

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. Maxim Portnyagin (Referee) mportnyagin@geomar.de
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This paper reports a new self-consistent (obtained in one lab) dataset for major tephra in New Zealand and its discussion aimed at defining robust criteria to distinguish different tephra on the basis of chemical data. This work is an important step toward a global database of tephra compositions and should be published. The dataset is proposed to be a reference for future studies and must be of high quality. Therefore my comments mainly focus on the analytical procedures and the quality of data included in the tables. I recognized some issues with the data, which should be solved before the manuscript and the database are accepted for publication. Discussion based on the data sounds valid. However, I cannot fully evaluate the discussion as I am not familiar with details of tephrostratigraphy in New Zealand.

We thank Dr Portnyagin for taking the time to give such a thorough review of our research, and appreciate his positivity toward the results. Dr Portnyagin highlights that as we are proposing this research as a reference set, the data should be of high quality. We wholeheartedly agree and we therefore very much appreciate his detailed comments on the analytical procedures and quality of the data. Below we have addressed the key themes of this review.

Samples studied Table 1 – list of tephra should be available as a part of the database in Excel format. This table can be linked to data tables.

SM Table missing/required: list of samples with coordinates, their description, name of tephra, age etc.

EMPA data Table 2. Analytical crystals should be indicated. Compositions of reference materials should also be included.

Table 1 with all the sample names and co-ordinate locations will be available as an excel spreadsheet, downloadable with the SM material. All the tables will be accessible in this format to ensure they are useful, and usable for future studies. The transparency of the glass-based data underpins the presentation of this research. We will update Table 2 to include the analytical crystals used and compositions of reference materials. The analysis dates for the standards are listed in SM Table 3 (EPMA) and SM Table 4 (LA-ICP-MS); we will add analysis dates for the samples to Table 3 for clarity.

Line 228: “. . . and Cl”.

Amended

Line 230: Source of reference data? I see in Table SM2 that reference data for VG-568 differ from Jarosevich et al. 1980. It is said in line 235 that the reference data came from GeoRem. However, Georem does not provide any recommended (preferred) values for this reference glass (and for VG-A99 either). So, how was this derived from the GeoRem data and why do the authors believe that the data is better than originally provided by the Smithsonian Institution? Anyway, the data for VG-A99 and VG-568 used for calibration and correction for instrumental drift must be clearly presented in table and justified if they differ from previously recommended values.

The reference data values for VG-568 and VG-A99 come from GeoREM. GeoREM reported 53 published analyses between 2006 and 2019 for VG-568, and 21 published analyses for VG-A99 between 2006 and 2015. We believe these to be more up to date than those provided by Jarosevich et al. (1980) but all are within error of Jarosevich et al's data, and are publicly

accessible, unlike the Jarosevich et al. (1980) publication. We have produced averaged data for the GeoREM values reported. However, because these values are updated frequently we chose to use the values reported by Streck et al. (2006) for consistency and continuity. In the database, Streck et al., are the only group to publish values for both VG-568 and VG-A99 for EPMA analysis. These values will be reported and appropriately referenced in the SM Table 3. Standard data for VG-A99 in SM Table 3 will also be provided as requested by Dr Portnyagin.

Line 238: Some analyses have H₂O_D as high as 32% (line 566. This analysis has also 1.2% Cl = a lot of epoxy trapped). This is not acceptable for reference data. The authors should exclude all data with calculated H₂O>8 wt% (more secondary water can hardly enter glass structure).

Yes, we have identified 19 data points throughout the 1190 that have H₂O_b values ≥ 8 wt%. These will indeed be removed from our dataset. This is an oversight on our part. There is only 1 sample with Cl value ≥ 0.72 wt%, and this is also one of the samples with high H₂O_b that will be removed.

Line 241: I recognized some problems with ATHO-G data, which must have influenced the calculated precision.

We thank Dr Portnyagin for pointing this out.

SM Table 2: Analysis date should be indicated here and for standards.

Amended

SM Table 3: poor reproducibility of ATHO-G. The data look very bad for Na. Drift is seen for Si, Ca, Al, Mn. What happened between points 51 and 100? Did the analytical conditions change? Was this different chip of ATHO-G? No data for VG-A99 provided. Was Cl calibrated on rhyolite glass VG-568? This cannot be precise calibration as Cl content is 0.1 wt% in the glass.

SM Table 3 shows the standard data for VG-568 (run as a primary standard) and ATHOG (run as the secondary standard). There is a jump in the data at point #51 and some drift observed after this point, as the machine was re-standardised after being left idle for two days (13/12–16/12). Besides this, no analytical conditions changed. The average and standard deviation for these data between these two periods are indistinguishable except for SiO₂, which show a variance in the average recorded value of 0.7 wt%. We will re-standardise using these separate analysis sessions to ensure the values reported are as accurate as they can be.

LA-ICP-MS SM Table 1: Very high level of oxides (ThO/Th=1.3-1.8%, whereas acceptable ratio is 0.5-0.7%). This must have effect on some mass number measured, which have interference with oxides. For example, Sc45 signal was likely strongly affected by interference with Si²⁹O¹⁶. This maybe the reason of large deviation of Sc from reference data in STHS standard (SM Table 4). As Sc was calibrated on ATHO with large input from SiO₂, Sc measured on samples with lower SiO₂ (as STHS) is underestimated.

The oxide levels reported for our analyses (SM Table 1) are ThO/Th = 1.3–1.8%. These values are comparable to those reported by other publications at similar operating conditions. For example, Pearce et al. (2011) reported ThO/Th values of “typically ~1.5” using a 193 nm laser ablation system with 5 Hz repetition rate and a 20s acquisition time. We note that these are higher than those reported by Portnyagin et al. (2019). However, we also report both ¹⁵³Eu and ¹⁵¹Eu values (which can be affected by ¹³⁷BaO). The concentrations measured

for these isotopes are very similar and show no relationship with Ba, thus we assume no problem with oxide interference on either the standard or sample data.

SM Table 2: For some elements two isotopes were measured. The authors should report just one value: the best or average value for these elements.

We will report the most common isotope for these elements.

Check cells [AB24] and [AC24] – misprints? Poor agreement between EMP and LA-ICP-MS data for Ti, for example, in lines 43, 45, 46 (contamination by orthopyroxene?), line 67 (contamination by Ti-magnetite) and in many other lines. About 5% of all data have this problem (See plot attached). This indicates contamination of LA-ICP-MS analyses by mineral phases. Outliers must be excluded based on some quantitative criteria. For example, data included in the dataset have better than 10% (or 15%, or 20% - this should be authors choice to place the level of their accuracy) agreement between EMP and LA-ICP-MS for Si and Ti, which were the only elements precisely analysed by both technique. EMP data for Mn are probably not precise enough for such comparison and data screening. Thus, the authors should manually check every LA-ICP-MS analysis and exclude outliers, which cannot be reliably proved as representing natural melt variability.

We realise that it is a common theme throughout our reviews: the data have not been thoroughly reduced. This is an oversight on our part, however, in some cases we did not remove outliers as we were unsure if these were indeed anomalous or if they were simple natural variability in the data. There is evidence for fractional crystallisation of mineral phases within the data, and we wanted the reference data to reflect (where appropriate) this natural variability within the samples. In some cases, this geochemical variability is the unique identifier for the tephra. We will add in a Supplementary file that shows a comparison between the elements that were analysed on both EPMA and LA-ICP-MS for clarity.

In the future, I strongly recommend to analyse all major elements by LA-ICP-MS (Agilent7900 is excellent for this job) as described, for example, by Portnyagin et al. 2020. This will ensure reliable identification of contaminated analyses.

We thank Dr Portnyagin for this advice and will endeavour to do this in subsequent analyses.

Fig. 2 Very strange data for Rb and Zr and calibration based on NIST-610 in runs # 8 and 9. The outliers do not look representative. NIST610 and NIST612 normally show very consistent calibration, but not in this study. This is unclear. In general, there are several comprehensive investigations of the matrix effect in LA-ICP-MS analysis of glasses. It is usually of the order of 10-20% or less, rarely larger as for Zn, which is volatile (low condensation temperature) and terribly difficult element for LA-ICP-MS analysis. Of course, NIST glasses differ compositionally very much from natural rhyolites. ATHO-G (Askjy rhyolite) should be better standard for natural samples.

This figure outlines our investigation into the most appropriate standard to use for our analyses, and we agree that our data show ATHO-G to be the most appropriate.

Line 347: 2sd value depends on analytical conditions and on concentration. Thus, comparison with the secondary standard maybe misleading if the tephtras have different composition. ATHO has 3.5%FeO, whereas the glasses from this work have on average 1.4% FeO. Using 2sd from ATHO is too conservative approach to define homogeneous populations in this case. CaO is also typically lower in the glasses compared to ATHO-G.

We thank Dr Portnyagin for pointing this out.

Fig. 3 -7: all should be updated after cleaning the dataset.

Amended

Line 399 and Figure 8: I strongly recommend to NOT use chondrite composition for multi-element plots like this one (Chondrite is Ok for REE plots). This is because chondrites are strongly enriched in some volatile elements, which were lost from the Earth mantle during accretion of our planet or shortly after it (e.g. Pb, Cs, Mo). Better use primitive mantle composition (e.g. McDonough and Sun, 1995, Chem Geology). In this case, normalized Pb, Mo, Cs will be much higher (Mo) and even strongly elevated (Pb) compared to neighboring elements (i.e. LREE for Pb) as it must be in typical subduction related magma. Chondrite normalized spectra like Fig. 8 look very confusing for geochemists working with trace elements in magmas from different tectonic settings. This figure also should be updated after cleaning the dataset (removing outliers contaminated by solid phases during analysis).

Amended

Line 403: Not Pr anomaly, but negative Pb anomaly relative to LREE. Not negative Sm anomaly, but positive Zr-Hf anomaly relative to Sm.

Amended

Line 410: Er and Lu peaks are likely analytical artefacts. We do not know high-T processes fractionating these elements from the neighboring HREE.

Noted

Line 445 and below: What is the advantage of using PCA analysis in comparison with simple “old-fashion” bi-plots of major elements and spidergrams for trace elements? Do we really need so many elements to distinguish different tephtras?

We have found in our research on New Zealand tephtras that more elements from the glass analyses are often required to distinguish between tephtras from different eruptions. This feature is discussed in the text. For this reason, we have chosen to run PCA analysis to further distinguish between samples that simple biplots cannot. This approach uses the theory of “handprinting” rather than “fingerprinting”, and it is often very successful, especially when statistical methods are used. In this way data can be looked at in multidimensional space, and thus variations in the data can be more readily distinguished and correlations made more robustly.

Fig. 15: Some of these plots make little sense to me. For example, Tb and Er are nearly elements-twins, their behaviour is always coupled.

These elemental couples, and all the plots, were chosen because they show the best distinction between the two tephtras.