reported to be discordant by up to 3%. The reason for discordance is suggested to be due to Pb loss from alpha recoil processes, thus resulting in Pb loss. The authors therefore use APT to analyze two baddeleyite grains, providing a single APT reconstruction from each respective sample. However, of the two samples, only one APT reconstruction exhibited U and Pb concentration profiles and a gradient in the $^{206}Pb/^{238}U$ ratio, which the authors suggest being a result of alpha recoil processes. The other sample showed no signs of disturbances, though concentrations of the relevant U and Pb isotope peaks were not detectable above background.

Although this work is relevant and needed, as baddeleyite is a widely used geochronometer in lithologies which do not saturate zircon, the data itself is quite sparse to support the quantity of related models and their interpretations presented in this manuscript. Their models for the calculation of alpha recoil are then technically based on one reconstruction – M5 (Ahmeyim Great Dyke). In contrast, M2 (Hart Dolerite) has a uniform U concentration and therefore the data from APT was inconclusive as to why these baddeleyite from the Hart Dolerite are discordant.

Specific Comments

My reserve with the manuscript as currently constructed is that it relies entirely on two APT reconstructions from two unique baddeleyite grains. Although they are quite large datasets for APT studies (65 and 62 million atoms), there is always the question of if the volumes analyzed are wholly representative of the system. Is there a reason more weren’t analyzed? As I expect the authors will not analyze more data, I would suggest that the authors take more care into at least displaying more of the two reconstruction volumes (display more images, more angles, the U clustering, an isoconcentration surface if you truly find planar features in the volume…).

With only one APT reconstruction per sample, it is difficult to correlate what is observed to a very specific feature in the grain. Complimented by the general lack of corresponding techniques to rule out alternative options – e.g., these two grains could be mounted perpendicular to the FIB sections and imaged for CL at the least to view zonation and evidence for disturbances in the crystal lattice.

I find it interesting that the authors chose different locations with respect to crystallography from the two samples. In the Ahmeyim baddeleyite, they took a lift-out from the surface perpendicular to the C-axis, while in the Hart Dolerite baddeleyite they analyzed perpendicular to the A-axis(?). Could this contribute to the observed differences in concentration profiles relating to potential anisotropic differences in elemental diffusivities?

Although other studies have detailed the tedious process of extracting U and Pb isotopic concentrations from TOF spectra (e.g., Valley et al. 2014; Blum et al. 2018), I find it imperative that the TOF of these

two reconstructions are presented for reader evaluation of the runs as the entire study relies on the ability to resolve and quantify these two peaks in the mass spectra.

It's challenging to follow the discussion of alpha recoil relating to the concentration and ratio profile depicted in Figures 3 and 4, versus U and Pb clustering and the result of alpha recoil from enriched clusters of Uranium? There are no figures depicting this clustering, even though there is an entire discussion section dedicated to this topic: "3.2 Constraints on alpha recoil distance from U clustering".

Most significantly, their interpretation of the $^{206}Pb/^{238}U$ ratio profile as reflecting alpha recoil is opposite to the measured profile. Processes of alpha recoil at the crystal surface would result in the loss of Pb and result in a younger date (i.e., lower $^{206}Pb/^{238}U$ ratio) at the surface – while the measured profile indicates the opposite and instead progressively gets older toward the rim. It is possible that these measured profiles instead reflect a diffusive boundary, mirrored by the profile of U concentration. See Figure 10 of Ibanez-Mejia et al. (2014; Chemical Geology) for an example of this process. The authors should thus provide an explanation as to why their Pb compositional gradient could not be diffusion related and more thoroughly defend their interpretation of a gradient due to alpha recoil.

Technical Corrections

[line 20] It would be better if you could confirm these are indeed oscillatory patterns – e.g., image the grains analyzed or at least grains from these separates.

[line 24] A comma between lattice and but.

[line 31] How does baddeleyite break down into zircon if there's no supply of Si from the baddeleyite. I understand when zircon ($ZrSiO_4$) breaks down into baddeleyite (ZrO_2) and quartz (SiO_2).

[line 83] What are the typical concentrations of U reported in these baddeleyite samples?

[line 84] Specify that these are ID-TIMS ages. Also, I read in the Ramsay et a. 2019 text that the Hart Dolerite Pb/Pb age is also an upper intercept age.

[line 94] How does the Cr cap ensure stable evaporation? I understood this would have the opposite effect…

[line 100] (mass spectrum in Dalton)

[line 104] Where are the TOF spectra for these two APT runs?

[line 112] "Lead was present as $^{206}Pb^{++}$ and $^{207}Pb^{++}$" – again we just have to take your word without the TOF spectra.

[line 116] Should the citations be ordered – either ascending or descending?

[line 120] I understand that APT is never the same as other methods, but it's interesting that the U is so low for the Hart Dolerite when the ID-TIMS gives U concentrations from 551 to 1682 ppm.

[line 127] "the largest U gradient should be encountered at the surface" – based on what? You could have oscillatory zones which have greater U concentration from earlier growth zones?

[line 153] "the planar symmetry of a zoned U distribution" - your reconstructions don't appear as having a plane of concentration change whereby indicating that this reflects a clear oscillatory zone/boundary? It's also challenging to see if this indeed is a boundary with only one view of the tip... the one chosen for Figure 3 is not particularly convincing.

[line 173] I’m sure you can find a source other than Wikipedia.

[line 235] The entire 3.2 constrains on alpha recoil distance from U clustering derives from U clustering which is never depicted in the figures?

[line 239] Do you have an explanation for why Ti of all elements is enriched in these clusters? No other elements?

[line 254] I think that Valley et al. 2014 and 2015 gave some explanations for clustering.

[line 262] You should also cite Peterman et al. 2019 for trace element enriched linear features.

[line 270] the clusters of U are primary, formed during initial crystallization: can you provide examples of this in the literature? Or explain this further?

[line 317] You confirm that you did not measure Pb depletion profiles yet go ahead and assume you can calculate alpha recoil from this profile? This Pb compositional gradient could be something other than alpha recoil: diffusion.

Figure 3: I suppose the concentration profiles are taken with respect to the observed volume? You should also plot the background levels with respect to each element analyzed here. What are the errors associated with each concentration point?

Figure 4: Where are the labels for each axis? Also the errors associated with these measurements??

Figure 7: Again what is the title for the y-axis? The points are incredibly difficult to see. I would suggest extending the graph to the full width of the page and spacing out the points so that you can see which correlate? Maybe use different symbols and not all circles?