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Interactive comment on "TephraNZ: a major and trace element reference dataset for prominent Quaternary rhyolitic tephras in New Zealand and implications for correlation" *by* Jenni L. Hopkins et al.

Anonymous Referee #2

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Review of gchron-2020-34

This manuscript sets out to be a database for the geochemical composition of glass in Quaternary rhyolite tephra layers in New Zealand. It provides an extensive data suite of major, minor and trace elements that is proposed to be a reference standard for identifying unknown layers (tephra correlation). The authors rightly point-out that the NZ tephra are well-studied, but there is no standard database, as previous studies are based on differing materials, techniques and labs, and the raw data is not always available. From this point of view the goal of work is valuable. But the question is

whether it has been executed correctly here considering the data suite and its quality (see below).

In addition, it is not clear whether a catalogue or inventory of data makes an actual scientific publication. Indeed, some the high quality tephra databases from elsewhere that the authors quote (line 95-100) are not actually published in refereed journals. The authors do not make a case for new discovery or methods – normally a requirement for science journals. Many (not all) of the conclusions about the homogeneity or heterogeneity of individual tephra and differences between volcanic centres are already thoroughly published by original workers (and re-cycled by previous reviewers – including reviews of reviews). In addition, it is unlikely that many of these local NZ tephra layers would be found beyond the NZ region, and hence the work is of regional rather than global interest. It should be noted the same applies to the other tephra databases.

Regardless, if the database is to become a standard, it must be comprehensive (even if unpublished but publicly available). This requires (1) relatively complete sampling of the known tephra both (i) regionally and (ii) sub-sampling within deposits; and (2) very robust geochemical results/methods.

1 (i) Geographic/stratigraphic coverage. There are some regional gaps in their sampling or sample choice. There is literature on well dated and documented tephra in SE North Island (e.g., Wairarapa and Cape Kidnappers) and northern NI (early Quaternary Auckland region). These have not been analysed and this needs to be explained. They cannot be dismissed as limited localities known or poor age control, because some of tephra layers from the Wanganui basin examined here have very limited known exposure and limited age accuracy.

1 (ii) Eruption deposit character. Although acknowledged as a limitation (near line 185), the work has not attempted to sub-sample within thick deposits despite numerous petrological studies showing time-sequential and azimuth differences in mineralogy and glass composition for some OVC and Taupo tephra layers. This becomes more

evident in proximal outcrops. Thus, creating a dilemma as to what is actual reference material for characterisation. The authors simply dismiss the problem by saying that distal deposits are the largest volume of the eruption (line 580). This is not always correct, and no published examples are offered in support – the old Walker citation provides no documented examples. It is possible that some of the widely dispersed glass from an eruption is homogeneous, but this is not always the case. There are published NZ examples of heterogeneity. Regardless, it becomes a circular argument unless it is documented that there is no spatiotemporal variation. This is difficult to solve. But the authors should expand the discussion to highlight the problem (rather than doing the reverse). As a result, the work implies some of the tephra are chemically very similar (e.g. near line 655). But there are petrology studies showing them to differ. This becomes an issue when you are attempting to make a reference database.

(2) Issues with the robustness of the geochemical data (a) Table 2 shows channels for elements analysed on the probe. This is meaningless unless it is spelt-out in the table which spectrometer crystals (e.g. TAP etc) were used. Its not obviously why channels are highlighted because it is glass standards that actually show achieved accuracy and precision. Spectrometer crystal set-ups will always vary between labs. A table of resulting standards would be better.

(b) (near line 235) It is stated that water in the glass is magmatic. This is unlikely. Most studies show modern pyroclastic glass as relatively anhydrous, and the high and variable water contents (by difference) like in this study is due to variable meteoric hydration. Actually, that in itself is a problem not discussed here.

(c) Water by difference in Supplementary files. A quick scan of the file reveals individual shards with water contents of in the range 10-32 wt %. This is impossible and reflects poor analytical data that should be removed. Most of the listed water data is in the range 0-7 wt %. But it is not clear why even that variation is so wide (within samples). Whether the water was magmatic (unlikely) or meteoric, why would some shards occurring side-by-side in a deposit have widely differing contents e.g. 0.7 and 7.5 wt

% water in sample Kaharoa P? This shows-up the problem with not directly measuring water (which is difficult). The water "by difference" is simply the sum of the analytical error. Unfortunately, this data suite highlights the problem. This needs to be discussed.

(d) The trace element variation is VERY wide in some samples. For example, Ti $\sim$300-1775 ppm and Sr 62-148 ppm in Taupo PY (also see wide Rb range in Waimihia and range Sr range in Whakatane). Is it likely that the melt is that highly heterogeneous on a micro-scale and is maintained during magmatic transport without mingling. Regardless, some of the co-variation elemental is not consistent with AFC processes. Petrologic studies at Taupo and Okataina volcanoes do not support such micro-variations. If fact many (not all) pumices are relatively homogeneous for the young Taupo eruption and other deposits examined here (OVC etc). The variability presented here could partly reflect the nature of the sample analysed. Were individual pumice or lapilli used? If not, then the matrix of many of these deposits contains xenolithic material including obsidians, dome glasses and other volcanogenic detritus. It is likely such fragments have been probed here, but they would not be representative of widely dispersed vitric ash found in deep-sea cores and elsewhere (as already published). Hence, a reference set of data must be based on juvenile lapilli where available. Lapilli is available for most of the post-20 ka deposits. Perhaps an appendix of lithology information is needed. Contributing to the problem is that some of the data are analytical outliers and reflect analytical problems. For example, data line 67 in Waimihia has V = 45 ppm and Cu = 79 ppm – wildly different to the other analyses and does not reflect petrologic processes. The entire dataset would need to be filtered for these types of errors. But this also raises the issue of how to filter it. It would need to be fully explained. I suspect the cause of the problem is ablation of microlites and micro-voids in the glass. This is a major problem in previous tephra studies using laser ablation and should be discussed in the text if you argue this is a reference database.

(e) There are some poor comparisons between element contents determined by EMA versus laser ICPMS (e.g. Ti). This needs to be discussed or explained. Data may need

to be filtered. But that requires a robust approach that is clearly explained.

In summary, (1) the geographic/stratigraphic sampling is not uniform (2) spatiotemporal within-deposit heterogeneity is not explored but is highlighted by other workers (3) the geochemical database has variable errors and outliers, and has not been filtered (4) filtering of the analytical database would require a robust rationale to avoid bias (5) suitable geologic material (individual lapilli) are needed to avoid xenolithic sources when proposing a reference standard

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