Comments on "TephAta - An online data collection of tephra data from the Atacama Desert" by

N. Leicher and co-authors submitted to ESSD

This manuscript introduces a large database of tephras from the Atacama Desert, northern Andes. The database comprises comprehensive information of the occurrence, high quality major, minor and trace element glass composition, and compilation of age determinations of about 100 individual tephra samples covering the age interval from Quaternary to Miocene. The majority of the data including Ar-Ar dating results were obtained by the authors; some literature data have been also included. The database is available in web and also as Excel files making it very convenient to use on-line or on local computer. The structure of the database is aligned with recommendations from the tephra community and thus is compatible with other databases (e.g. EarthCHEM). I want to specially emphasize that all the data is accompanied by comprehensive information on reference materials analyzed during the same analytical sessions. This is excellent example of how geochemical tephra data should be reported in any publication. The manuscript provides quite detailed analysis of the age data, compositional variations of tephras, their clustering, and possible implications for the ongoing and future research. The manuscript is very well written and without doubts is a major contribution to the tephrochronology of Andes with many important applications.

My major recommendation to authors is to try clean the database as thoroughly as possible already on this stage (when it is not too large), exclude all data of questionable quality or not supported by data on reference materials, exclude data with totals less than 90-92% and more than 101.5%, exclude obvious compositional outliers, check the correctness of web output (I specify the questions below).

Overall, I strongly recommend publication of this contribution after minor revisions, suggestions for which are placed below and mainly concern geochemical methods and results.

Thank you for reviewing our manuscript and acknowledging our work. We appreciate your comments and thoroughly reviewed the data within the database. A point-by-point reply is found below, including a statement (red text) and the adjustments made in the manuscript (blue text in italics).

Line 65: Perhaps magma-crust interaction is particularly important in Andes, but in general it is not prerequisite for eruption- or volcano-specific fingerprint. Common factors resulting in volcanic glass variability is different extent of crystallization and variations in parental magma compositions.

We rephrased the sentence to provide a more general explanation for the evolution of volcano-specific fingerprints.

Geochemical variations specific to individual volcanoes and eruptions are driven not only by parental magma composition and the degree of crystallization, but also by the geodynamic evolution of the Andes. The spatial and temporal differences in the thickness and composition of the crust, led to varying degrees of magma-crust interactions and thus to variable/additional magmatic differentiation of individual eruptions (Kay et al., 2010; Brandmeier and Wörner, 2016; Burns and De Silva, 2023).

Line 71: Are sedimentation rates high enough in the Atacama Desert to provide high temporal resolution of the archives?

We adjusted the sentence and incorporated a statement on the temporal resolutions of archives. We further clarified our originally addressed statement, that the "dry" environmental conditions of the Atacama Desert with low physical and chemical weathering ensured a good preservation of tephra layers in sedimentary archives, being less affected by alteration as tephra in other, more humid environments.

The Atacama Deserts' long-term aridity, is thought to have initiated as early as ca. 25 Ma ago (Dunai et al., 2005; Evenstar et al., 2017) and sets with the low degree of erosion and weathering (e.g., Ritter et al., 2023) suitable climatic conditions for the preservation of volcanic deposits. Despite dominating easterly wind systems, tephra deposits can be found abundantly from the Andes to the Pacific coast (Marquardt et al., 2005; Vásquez and Sepúlveda, 2013; e.g., Breitkreuz et al., 2014). Tephra layers serve as crucial isochronous markers for dating sedimentary sequences within this arid environment, where other dateable materials are scarce and the temporal resolution often sediment records is often low.

Line 82: Whole-rock analysis is also technically more complicated, time-consuming and expensive compared to glass analysis by microanalytical techniques

We agree that whole-rock analyses can be more complicated, time-consuming and expensive compared to glass analysis by microanalytical techniques. We adjusted the paragraph to make clear that we rather addressed the general comparability of data (single component vs. bulk analyses), which affects tephra correlations (for changes see also comment on line 83 below).

Line 83: not only lateral variations; crystal/glass in tephra layers are often vertically/temporally variable.

We included this in the adjustment of the paragraph.

Comprehensive results of this research including geochemical (whole-rock compositions and isotopes) and chronological data are made available within the Central Andes Geochemical and Geochronology database (https://andes.gzg.geo.uni-goettingen.de/). Whole-rock analyses, however, have been found to be less suitable for tephrochronological alignments due to site-dependent variations in their main components (variable relative abundances of glass, crystals and lithics) caused by aeolian fractionation, temporal eruptive variations and the influence of alteration (Tomlinson et al., 2012a; Lowe et al., 2017).

Line 165 and the above description of the database and web interface:
This is great web tool! I really like it. However, the authors may want to check the data and web output more thoroughly. For example, for randomly selected sample #TSdU, the output table contains wrong original totals (117% etc.). Supplementary table is correct.

We reviewed all data stored within TephAta to ensure data quality. We revisited original data to exclude data of sessions with reduced analytical uncertainty and further inspected major, minor and trace element glass data for the influence of potential mineral phases or technical malfunction of individual analysis. We apologize for copy/edit mistakes in the previous version (such as wrong totals), which now have been corrected. All geochemical data is removed from the database, and the revisited datasets are currently being reuploaded. A compilation of all reviewed data will be made available within a revised version as supplementary material, which will be also made available at EarthChem.

Apparently, the 100%-normalized data in the web tables and supplementary table to this manuscript does not account for the substitution of halogens for oxygen, though it is said in the heading line of the supplementary table. Minor thing but better do it or explain clearly that Cl, F and S were not included in normalization and this is deviation from the recommended by Wallace et al. 2022 procedure.

Our EPMA-WDS data (totals) does account for the substitution of halogens (Cl, F) for oxygen during data reduction by the JEOL software. We apologize for a formatting issue, which presented an excel-calculated sum and not the halogen-corrected value. We have replaced the affected data with the corrected values. We did not include volatiles (Cl, F, SO_3) in the normalization for 100% water-free compositions, as recommended in Lowe et al., 2011 and commonly applied within the community. We did not find such recommendations (including volatiles in water-free normalization) in Wallace et al. (2022). We rephrased the methods section and included information about our data reduction.

Data reduction included ZAF correction and substitution of halogens (Cl, F) for oxygen using the JEOL Ltd JXA8900 Basic Software V3.02. Only EPMA-WDS geochemical analyses of glass fragments with analytical totals >90 wt. % were considered and normalized to 100% on a loss on ignition free basis, excluding volatiles (Cl, SO_3 and F).

Presumably, the authors did quality checks before entering this data into database. Or not? Was there any screen based on the values of original total? Do authors believe that totals as low as 90% and less are real, that is, due to glass hydration? One of the samples in Supplement has original total of 58% - check it.

We apologize for erroneous data with totals <90%, which accidentally was copied to the supplementary data. We removed such data from the database and data stored at EarthChem/Supplement. Our quality cutoff value has been chosen at 90% to account for high magmatic water contents, any post-depositional hydrations and/or alteration, not measured elements and analytical uncertainties. We agree that 90% is at the lower end of values being heterogeneously discussed within the community (cf. Lowe, 2011). However, we suggest to keep this value, so that people reusing the data can apply own quality criteria, e.g. if higher values are preferred as also applied within other tephra-databases (Portnyagin et al., 2020). We have also added information about the 90% cutoff-value to the methods section, to make it aware during reuse of the data (see comment above). We also flagged data with low totals (>90-<92 wt.%) within the datasheets (comment in column H: data_point_notes).

Line 277: Please, clarify that grain-specific SiO2 was applied only to samples with heterogeneous composition (as explained below). What was criteria of “heterogeneous composition”? SiO2 range?

After a comprehensive review of the entire dataset, we re-examined the two samples for which LA-ICP-MS data reduction had been based on grain-specific SiO_2 values. We recognize that our previous description of this approach was unclear and, in part, inaccurate, and we sincerely apologize for this oversight. The grain-specific SiO_2 data in question were obtained during SEM-EDS sessions for which no secondary standard measurements are available. Although these values showed good agreement with the corresponding EPMA-WDS data of the sample, the lack of secondary standard data limits their analytical robustness. Consequently, we excluded these grain-specific SEM-EDS data and instead applied the median SiO_2 concentrations determined by EPMA-WDS consistently across all samples in the dataset as also SiO_2 concentrations appeared homogenous. The methods descriptions within the manuscript have been corrected. (see also comment below)

Line 296: Was Ca by LA-ICP-MS compared with Ca from EMPA data to monitor potential contamination by mineral phases? In general, how precisely was Ca content reproduced by LA-ICP-MS? This is unfortunate that some more major/minor elements were not analyzed (Ti, Na, P etc.); this precludes rigorous analysis of the data quality and screening out of contaminated data.

After having a quick look at the data, I suggest that some variations of trace elements can be compromised by contamination during laser ablation. As an example, let us look at the composition #TIB4-TEPH1. Major elements are relatively homogeneous with SiO2 range of 76.5-78% with only one obvious outlier having Na2O=1.5%. Trace elements were calculated using sample-averaged SiO2. The trace element and also Ca concentrations are quite variable (~2x variations, 2 points have very contrasting compositions). How the authors can prove that these variations reflect heterogeneous glass composition and do not result from contamination by mineral phases during laser ablation? Another example, analysis #52.4-PAG17.2/008-12 with high Ca and Sr, which is very likely contaminated by plagioclase during analysis.

I should mention that this is a common problem of all studies which do not analyze major elements by LA-ICP-MS. Perhaps, the authors can write a kind of disclaimer that some contaminated data may be present in the database and should be used with caution.

We added information about data reduction of LA-ICP-MS data to the method section, explaining how crystal-contaminated data was detected. The median accuracy of Ca measurements of LA-ICP-MS measurements at the UoC was at about 8.5% and at the UoB at 4.1 %. We also stated that no other major elements were measured for considering the influence of crystal-contamination, so that during re-use of the data, people are aware of potential contamination being undetected. However, we revisited all LA-ICP-MS data to screen for glass compositions, which may have been influenced by minerals within ablation and were overseen in the first data compilation. Such data, as the one form the given example (PAG17.2/008) were excluded from that data (e.g. like the given examples) to minimize the bias.

As an internal standard ^{29}Si was incorporated using median SiO2 concentrations obtained from EPMA-WDS data of respective samples. Since major and minor elements such as Ti, Na, K, or P were not analyzed by LA-ICP-MS, they could not be considered for detection of potential contamination by mineral phases during ablation. However, during data reduction in Iolite, the full analyzed trace element spectrum and Ca were screened to identify and exclude potential mineral inclusions (e.g. relatively elevated Ca, Sr, or Ba counts indicating feldspar inclusions) from data selection.

Line 309: One standard deviation or two? Two SD (or RSD) should be reported that corresponds to ~95% probability.

We had calculated the relative standard deviation using a one standard deviation. We have now changed this according to the suggestion of both reviewers using a relative two standard deviation (two standard deviation/mean).

Line 340: "Crypto" refers to invisible tephra layers, disseminated in host sediments/ice.

We agree on that definition and have adjusted the sentence to clarify the meaning.

The typical thickness of tephra layers is in the scale of centimeters, but also include several m-thick to sub-cm thin and tephra deposits, whose lateral extent ranges from decimeter to hectometer. In addition, cryptotephra horizons have been identified in sediment cores.

Line 428: This is unclear why the legacy data for sample #2-3-5-2, which are not supported by standard measurements, are included in the database. I suggest to delete all questionable data from the database. This will increase the database value, consistency and reliability.

We included the legacy data to have a most complete dataset that also accounts for existing data but had flagged this data as not reliable within the download file of the EPMA-WDS data. This should also serve as an example that the database is suitable for storing legacy geochemical data. However, we see the point that flagging of the data might by overseen and thus removed these entries.

Line 453: As most of the samples are rhyolites, many trace elements behave as rather compatible elements due to strong partitioning into major and accessory mineral phases: Zr-Hf, U in zircon, Sr in plagioclase, Rb, Nb, Cs, Ba in biotite, Ba, Sr is sanidine, LREE in apatite and allanite, HREE in garnet and amphibole. Thus, the argument for using trace elements should be reformulated.

We revised the argument and included further arguments why trace element compositions can be more diagnostic to distinguish between rhyolitic compositions compared to major and minor element compositions.

Due to their generally more incompatible behavior and lower concentrations of trace elements compared to major and minor elements within the melt, trace elements effectively amplify compositional variations driven by differences in the parental magma source and magmatic history (e.g. fractional crystallization, degree and depth of melting, or residual mineral *assemblages). Thus, trace element geochemistry of glass shards have been shown to be a reliable parameter for distinguishing between eruptions with similar major element composition (Tomlinson et al., 2012; Pearce, 2014; Hopkins et al., 2021).*

Figure 4. Lead should be placed between Ce and Pr on spider-diagrams if the elements are ordered according to their incompatibility in basaltic systems. Then, the subduction-related Pb enrichment will be seen better.

We changed the order as requested.

In plots 4 (f-i), what is shown by black symbols placed between 1 and 2?

We adjusted Figure 4 according to the revisited dataset and clarified the assignment of compositional groups in the figure.

Line 501: It is clear from the above that CG1, CG2 and CG9 are not "layers" but "groups of tephras of similar composition".

We rephrased this paragraph to make clear that tephra layers of compositional groups are addressed.

Some tephra layers were found in different sedimentary archives (e.g., tephra layers of CG1, CG2, CG9).

Line 540: Perhaps I missed some text but would it be possible to identify volcanic sources of some tephras and give this information in separate chapter?

We avoided an in-depth discussion about potential volcanic sources at the present state, as the lack of suitable data (glass geochemical data, precise chronological data of young eruptions) from proximal volcanic deposits does not enable a robust correlation at present and is beyond the scope of the current paper, presenting the database. We planned to investigate the source of the identified eruptions within future work, including more proximal data and refined chronological information to ensure robust alignments.

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