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Climate of the Past Discussions

Interactive comment on "Volcanic ash layers in Lake El'gygytgyn: eight new regionally significant chronostratigraphic markers for western Beringia" *by* C. van den Bogaard et al.

Anonymous Referee #1

Received and published: 22 November 2013

General Comments.

This paper reports eight significant tephra layers found in the El'gygytgyn crater lake record from NE Siberia. This record is incredibly valuable palaeoclimate archive for the region of Beringia and the Siberian Arctic and has the potential to rival Pacific marine records in both length and palaeoenvironmental data resolution. Identifying and robustly characterising the tephra layers within this archive has, as the authors conclude, the potential to begin the construction of an important stratigraphic framework that will allow robust comparisons between regional palaeoclimate archives. In seeking the source areas of the tephra layers, the authors provide a concise and well-referenced review of the volcanism around the North Pacific region and highlight the areas and

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time periods that require further research. However, I have a few areas of concern with regards to this article: most significant is the chemical data central to the paper, which I will expand upon first. Then I will address the papers layout and treatment of chronological data in the “specific comments” section. I also append a list of minor technical corrections.

Major concern: inaccurate LA-ICP-MS data.

I strongly disagree with the publication of the LA-ICP-MS data presented in this manuscript and recommend that these issues are addressed fully before this article is published and the data made widely available. This will not be a small undertaking and with regret I suggest that the paper is rejected until either the trace element data is removed, or improved datasets can be produced.

The authors are commendably honest about the disagreement of the data produced by the LA-ICP-MS systems in Aberystwyth and Kiel. However the differences in the compositional data generated on the same tephra layers is NOT insignificant and cannot be worked around. One or other (or both) of these instruments has generated inaccurate data and this data should not be published as it will be reproduced and will trigger mis-correlations between layers in future studies. Tephrochronology relies upon correlations between datasets generated in multiple laboratories. The recognition of this by the community has led to improved methodologies and protocols for data generation and data sharing, particularly with regards to the longer established EPMA technique (Hunt et al., 1998, Kuehn et al., 2011). Trace element analysis of tephra using LA-ICP-MS has more recently been widely adopted by the community and has also undergone many methodological developments (e.g. Pearce et al., 2007, 2011; Tomlinson et al., 2010). Consequently the number of laboratories now producing this type of data is steadily rising. The admission in this manuscript that two laboratories cannot produce comparative data, despite agreement of their standard analyses, has consequences not only for this manuscript, but for all tephrochronlogists generating data by this method and making (mis)correlations between tephra layers. It raises the

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question of how much of the data already existing in the literature is also inaccurate and this issue must be addressed. Clearly the use of fused glass standards, which are larger size and a different matrix than actual tephra glass shards, is not sufficient for checking the accuracy of LA-ICP-MS data and this paper highlights that fact extremely well. The authors might consider using their findings as a basis for initiating an inter-laboratory comparison of LA-ICP-MS trace element analyses of tephra glass shards, as has been carried out for EPMA (Kuehn et al., 2011).

If the trace element data were to be removed from this article and only the EPMA data presented, it would be a more useful contribution to the research community. However the ideal result would be for the instrument errors to be traced and explained and the LA-ICP-MS data re-run and included in a resubmission of the manuscript.

Specific Comments.

Paper layout: Introduction and background. (Section 1 and parts of section 5).

1. Sections 5.2.1 and 5.2.2 (P5991, lines 5-22 and P5993 line 15 – P5995 line 8): These detailed (and valuable) reviews of regional volcanism are out of place in the "results" section and should be moved up into the introduction/background sections. I recommend moving this ahead of the existing Section 2 as it gives important regional context.

Reporting of age estimates. (Section 4, Table 1, Section 5). 1. All age estimates in the manuscript should be accompanied by an estimate of their uncertainty, or a clear indication that the age is an "approximate" age only, by use of a prefix: c. or $\sim$. 2. There is inconsistency in reporting of radiocarbon ages. These MUST be quoted as calibrated ages, with their uncertainties, e.g. P 5994, lines 13- 15. 3. Nowaczyk et al., 2013 give an assessment of the precision of the age model for Lake El'gygytgyn based upon the $\sim$3000 year uncertainty of orbital tuning between different marine stacks. This information should be made clear in this manuscript, in table 2 and also in the text when ages are given as single point estimates. 4. Section 4, line 2: The age model is

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specified as being *high resolution* – this phrase can be interpreted in many different ways and needs quantifying (10's of years – 1000's years precision?). Therefore I would suggest this is a good point to be up front about the age uncertainties associated with the El'gygytgyn core.

Additional comments on analytical protocols and presentation of data. (Section 2 and Supplementary). 1. EPMA was carried out with only the Lipari Obsidian secondary standard to compare the data between instruments. As most of the tephra samples (excepting T5) are also dacite-rhyolites, this is probably sufficient. But in order to check the accuracy of all elements being analysed, the authors should consider using a suite of secondary standards which contain the full range of elements in abundances well above detection levels. 2. Presentation of means and standard deviations in table 2 is inappropriate, representative data should be given in these tables that reflects the true variability of the tephra layers. In particular, T5 and T3 show chemical trends that are entirely lost when the data is averaged in this way. 3. I have concerns about the quantification of the LA-ICP-MS data carried out using average values of the internal standard element(s), as stated in A3.2. Please can the authors specify how they selected Si values for T3 and T5 which show widely variable SiO2 concentrations? The value of single grain trace element analysis is that it records the true (and variable) glass composition of tephra layers, however important detail will have been lost if non-grain-specific data was used to quantify the datasets.

Technical Corrections.

These points are all minor typographical corrections or suggestions of clarifications that will aid the reader's understanding of the manuscript.

Section 1.

P5979,

Line 15: remove either "possible" or "probable".

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Line 21: correct “records” to “record”. P5981,

Line 21: Clarify “a minimum of eight visible tephra layers” – if they are visible they should be countable. Please specify why the number is uncertain. P5982,

Line 7: Suggest to re-iterate that only visible layers were studied, correct to “each individual visible tephra layer”.

Section 2.

P5983,

Line 26: Please clarify that “under the same conditions” is referring to analysis of secondary standards under the same conditions as the tephra shards, or between the two labs (the former I think?).

Line 28-29: Suggest correction to “. . .resulted in different measured trace element concentrations. . .”.

Line 29: please add units (ppm?) to the values stated.

P5984, Line 5: delete “relative”.

Section 3. P5985, Line 4: Suggest that the areas of “mixed in material” be marked on (some?) of the photographs in Figure 2 to aid the reader’s interpretation of this description.

Line 9: tephra layers are described as “light grayish to dark brown” in the text, whilst T0 and T1 are “yellowish” in Table 1. Can these descriptions be checked and corrected.

Line 14: Please clarify “distinct individual characteristics” – does this refer to visual, chemical, structural characteristics? All of the above?

Section 5. P5995, Line 27: Correct to either “the only plausible source” or “a plausible source”.

Section 6. P5997, Line 12: Either “the sources. . .lie” or “the source. . .lies”.

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Appendices.

A1. P5999, line 4: please state the sieve size used to remove the “finest grains”.

A2. Is the introduction needed here? Most of it is said in the main manuscript, so cut to just the lab-specific operating conditions.

A2.2. It is not clear why the full EPMA dataset from the UofA is available but the Kiel dataset provided is only representative, given as average compositions and standard deviations. It would be preferable if all data should be presented within the article, making use of online supplementary tables.

A3. Again, much of this pre-amble is included in the main manuscript and could be omitted here. P6001 line 25 to P6002 line 2: I do not understand this final sentence. Why were the analyses done on “somewhat different materials” – what does this mean?

Table 1.

1. The composite depth for T1 appears to be in cm.

2. Please add a comment on the age uncertainties into the caption.

Table 2.

1.Remove decimal places in “52.00” for T2 UA n value.

2.The T4 “both” n value does not equate to the sum of the UA and Kiel n values – please check.

Table 3a.

Please check: is the fourth line from the top definitely T3? The values seem closer to T2 in the line above.

Tables 3a and 3b.

1. The data for “selected data for widespread Alaskan tephra” at the base of each of

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these tables should be referred to, and referenced if appropriate, in the captions. Was this data generated for this study? If so details of the samples should be given. It is not clear why solution ICPMS is appropriate for these reference materials (Table 3a), rather than single grain analyses as implemented throughout the rest of the paper.

2.For consistency, please include the Kiel ATHO-G data in table 3b, as has been done for the Aberystwyth data.

Figure 1.

1. Figure 1 could be supplemented with a figure showing the lake basin and the positions/lengths of the different cores investigated. The reader wishes to understand why some tephra were not found in all of the cores and a simple figure (or addition of information on the cores lengths, water depths, lake floor bathymetry etc in the text of section 1) would make this clear.

2. Correct to “additional triangular markers”.

3. Correct to “are either too far afield”.

Figure 7.

These two figures present the same data, why not add just one figure that shows both the comparison and the error bars. If the error bars were added as light grey lines they should not make the figure illegible.

Tables S6-S8.

Please spell check “Kiel” and “Aberystwyth” in the table captions.

References used: Hunt, J.B., Clift, P.D., Lacasse, C., Vallier, T.L. and Werner, R., 1998. Interlaboratory comparison of electron probe microanalysis of glass geochemistry. Proceedings of the Ocean Drilling Program: Scientific Results, 152, 85-91. Kuehn, S.C., Froese, D.G. and Shane, P.A.R., 2011. The INTAV intercomparison of electron-beam microanalysis of glass by tephrochronology laboratories: Results and recommenda-

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tions. Quaternary International, 246, 19-47. Pearce, N.J.G., Denton, J.S., Perkins, W.T., Westgate, J.A. and Alloway, B.V., 2007. Correlation and characterisation of individual glass shards from tephra deposits using trace element laser ablation ICP-MS analyses: Current status and future potential. Journal of Quaternary Science, 22, 721-736. Pearce, N.J.G., Perkins, W.T., Westgate, J.A. and Wade, S.C., 2011. Trace-element microanalysis by LA-ICP-MS: The quest for comprehensive chemical characterisation of single, sub-10 μm volcanic glass shards. Quaternary International, 246, 57-81. Tomlinson, E.L., Thordarson, T., Müller, W., Thirlwall, M. and Menzies, M.A., 2010. Microanalysis of tephra by LA-ICP-MS - Strategies, advantages and limitations assessed using the Thorsmörk ignimbrite (Southern Iceland). Chemical Geology, 279, 73-89.

Interactive comment on Clim. Past Discuss., 9, 5977, 2013.