Dating peat profiles using tephra: stratigraphy, geochemistry and chronology

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SUMMARY

In this article we provide a brief overview of the protocols for dating peat profiles using tephrochronology. A standardised methodology for the detection, extraction and analysis of tephras is presented and the relevant problems and limitations are discussed.

KEY WORDS: cryptotephra, tephrochronology, volcanic ash layers.

1. INTRODUCTION

Tephrochronology (dating using volcanic ash layers) is a particularly useful tool for developing robust chronologies from peat sequences (e.g. Langdon & Barber 2005) and for examining inter-site records across specific *isochrons* or 'snapshots in time', allowing the spatial synchroneity of environmental changes to be scrutinised (Hall *et al.* 1994, Hall 2003, Langdon & Barber 2004). Tephrochronology may also prove helpful during periods when the chronological precision of ^{14}C is limited (Plunkett *et al.* 2004, Swindles *et al.* 2007).

Tephra layers are sometimes visible to the naked eye, for example in Iceland, New Zealand and Kamchatka (Braitseva *et al.* 1997, Larsen *et al.* 1999, Lowe *et al.* 2000), but invisible (and often microscopic) *cryptotephra* layers (*sensu* Lowe & Hunt 2001) have been found in many more areas of the world at a distance from volcanic sources (e.g. Persson 1971, Dugmore 1989, Dugmore *et al.* 1995, Hall & Pilcher 2002, van den Bogaard *et al.* 2002, Zillén *et al.* 2002, Boygle 2004, Chambers *et al.* 2004, Pilcher *et al.* 2005, Wastegård 2005, Gehrels *et al.* 2006, Hang *et al.* 2006, Payne *et al.* 2008). Some historic tephras can be assigned a known calendar date such as the eruptions of Hekla in Iceland in 1947, 1510 and 1104 (*cf.* Swindles *et al.* 2008). The ages of other tephras have been constrained through high-precision radiocarbon techniques including wiggle-match dating of the deposits in which they are found (Pilcher *et al.* 1995, Plunkett *et al.* 2004, Barber *et al.* 2008, Wastegård *et al.* 2008) and Bayesian age modelling approaches (Blockley *et al.* 2008). Tephro-chronology is an extremely powerful tool for constraining past environmental events registered in peat sequences. However, this can be achieved only if accurate, quantitative distributional and geochemical data are obtained from the tephra layer in question. The chemical stability of tephras in peat has been recognised and repeatedly demonstrated by the successful correspondence of distal tephra geochemistries with material from source eruptions (e.g. Dugmore *et al.* 1992, Wastegård 2005).

This paper describes the analytical procedures for dating peat profiles using tephrochronology. Tephras are firstly detected in peat ashes using light microscopy. Where tephra layers are encountered, an acid digestion technique is used to extract the shards from the peat matrix and the tephras are then mounted on slides for electron probe microanalysis. Identification of tephras is carried out through comparisons of geochemical data with results from previous studies.

2. FINDING TEPHRA LAYERS IN PEAT PROFILES

2.1 Detecting and isolating tephras

Several non-destructive approaches may be used as a first stage in the detection of microscopic tephra layers in peat profiles, such as magnetic susceptibility, spectrophotometry and X-ray fluorescence (*cf.* Gehrels *et al.* 2008). The methods for analysis of tephra in peats that we present here are adapted from Dugmore *et al.* (1992) and Hall & Pilcher (2002). For an initial, rapid assessment of the occurrence of tephra, peat sequences can be subdivided into contiguous 5 cm-long samples along the length of the core or monolith, then the samples placed into crucibles and burnt in a muffle furnace at 600°C for six hours (Hall & Pilcher 2002). The resulting ashes are suspended in 10% HCl for up to 24 hours, and then washed with deionised water to

remove all traces of acid. The aqueous samples are centrifuged at 3,000 r.p.m. for 10 minutes (no brake set) to concentrate the tephra at the bottoms of the tubes. For samples containing a significant proportion of minerogenic material, such as those from minerotrophic peats, sieving at 10 µm in an ultrasonic bath for 5–10 minutes can be carried out, although there is a risk that this may damage some fine glass shards. This stage is not usually needed for ombrotrophic peats. Samples rich in biogenic silica (e.g. diatoms, phytoliths) can be treated with hot 5% NaOH or KOH (Rose *et al.* 1996) but treatment should be limited to one hour to prevent chemical alteration of the volcanic glass.

2.2 Slide preparation for petrography

Samples are added in drops (using a Pasteur pipette) to a glass microscope slide on a hotplate at a low heat setting, and left until all the water evaporates. A drop of Histomount (or similar) is added to the slide and a coverslip applied. The slides should be left to dry and must be stored horizontally until the mounting medium has hardened.

2.3 Petrography

Slides are scanned using a transmitted light microscope at a total magnification of 100–400x. Plane-polarised light may be used to differentiate between tephra and other minerogenic material (Hall & Pilcher 2002, Chambers *et al.* 2004). Tephra can be recognised on the basis of its isotropism, colour, shape and vesicularity (Heiken 1974, Westgate & Gorton 1981). Individual shards should be counted in transects and their colour and morphological characteristics may be noted (Figure 1).

A quantitative estimation of the mineral *vs*. the glass shard content can be achieved by counting a minimum of 300 grains using the method of Van Harten (1965). Glass shards can be described in terms of their size and shape, but also the size and shape of their gas inclusions (Heiken 1972, 1974; Schmid 1981). Thin sections of the dense mineral residue can also be analysed to give a better idea of the relative proportions of the principal minerals found in the tephra. The minerals present in thin section can provide an insight into the formation of the tephra in question (type of magma, geotectonic context) (*cf.* MacKenzie & Guilford 1980).

Specific minerals may be helpful in distinguishing volcanic centres when glass shards are absent or in such a low concentration that they do not allow for a subsequent chemical investigation. For example, titanite is a typical

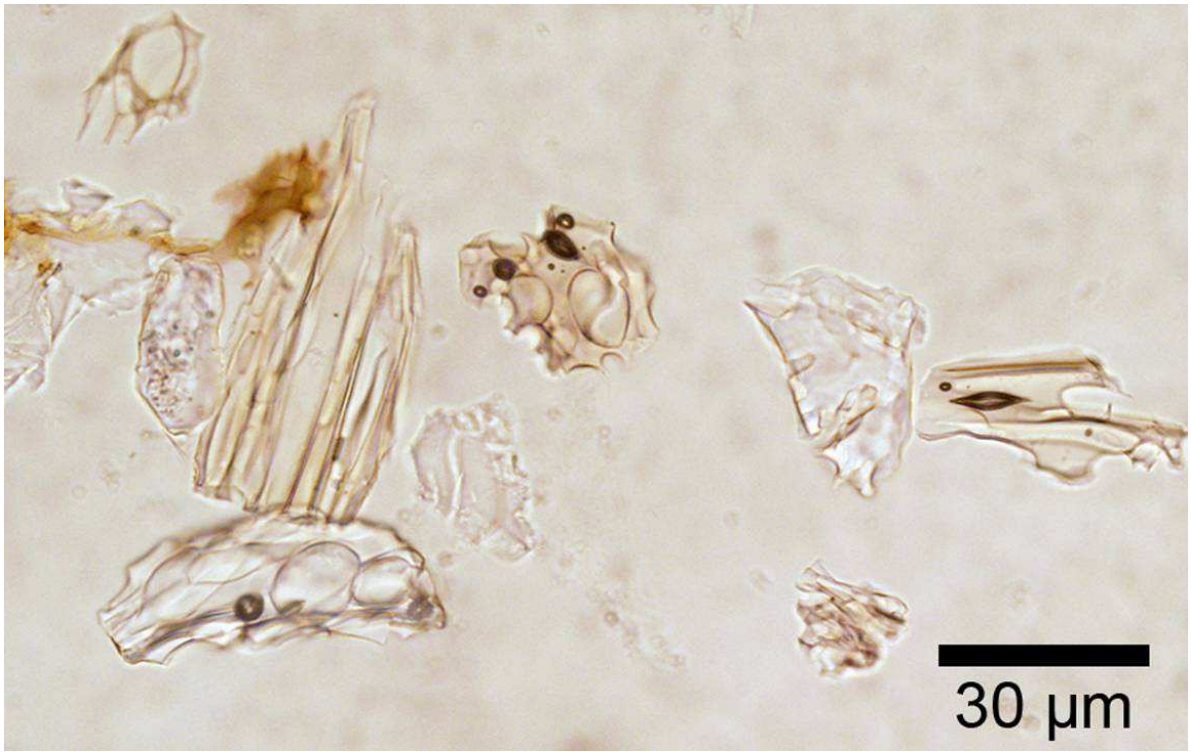

Figure 1. Photograph showing tephra shards with characteristic fluted and vesicular morphologies. The shards are from a currently unidentified tephra layer from the Shetland Isles, UK.

heavy mineral from the Laacher See tephra (van den Bogaard & Schmincke 1985), and has been used to identify the event when glass shards were absent from sediments (Juvigné 1991).

2.4 Quantitative analysis

Following the initial detection of tephra at coarse resolution, the above procedures should be carried out using contiguous samples of peat in the section(s) of the core where shard concentrations have been identified to develop a tephrostratigraphy, i.e. a stratigraphic outline of tephra horizons, for the profile. Peat volume can be measured by calibrated syringe or a similar procedure. This stage can be combined with loss-on-ignition analysis if desired. Tablets of *Lycopodium clavatum* spores (*cf.* Stockmarr 1971) (or similar) may be added to the ashes during suspension in HCl for semi-quantitative determination of tephra shard concentration (*cf.* Gehrels *et al.* 2006). If this procedure is not used, then each individual tephra shard per 1 cm^3 sample must be counted to determine concentration accurately. Tephra concentration can be presented as number of shards per cm^3 (Figure 2).

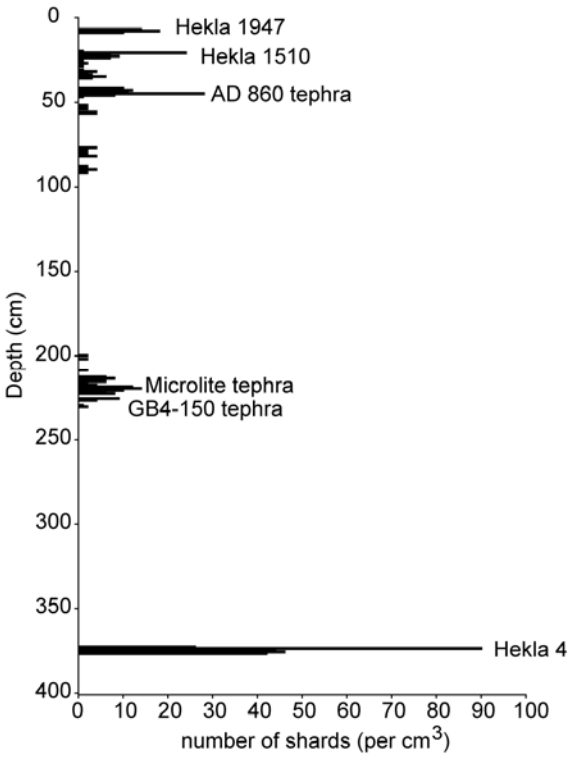

Figure 2. Tephrostratigraphy of Dead Island Bog (Northern Ireland), from the Hekla 4 isochron (Larsen & Thorarinsson 1977) which has been ^{14}C wiggle-match dated to 2339–2279 cal. BC (Pilcher *et al.* 1995) to the historically dated Hekla AD 1947 tephra (Thorarinsson 1967) (after Swindles *et al*. 2010). Tephra counts are expressed as number of shards cm^{-3}.

3. ANALYSIS OF TEPHRA SHARDS

3.1 Preparation for chemical analyses

Tephra extracted by the combustion method cannot be used for geochemical analysis because the procedure alters the chemistry of the glass, so an acid digestion technique is used (Hall & Pilcher 2002). A sample of at least 1–3 cm^3 of peat, representing the horizon of maximum tephra concentration, is placed in a beaker on a hotplate (medium heat) inside a fume cupboard, then up to 200 ml of concentrated H_2SO_4 is added until water is driven off. A small amount of concentrated HNO_3 can then be added; the solution reacts vigorously and dark fumes of NO_2 are given off. Further small amounts of HNO_3 are added until the reaction stops. When digestion of the peat is complete, the end product should be a straw yellow coloured solution. The solution should be left to cool and then diluted in one litre of water before fine-sieving (e.g. 10 µm). The sample must be washed with copious amounts of deionised water (2–5 L) to ensure that all traces of acid are removed. The sample can then be pipetted into a centrifuge tube and centrifuged at 3,000 r.p.m. for ten minutes (no brake set) to concentrate the tephra, and the supernatant is decanted. In addition we recommend that, if organic or waxy deposits remain, the digestion should be repeated (Hall & Pilcher 2002). Hot dilute alkali treatment may also be required if the sample is rich in biogenic silica. The size of the peat sample should be chosen to ensure that enough glass shards are concentrated to obtain sufficient analyses.

3.2 Slide preparation for geochemical analysis

As each electron microprobe laboratory may have specific requirements regarding the way in which samples for analysis are mounted, it is worth contacting the system administrator in advance of slide preparation. Typically, the surface of a glass slide is coarsely ground using 600 µm alumina grit or carborundum paper to improve sample cohesion (note that the slide must be of suitable dimensions to fit within the instrument that will be used to analyse the tephra geochemistry). The slide should be labelled using a diamond scriber on the un-ground side and a pencil on the ground side. Small square cells and labels for the tephra samples can also be drawn (using a pencil) on the ground side depending

on sample size (up to six per slide). The samples are pipetted onto their individual cells and the water evaporated on a hotplate at a low heat setting. One drop of epoxy resin (e.g. Araldite or equivalent, following the laboratory instructions) is applied over the dry specimens (ensuring a clean spatula is used for each sample) and left to dry on a hotplate. The slide should be ground on alumina grit or carborundum paper using progressively finer grades to leave a layer of resin 30–50 μm thick. Grinding should continue until tephra shards are nearly exposed (which should be checked regularly using a reflected light microscope to prevent over-exposure and loss of shards). The slide should then be washed in deionised water in an ultrasonic bath and polished using fine grade abrasive paper or polishing paste (alumina or diamond) at 6 μm, 3 μm and 1 μm (washing in an ultrasonic tank before each stage) to achieve a fine polish on the slide surface. The slide should then be meticulously washed in deionised water and carbon coated under a vacuum following the procedures of the electron probe laboratory. Instead of the glass slide method, some laboratories use brass or epoxy resin disks in which the tephra is mounted before being ground and polished.

3.3 Geochemical analysis

It is crucial that geochemical analysis of tephra follows protocols that provide consistently reliable data and researchers should be aware that inter-laboratory discrepancies have been noted (Westgate & Gorton 1981, Hunt & Hill 1993, 1996; Potts *et al.* 2002, Coulter *et al.* 2010). Such discrepancies are currently being examined in the Intercomparison of Tephrochronology Laboratories project, conducted by the International focus group on tephrochronology and volcanism (INTAV, http://home.wlu.edu/~kuehns/INTAV/interlab.html). Tephra geochemistry should be determined using wavelength-dispersive electron probe microanalysis. Although settings of the instrument may vary between laboratories, a defocused beam of 5–10 μm should be used and Na should be counted first to guard against migration (Hunt & Hill 1993, 2001). Algorithms such as ZAF, PAP or X-PHI should be used to correct for absorbance and fluorescence effects (Sweatman & Long 1969, Pouchou & Pichoir 1991, Merlet 1994). Primary and secondary standards such as pure synthetic oxides, simple silicates, andradite garnet, standard basalts and Lipari obsidian should be used for calibration and to check the accuracy of the analyses before and during analysis runs (Hunt *et al.* 1998). The main species that should be obtained are SiO_2, TiO_2, Al_2O_3, K_2O, CaO, $FeO_{(total)}$, Na_2O, MgO and MnO. Other species, such as F and P_2O_5 can be analysed if possible. Systems with linked energy dispersive systems (EDS) may be of particular use to help pinpoint very sparse tephra shards in thin section. The tephra geochemistry can be compared with previous analyses from online databases (e.g. Tephrabase, http://www.tephrabase.org/) or published works, and presented in biplots and/or ternary diagrams (Figure 3). Principal Components Analysis (PCA) may also be useful for tephra discrimination in certain circumstances (Pollard *et al.* 2006). However, it should be interpreted alongside the more traditional bivariate or trivariate major oxide diagrams (Pearce *et al.* 2008).

It is common practice to omit data with less than 95% of the analytical total, and this may be appropriate in many cases (Hunt & Hill 1993). However, it is not always possible to obtain totals >95%, especially from tephras containing a large amount of water (either primary magmatic or through post-depositional hydration of the glass) (Pearce *et al.* 2008). The number of analyses needed for the identification of the tephra is variable and dependent on the discretion of the researcher. It is often said that twenty or more is a suitable number, but this may not be attainable with very sparse layers. Sometimes distinct tephras can be identified with five (or even fewer) analyses, especially if other dating evidence is available. However, researchers should strive to get as many analyses as possible from a tephra layer. Normalisation of tephra geochemical data is common practice in the Southern Hemisphere and in North and South America, as this can remove the variable effects of hydration in different samples (e.g. Pearce *et al.* 2008). This practice is probably best avoided, however, as it masks the quality of the data (Pollard *et al.* 2006) and does not allow other researchers access to the raw data.

3.4 Density separation

In peats containing a large amount of minerogenic material, density separation procedures may be needed to extract and concentrate the shards (*cf.* Turney 1998). We have achieved good results using LST Fastfloat (http://www.polytungstate.co.uk/), which is a solution of low toxicity sodium heteropolytungstates in water. Densities of 2.3–2.5 g cm^{-3} are commonly used in tephrochronology, which can be checked using a hydrometer (Turney 1998). Bromoform (density 2.8 g cm^{-3}) can also be used for the separation of glass shards. This method is relatively fast and allows the separation of minerals with grain sizes below 300 μm, which is typical of tephra layers (Juvigné 1979). However, bromoform should be used with caution as it is toxic to humans and the environment.

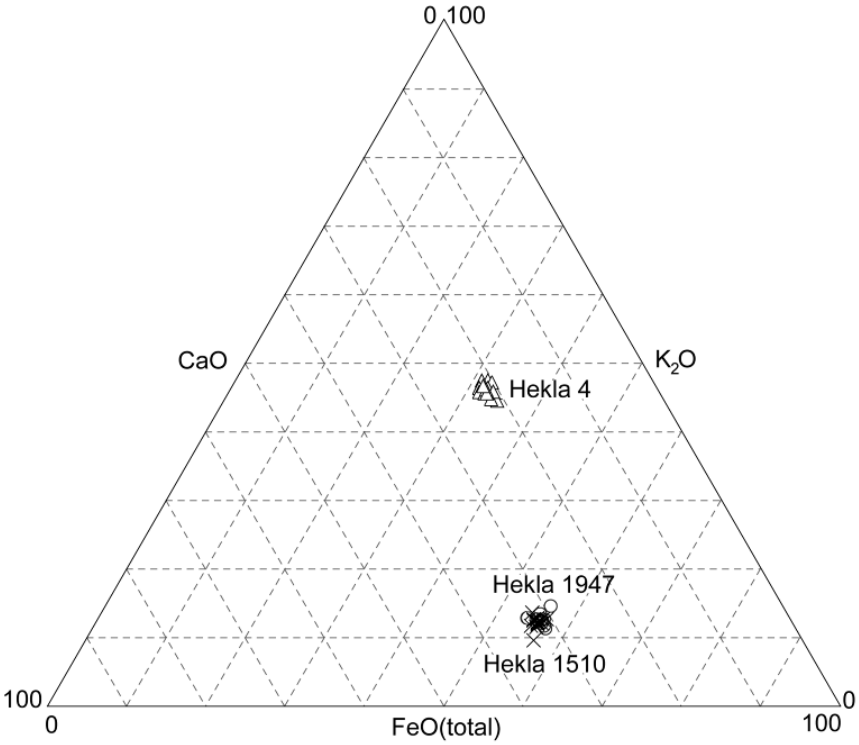

Figure 3. Ternary plot showing $FeO_{(total)}$, CaO and K_2O for the Hekla 1947, 1510 and Hekla 4 tephra layers encountered in two peatlands in the North of Ireland (after Swindles *et al*. 2010). It is evident that Hekla 1947 (circles) and 1510 (crosses) are indistinguishable on the grounds of their major element oxide geochemistry, whereas Hekla 4 (triangles) can be easily distinguished from these layers.

4. POTENTIAL AND LIMITATIONS

Although a standard protocol for tephrochronology is presented here, there is a growing body of literature presenting experimental methods for the detection, extraction, analysis and dating of tephra (e.g. Caseldine *et al.* 1999, Buck *et al.* 2003, Blockley *et al.* 2005, Payne & Blackford 2005, Auclair *et al.* 2007, Gehrels *et al.* 2008, De Vleeschouwer *et al.* 2008). Tephrochronology is firmly established as a useful chronological tool for peat-based studies, but a number of problems and limitations are apparent. One limitation is that tephra layers are not found everywhere in the world, or are sometimes characterised by very low shard concentrations, making identification difficult. A further problem is that tephra fallout is often not spatially coherent, leading to a distinct 'patchiness' of tephra layer distribution (Dugmore *et al.* 1996). Modelling approaches have illustrated that climate variability is an important factor in the atmospheric transport of Icelandic tephra in the subpolar North Atlantic (Lacasse 2001). 'Taphonomic' problems may also occur in peats as the tephra may have been deposited on an uneven surface and re-working can occur (Holmes 1998, Payne *et al.* 2005, Payne & Gehrels 2010). In volcanic regions it is often difficult to interpret the abundance of inter-mixed tephra layers. Also, the zone of highest concentration of glass may not necessarily represent the primary ash-fall layer but instead reflect the erosion of exposures or surfaces containing tephra adjacent to a peat bog.

Some studies have suggested that there is chemical alteration of tephra shards in the post-depositional environment due to cationic leaching from the matrix, or complete destruction of the silica network (e.g. Pollard *et al.* 2003). From their experimental work, Wolff-Boenish *et al.* (2004a, 2004b) proposed a relationship between the lifetime of 1 mm-radius natural glass spheres and their silica content at 25°C and pH 4. The dissolution rate depends mainly on the silica content of the tephras: rhyolitic tephras are generally more stable than basaltic (Oelkers 2001, Pollard *et al.* 2003, Wolff-Boenish *et al.* 2004a, 2004b). The dissolution processes are slow and a 1 mm thick layer of glass can take up to 4,000 years to dissolve under these

conditions (Wolff-Boenish *et al.* 2004a, 2004b). On the other hand, Hodder *et al.* (1991) reported how glass and ferromagnesian minerals in very acidic anoxic peat bogs could be partly or totally dissolved, sometimes leading to complete dissolution of certain minerals (e.g. biotite) in relatively short time periods.

These different observations illustrate that a systematic and thorough analysis of sediments, tephra and related alteration products may be needed when studying distal tephras in acidic peatland environments. Nevertheless, the successful linkage of distal tephras to source material in peatlands across Europe (e.g. Hall & Pilcher 2002, van den Bogaard *et al*. 2002, Wastegård 2005) and North America (e.g. Payne *et al*. 2008) demonstrates that chemical alteration is probably not a critical problem when working with peat profiles.

Several studies have also provided insights into the effects of bacterial activities on glass dissolution (e.g. Thorseth *et al.* 1995, Staudigel *et al.* 1998, Brehm *et al.* 2004). Experimentally, Thorseth *et al.* (1995) found that the dissolution rate can increase by a factor of ten after six months of glass alteration due to the formation of new bacterial communities. Birkefeld *et al.* (2006) also emphasised that dissolution rates are greater in the field than in the laboratory, due to extensive biological influence from fungi, bacteria and plant roots. However, although bacterial action could induce a rapid destruction of the glass walls, bacteria will also form and/or adsorb amorphous particles (from organic or mineral composition) at the grain surface, developing an alteration film that could decrease or stop the alteration of tephra. Such protective barrier films have been studied in the case of basaltic glass alteration and the use of this material as radioactive stockpile (e.g. Techer *et al.* 2001).

There may also be problems in discriminating tephra layers using major element geochemistry. For example, the historical Hekla 1510 and 1947 tephras cannot be separated on the basis of their major element geochemistry, and other stratigraphic or chronological information is needed for their reliable identification (Swindles & Roe 2006). Trace and rare earth elemental composition of glass shards using laser ablation ICP-MS or ion probe analysis may be needed to discriminate between such tephras (Pearce *et al.* 2007, Coulter *et al.* 2010).

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