

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

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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. We thank Reviewer2 for

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taking the time to read and comment on our manuscript. Below we address some of the key concerns highlighted by R2 in their comments.

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 of 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. Despite agreeing that this manuscript provides an “extensive data suite” and that we “rightly point-out that there. . .is no standard database” for New Zealand tephra, we are surprised that R2 thinks this research is not valuable enough for a scientific publication. We (and the other two invited reviewers) strongly disagree that this research has no new “discovery or method” as described by R2. This manuscript includes many firsts for New Zealand tephrochronology that are clearly worthy of publication including (but not limited to): 1. The first time almost all of these tephra (of known source) have been analysed for glass trace element compositions – allowing more robust correlations where major elements are not distinct enough, as shown by our work and previous publications. 2. The first time a comprehensive and systematically analysed data set has been produced, which allows rigorous assessment of the relationship between the geochemical signatures of glass not only from different tephras but also from different caldera systems and their evolution through time. 3. The first open access, fully holistic dataset that has been produced, including not just mean and standard deviation values, which have limitations when producing robust correlations, but also full standard data information (i.e.

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individual shard analyses) and data reduction methods, which are critical for producing comparable data in future projects.

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

(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. Reviewer 2 rightly points out that there is extensive research on tephra in many regions of New Zealand. However, we believe R2 misses one of the main themes of this reference dataset, namely providing reference data from known and well-documented tephra deposits. Even in the abstract we plainly state that “we target original type sites or reference locations where the tephra’s identification is unequivocally known based on independent dating or mineralogical techniques”. Therefore, many of the sites highlighted by R2 (e.g. Auckland, Wairarapa, Hawke Bay), and indeed other sites in New Zealand, were deemed inappropriate for this study as their assigned eruptives are commonly just correlations based on other research. By adding such sites could potentially perpetuate misinformation and miscorrelation, which is why we have chosen to pointedly target the type sites for these tephras, or where their correlation is unequivocally known through multiple criteria (e.g. Kaipo bog sites).

(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

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and glass composition for some OVC and Taupo tephra layers. This becomes more paper 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. We recognise that past literature (which we have cited) has identified variability in composition for the same eruption’s deposits, linked dominantly to changing wind direction during the eruption coupled with magma source dynamics and compositional variations, and this limitation is discussed in Section 4.1.3. Because of this we sampled both proximal and distal locations (where possible) to emphasise that there is sometimes variability in the geochemical compositions of these deposits from a single eruptive episode, and our results show this is true for some, but not all, of our samples, which is discussed in the text. As R2 suggests, we will expand our discussion on this to give more clarity to the reader with regards to the complexity of geochemical variations throughout an eruption.

We would like to reiterate that this foundation dataset, is proposed to be the beginning of what we hope will be a constantly updating and evolving tephra data base for New Zealand (in our case, based on glass-shard analyses). Indeed, we have financial support for the next two years for projects to gather more samples and data where appropriate.

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(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. It's 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. Additional information will be added to this table. We highlight that SM Table 3 shows all the standard data for major elements run on the EPMA.

(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. Amended in the text

(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. Yes, there are 19 data points in the 1190 that have H<sub>2</sub>O values  $\geq 8$  wt%. These have been removed from our dataset and additional discussion will be added to the text to explain this.

(d) The trace element variation is VERY wide in some samples. For example, Ti 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 with-

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out 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. In 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.

We are aware of the high variability in the trace element data we have produced. As R2 points out, it is well known in the literature the difficulty in analysing glass shards without accidentally including microcrysts. Therefore, we realise we need to be even more rigorous in our data reduction. Additional data reduction will be fully explained in the text, as has been done for data reduction and standardisation already (sections 2.3-2.6).

We highlight to R2, as discussed frequently in the text, that these analyses were run on glass shards in 60–250  $\mu$ m size fraction, thus negating contamination by what R2 suggests could include "xenolithic material including obsidian, dome glasses and other

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volcanogenic detritus". The whole point of this study is to provide a comparable data set to distal deposits (including from deep sea cores as identified by R2), hence our exclusive use of the same material (juvenile glass) found at these distal sites.

We also note that heterogeneity and homogeneity are often defining features of an eruption and, by analysing a juvenile clast (e.g. lapilli) you are effectively producing a whole rock analysis, which can homogenise the dataset. For example, small scale heterogeneity is less likely to be picked up as the juvenile clast will represent only a small part of the magmatic system. Selecting glass shards from ashfall is far more likely to sample a wider range of the magmatic system, depending on which part of the magma chamber they come from (and what minerals they are in equilibrium with). This is confirmed by melt inclusion work. For example, glass shards that formed interstitially to plagioclase-dominated crystal mush will be very different in composition to those formed when surrounded by biotite, or those from areas of high melt proportion and few crystals. We believe that many previous studies have "over-reduced" their data, removing "outliers" or "inherited shards" and therefore skewing the geochemical composition results. This detail is also lost where means and standard deviations of individual shards are reported rather than the full data set. The point of reporting all of our data (even when the internal variability seems high) is in the hope that these details are retained.

(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. This data will be plotted and added as an appendix into the Supplementary Files once further data reduction has been undertaken.

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

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(5) suitable geologic material (individual lapilli) are needed to avoid xenolithic sources when proposing a reference standard.

Please also note the supplement to this comment:

<https://gchron.copernicus.org/preprints/gchron-2020-34/gchron-2020-34-AC2-supplement.pdf>

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Interactive comment on Geochronology Discuss., <https://doi.org/10.5194/gchron-2020-34>, 2020.

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