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Discussions
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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.

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This paper reports a new self-consistent (obtained in one lab) dataset for major tephras in New Zealand and its discussion aimed at defining robust criteria to distinguish different tephras on the basis of chemical data. This work is 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 tephrastratigraphy in New Zealand.

Samples studied Table 1 – list of tephras 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.

Line 228: ". . . and Cl".

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 VGA99 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.

Line 238: Some analyses have H2OD 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).

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

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

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.

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 SiO+, Sc measured on samples with lower SiO2 (as STHS) is underestimated.

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.

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.

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.

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 natuarl samples.

Line 347: 2sd value depends on analytical conditions and on concentration. Thus, comparison with the secondary standard maybe misleading if the tephras 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.

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

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).

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

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

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 tephras?

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.

C5
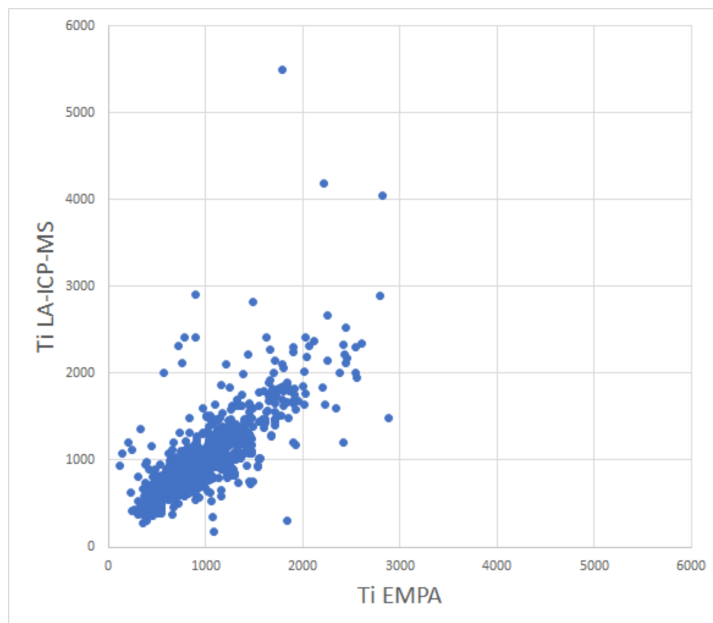
This figure illustrates poor agreement between Ti content in glass obtained by EMP and LA-ICP-MS in some analyses included in the dataset. Acceptable deviation is about 20% relative or less. Larger discrepancy indicates contamination by mineral phases, which are present in glass and were likely ablated during analysis. These bad analyses should be excluded from the dataset.

Fig. 1. Ti EMPA versus Ti La-ICP-MS