Quaternary Science Reviews 175 (2017) 1–44

Contents lists available at ScienceDirect

Quaternary Science Reviews

journal homepage: www.elsevier.com/locate/quascirev

Invited review

Correlating tephras and cryptotephras using glass compositional analyses and numerical and statistical methods: Review and evaluation

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ARTICLE INFO

Article history:
Received 12 May 2017
Received in revised form
2 August 2017
Accepted 2 August 2017
Available online 19 September 2017

Keywords:
Tephra
Cryptotephra
Tephrochronology
Tephrostratigraphy
Glass-shard analysis
Microshard
Volcanic glass
Crystal
Microlite
Melt inclusion
Electron probe
Laser ablation
LA-ICP-MS
EPMA
Multivariate statistics
Similarity coefficients
Machine learning
Cluster analysis
Statistical distance
Bivariate plot

ABSTRACT

We define tephras and cryptotephras and their components (mainly ash-sized particles of glass ± crystals in distal deposits) and summarize the basis of tephrochronology as a chronostratigraphic correlational and dating tool for palaeoenvironmental, geological, and archaeological research. We then document and appraise recent advances in analytical methods used to determine the major, minor, and trace elements of individual glass shards from tephra or cryptotephra deposits to aid their correlation and application. Protocols developed recently for the electron probe microanalysis of major elements in individual glass shards help to improve data quality and standardize reporting procedures. A narrow electron beam (diameter ~3–5 μm) can now be used to analyze smaller glass shards than previously attainable. Reliable analyses of 'microshards' (defined here as glass shards <32 μm in diameter) using narrow beams are useful for fine-grained samples from distal or ultra-distal geographic locations, and for vesicular or microlite-rich glass shards or small melt inclusions. Caveats apply, however, in the microprobe analysis of very small microshards (≤~5 μm in diameter), where particle geometry becomes important, and of microlite-rich glass shards where the potential problem of secondary fluorescence across phase boundaries needs to be recognised. Trace element analyses of individual glass shards using laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS), with crater diameters of 20 μm and 10 μm, are now effectively routine, giving detection limits well below 1 ppm. Smaller ablation craters (<10 μm) can be subject to significant element fractionation during analysis, but the systematic relationship of such fractionation with glass composition suggests that analyses for some elements at these resolutions may be quantifiable. In undertaking analyses, either by microprobe or LA-ICP-MS, reference material data acquired using the same procedure, and preferably from the same analytical session, should be presented alongside new analytical data.

In part 2 of the review, we describe, critically assess, and recommend ways in which tephras or cryptotephras can be correlated (in conjunction with other information) using numerical or statistical analyses of compositional data. Statistical methods provide a less subjective means of dealing with analytical data pertaining to tephra components (usually glass or crystals/phenocrysts) than heuristic alternatives. They enable a better understanding of relationships among the data from multiple

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Abbreviations: ANOVA, analysis of variance; AVF, Auckland Volcanic Field; BSE, back-scattered electron (image); CV, coefficient of variation; CVA, canonical variates analysis; DFA, discriminant function analysis; EPMA, electron probe microanalysis; FMAZ, Faroe Marine Ash Zone; HFSE, high field strength elements; INTAV, International Focus Group (IFG) on Tephrochronology and Volcanism; IS, internal standard; LA-ICP-MS, laser ablation inductively coupled plasma-mass spectrometry; LLQ, lower limit of quantitation; MANOVA, multivariate analysis of variance; μ-XRF, micro-X-ray fluorescence; MTT, Middle Toba Tuff; OTT, Oldest Toba Tuff; PAM, partitioning around medoids; PC, principal component; PCA, principal components analysis; REEs, rare earth elements; SC, similarity coefficient; SEM, scanning electron microscope; SN-ICP-MS, solution nebulisation inductively coupled plasma-mass spectrometry; SVM, support vector machines; YTT, Youngest Toba Tuff; XRF, X-ray fluorescence.

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http://dx.doi.org/10.1016/j.quascirev.2017.08.003

viewpoints to be developed and help quantify the degree of uncertainty in establishing correlations. In common with other scientific hypothesis testing, it is easier to infer using such analysis that two or more tephras are different rather than the same. Adding stratigraphic, chronological, spatial, or palaeoenvironmental data (i.e. multiple criteria) is usually necessary and allows for more robust correlations to be made. A two-stage approach is useful, the first focussed on differences in the mean composition of samples, or their range, which can be visualised graphically via scatterplot matrices or bivariate plots coupled with the use of statistical tools such as distance measures, similarity coefficients, hierarchical cluster analysis (informed by distance measures or similarity or cophenetic coefficients), and principal components analysis (PCA). Some statistical methods (cluster analysis, discriminant analysis) are referred to as 'machine learning' in the computing literature. The second stage examines sample variance and the degree of compositional similarity so that sample equivalence or otherwise can be established on a statistical basis. This stage may involve discriminant function analysis (DFA), support vector machines (SVMs), canonical variates analysis (CVA), and ANOVA or MANOVA (or its two-sample special case, the Hotelling two-sample T^2 test). Randomization tests can be used where distributional assumptions such as multivariate normality underlying parametric tests are doubtful.

Compositional data may be transformed and scaled before being subjected to multivariate statistical procedures including calculation of distance matrices, hierarchical cluster analysis, and PCA. Such transformations may make the assumption of multivariate normality more appropriate. A sequential procedure using Mahalanobis distance and the Hotelling two-sample T^2 test is illustrated using glass major element data from trachytic to phonolitic Kenyan tephras. All these methods require a broad range of high-quality compositional data which can be used to compare 'unknowns' with reference (training) sets that are sufficiently complete to account for all possible correlatives, including tephras with heterogeneous glasses that contain multiple compositional groups. Currently, incomplete databases are tending to limit correlation efficacy. The development of an open, online global database to facilitate progress towards integrated, high-quality tephrostratigraphic frameworks for different regions is encouraged.

1. Introduction

1.1. Tephra and cryptotephra deposits and their componentry

Tephras are the unconsolidated, pyroclastic or fragmental products of explosive volcanic eruptions (Greek *tephra*, 'ash' or 'ashes') (Thorarinsson, 1981; Lowe, 2011). Erupting pyroclasts propelled through the air, together with volcanic gases, typically comprise three main components: (*i*) volcanic glass (including glass shards, pumice, and scoriae); (*ii*) crystalline mineral phases (hereafter crystals); and (*iii*) lithics or rock fragments. *Volcanic glass*, a non-crystalline phase, occurs in multiple morphologies including individual bubble-wall (cuspate) or platy glass shards, pumiceous or 'inflated' shards, and pumice or scoria clasts, which all originate from the rapid quenching of molten magma during eruption (Fig. 1). The degree of ordering and linkage of SiO_4^{4-} tetrahedra (so-called 'polymerisation') within these glasses is dependent on composition, and reflects the structure of the magma from which the glass formed. Basaltic magmas are less polymerised than rhyolitic magmas, and are thus less viscous and erupt more effusively. The space between the partly-linked SiO_4^{4-} tetrahedra in the melt is occupied by cations such as Na, K, Mg, Ca, and Fe, which act to depolymerise the melt. Glass may also occur as coatings or rims on crystals (selvedges). Pumice and scoria clasts consist mainly of glass with vesicles (voids) formed by expanding gases during eruption and various quantities of crystals or crystal fragments (loose or as phenocrysts) and occasionally lithic fragments. Pumice is most commonly silicic and pale-coloured (although dark-coloured basaltic pumice also occurs) and has a low density, whereas scoriae (or 'cinders') are mafic and dark-coloured, typically basaltic to andesitic, and have a greater density (Fisher and Schminke, 1984). *Crystals* and crystal fragments are mainly formed in the magma prior to eruption (Jerram and Martin, 2008). *Lithic fragments* are pieces of pre-existing rock that became incorporated into the tephra during eruption, transport, or deposition (Fisher and Schminke, 1984; Sarna-Wojcicki, 2000). Volcanic glass, pumice/scoria, and most crystals (including tiny crystals, i.e. microcrysts/microlites or microphenocrysts) within glass are juvenile or co-magmatic constituents of the tephra (i.e. formed from magma involved in the eruption), and provide the materials for tephra characterization using physical properties and compositional analyses. Lithic fragments (xenoliths) may be related (cognate xenoliths, or autoliths) or unrelated to contemporaneous magmatic activity. Similarly, crystalline material may be physically removed from older rocks surrounding the magma chamber or vent (becoming xenocrysts), it may be 'reincorporated' from earlier cumulates in the current magmatic cycle (antecrysts, e.g. zircon, *sensu* Jerram and Martin, 2008), or it may be a restite phase from assimilation of unrelated, older country rock. In some cases material, termed 'detrital' (Sarna-Wojcicki, 2000), may be entrained from clastic sources during transport and emplacement of the tephra deposit.

The proportions of these various components (glass, pumice/scoria, crystals, lithics) differ widely according to eruption composition and style, proximity to vent, atmospheric conditions, and other factors (Fisher and Schminke, 1984; Alloway et al., 2013; Edmonds and Wallace, 2017). Large-magnitude, very explosive, and voluminous silicic eruptions with dacitic to rhyolitic bulk compositions and dacitic (~63–69 wt % SiO_2) to rhyolitic (>69 wt % SiO_2) glass tend to generate extensively dispersed tephras that persist as relatively thick layers of ash over large distances (e.g. Froggatt et al., 1986; Machida, 2010). Basaltic tephras, much less siliceous (<52 wt % SiO_2), derive from typically lesser-magnitude eruptions and lower eruption columns (but with notable exceptions, e.g. Laki and Grimsvötn eruptions 1783–1785: Thordarson and Self, 1993; Tarawera eruption 1886: Walker et al., 1984). The bulk of associated basaltic tephras are mainly locally dispersed but many finer particles of ash are now