How reliable is µXRF core scanning at detecting tephra layers in sedimentary records? A case study using the Lake Suigetsu archive (central Japan)

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ABSTRACT: Here, we evaluate the ability of micro X-ray fluorescence (µXRF) core scanning to identify non-visible volcanic ash (cryptotephra) layers in sedimentary records. Its suitability is assessed using the annually resolved lacustrine sediments of Lake Suigetsu (Japan) for which there is high-resolution ITRAX µXRF core scanning data, and a detailed cryptotephrostratigraphy (formerly established via density separation techniques). The studied core sections contain 10 visible and 30 cryptotephra markers that span a range of glass concentrations (from 1000 to >20 000 shards per gram of dried sediment) and compositions (basalts, trachyandesites, phonolites, trachytes and rhyolites), thus providing an ideal case study. The ITRAX core scanner produced recognisable µXRF elemental responses for the visible ash layers, including those just 1 mm thick. However, just 10% of the cryptotephra layers could be unequivocally identified. Although this study demonstrates that µXRF core scanning should not be used as an independent method within a similar geological setting, we show it can provide a powerful tool alongside traditional techniques. Where detected, µXRF profiles can verify and refine cryptotephra positions (here to a sub-millimetre precision), and help establish reworking signatures. These insights create possibilities for ultra-precise synchronisation of records, improved chronological modelling and help generate more complete eruption histories.

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Introduction

Distal deposits of volcanic ash (tephra) preserved in sedimentary sequences (lacustrine, peat and marine) are excellent chronological markers for dating and correlating palaeoenvironmental and archaeological records (Davies et al., 2012; Smith et al., 2013; Blockley et al., 2014; Lane et al., 2014; Lowe et al., 2015; Lane et al., 2017) and thus are highly sought after within Quaternary studies. In addition, these layers provide an important resource for volcanologists investigating the frequency, eruptive magnitude and dispersal of past explosive events (e.g. Costa et al., 2012; Schindlbeck et al., 2018; Di Roberto et al., 2018; Albert et al., 2018, 2019; Buckland et al., 2020; McLean et al., 2020a). Such is the value of these markers, it is increasingly worthwhile to search for fine ash layers, which due to their low or diluted glass concentrations are only microscopically preserved (i.e. cryptotephra layers) in sedimentary profiles (Pyne-O’Donnell et al., 2012; Barton et al., 2015, 2021; Davies, 2015; Wulf et al., 2018; Chen et al., 2016, 2019; Timms et al., 2019; McLean et al., 2018; Panaretos et al., 2021). Detailed cryptotephra investigations have meant that coeval isochrons can be identified over wide geographical regions (over thousands of kilometres; Lane et al., 2011; Jensen et al., 2014; Ponomareva et al., 2015; McLean et al., 2016; van der Bilt et al., 2017; Cook et al., 2018; Kearney et al., 2018; Jones et al., 2020), and permit the construction of more complete volcanic records, allowing the integration of lower magnitude events and/or eruptions from more distal sources (e.g. Albert et al., 2018). Indeed, in some instances cryptotephra layers may prove to be the only geological evidence of some eruption events (McLean et al., 2020b).

Conventional density separation methods for the identification and characterisation of cryptotephra layers are notoriously time-consuming (e.g. >30 h to process 1 m of sediment), highly iterative, and can require significant amounts of valuable core material. As a result, it is often not feasible to undertake detailed cryptotephra investigations over long stratigraphic intervals. Even for benchmark Quaternary palaeoclimate records, and those providing the most robust...
...many sequences have only been assessed in part, or at low resolutions over certain time periods (e.g. the Greenland ice cores). The most reliable and widely utilised method to identify low-concentration ash layers in marine and lacustrine records is achieved by separating the volcanic glass grains from the host sediments. This is typically accomplished using density separation techniques that are able to extract the volcanic glass shards from the lighter (typically organic) and denser (minerogenic) components, and allow for the primary positioning of the cryptotephras, i.e. the eruption event. It is possible to detect the positioning of these markers due to the contrast between the geochemical and mineralogical composition of the ash and the matrix/host sediments. µXRF core scanning is well suited to the analysis of long sedimentary cores, as the technique is non-destructive, can be operated at relatively high speed, high spatial resolutions (up to a 20 µm stepping interval on some systems) and requires almost no sample preparation. It is therefore possible to generate a comprehensive time series of geological data and detect changes in particular single element profiles or profiles of element ratios. The composition of ash (glass and minerals with decipherable amounts of Si, K, Ca, Ti, Fe, Rb, Sr and Zr) are therefore likely to be reflected in the core scanning data and potentially show the precise position of high concentrations of ash and cryptotephras. Previous studies have shown that the elemental data generated for tephra layers using µXRF core scanning are not, however, comparable to individual shard analysis by electron microprobe (e.g. Kylander et al., 2012; Petti et al., 2020). Significant questions still surround the ability of µXRF core scanning to detect both fine ash (i.e. <1 mm in thickness) and cryptotephras preserved in high-resolution sedimentary sequences, although the technique has been combined in a range of multiproxy studies to date (e.g. De Vleeschouwer et al., 2008; Vogel et al., 2010; Wulf et al., 2013; Zawalna-Geer et al., 2016; Jouannic et al., 2022). Earlier work has shown that, as for visible ash deposits, detection may strongly depend on the contrast of the host sediment and the glass shards, in addition to the concentration of the grains (Moreno et al., 2007; Langdon et al., 2011: Kylander et al., 2012; Cassidy et al., 2014; McCanta et al., 2015). As a result, its usefulness is thought to be more variable, depending on the archive and neighbouring volcanic region. Most commonly, useful elements for the detection of volcanic ash are typically K, Ca, Fe and Zr, with element ratios such as Ca/Ti and K/Ti being able to minimise the overlap of environmental signals also captured in the sediment. Experimental approaches have shown that the grain size can also play an important role when using techniques such as backscattered electron imaging (see Davies, 2015). Further studies are required, particularly in different geological and volcanic settings, to determine the percentage of (crypto)tephra layers that remain undetected when using µXRF core scanning as a first-order means of discrimination. Further work is required to quantify the success identification rate, potential thresholds for detection (i.e. glass compositions, grain size, concentrations) and provide an understanding of which elements and element ratios are useful for different volcanic centres/compositions. Moreover, it is also possible that µXRF core scanning could help to alleviate other longstanding problems faced by tephrachronologists when interpreting low concentrations of glass (e.g. discriminating primary/secondary peaks, identifying their precise positioning, and evaluating sediments with high background concentrations of volcanic glass). The applications of µXRF core scanning of cryptotephras alongside traditional methods are currently untested. If verified, this technique would have significant potential for the identification of sampling targets (i.e. sediments most likely to contain cryptotephras layers), speed up the processing time of searching for specific cryptotephras layers, and also increase the application of cryptotephras investigations.

Further work has shown that, as for visible ash deposits, detection may largely depend on the contrast of the host sediment and the glass shards, in addition to the concentration of the grains (Moreno et al., 2007; Langdon et al., 2011: Kylander et al., 2012; Cassidy et al., 2014; McCanta et al., 2015). As a result, its usefulness is thought to be more variable, depending on the
sediments (50 to 30 ka; McLean et al., 2020b) of Lake Suigetsu. These 40 tephra originate from 16 different volcanic centres across east Asia (e.g., Japan, South Korea, North Korea, China) and therefore incorporate a range of glass compositions and concentrations suitable for assessment.

2. Ultra-high µXRF elemental data (60 µm step-width, 100 µm vertical beam-width; see Section High-resolution µXRF elemental scanning) have been obtained from the Lake Suigetsu sediments (from the core top to 45 m composite depth (CD); Marshall et al., 2012; Schlolaut et al., 2012) providing detailed quantitative profiling across all identified cryptotephra and visible tephra layers.

3. A comprehensive analysis of event layers (e.g., those recording evidence of past flood and earthquake events) has been performed using thin-section microscopy and the µXRF elemental data (Schlolaut et al., 2012, 2014, 2018). This work can be utilised and applied to investigate the characteristics of high-energy events that are known to have remobilised volcanic glass shards in the catchment and could skew cryptotephra assessments.

4. Thin sections of the sediments were previously prepared for microanalytical and varve analysis (Schlolaut et al., 2014) and can be used here to further investigate the stratigraphic positioning of cryptotephra within the varved sediments.

This study is the first to investigate high-resolution µXRF elemental responses (e.g., 60 µm) across a long stratigraphic sequence (>30 m with varved and non-varved sediments), and for an abundance of glass shard concentrations and compositions (i.e., 40 tephra layers erupted from at least 16 different volcanic centres across east Asia).

Study site and sediments

Lake Suigetsu, catchment and coring campaigns

Lake Suigetsu (35°35′N 135°53′E, 0 m above sea level) is a small tectonic basin located close to the Sea of Japan, and situated in Fukui Prefecture (Fig. 1). The lake is 34 m deep and covers an area of 4.3 km² with a diameter of ca. 2 km. It is part of a tectonic lake system (the Mikata Five Lakes) with a small catchment area, vegetated by warm mixed forest and is surrounded by a ring of Palaeozoic hills (maximum elevation 400 m) (Nakagawa et al., 2005). The main tributary feeding freshwater to the five Mikata lakes is the River Hasu (ca. 10 km in length), which enters on the southeastern side of Lake Mikata and flows through the Seto Channel into Lake Suigetsu. This channel is particularly shallow (ca. 2 m in depth), meaning that during high-energy hydrological events (such as floods), Lake Suigetsu receives only a small proportion of detrital material from the Hasu River catchment (Nakagawa et al., 2012).

The geology around the lake is dominated by a large granite pluton to the east and southeast. To the south mudstone dominates, but sandstone, chert, limestone, basalt and dolerite also occur. There is sandstone at the northeast coast of the lake, while at the north and west coasts basalt, dolerite and chert are dominant (Schlolaut et al., 2014). Schlolaut et al.
produced by flood events (362 of the 369) (Schlolaut et al., 2014). Flood events could be distinguished from other major depositional events, such as landslides or subaqueous slope failures. In particular, the clastic event layers could be characterised in the SG06 profile using elements Ti, K, Ca and Si fluctuations. Indeed, Ti is a well-established tracer for terrigenous input in lacustrine sequences (Yarincik and Murray, 2000). Peaks in K concentrations often indicate the presence of clays and/or K-feldspar, and Ca likely derives from detrital carbonates or plagioclase. The Si signature of the event layers is not as distinct as that of the other elements since the sediment is rich in diatoms and hence generally rich in Si. In general, Fe and Mn are also considered as two elements that show changes in the hydrology and sedimentation of the lake (Katsuta et al., 2007; Marshall et al., 2012). From the top down to 3095.9 cm SG06 CD the sediments are usually dominated by autochthonous components, while below (>38 213 cal. yrs BP) they contain a higher proportion of detrital mineral grains. This is evident in the µXRF signals that show a significant drop in Ti and Ca in the upper core sections, as well as a weak drop in K (Schlolaut et al., 2014). It is proposed that the change from a clastic-rich to a clastic-poor facies may be related to change in the inflow point for the Hasu River, potentially shifting the estuary from Lake Suga to Lake Mikaka and ‘turning the filter on’ (Schlolaut et al., 2014).

Lake Suigetsu tephrostratigraphy

The Lake Suigetsu tephrostratigraphy provides the single most comprehensive record of east Asian volcanism established to date. Thirty-two visible ash layers have been identified in the SG06 core (Smith et al., 2011, 2013; McLean et al., 2016; Albert et al., 2018, 2019; Fig. 1), most of which originate from eruptions at calc-alkaline to high-K calc-alkaline arc volcanoes situated southwest of Suigetsu and were dispersed via the prevailing westerly winds. The thickest tephra beds preserved in the Lake Suigetsu sediments are therefore correlated to well-known caldera-forming eruptions (VEI 6–7) of four active or buried volcanoes situated on Kyushu Island (Kikai, Aira, Aso and Aka; see Smith et al., 2013; Albert et al., 2019). Many of the thinnest visible ash layers preserved in the SG06 core possess overlapping yet heterogeneous rhyolitic glass chemistries, and are correlated using their distinctive trace element signature to activity at two of the closest volcanoes, Daisen and Sambe, situated on the southwestern Japan Arc (Albert et al., 2018). Other ash layers originate from alkali-rich intraplate volcanoes Ulleungdo (South Korea) and Changbaishan (North Korea/China border), which have also been very productive throughout the Late Quaternary (McLean et al., 2020a). In general, most of the tephra layers vary in their relative abundances of major, minor and trace elements as shown by the electron microprobe and LA-ICP-MS analyses of the glass shards, although layers from Ulleungdo (U-2, U-3, U-4 and U-Ym) are largely geochemically indistinguishable (McLean et al., 2020a).

Detailed cryptotephra analysis through the Lake Suigetsu sediments has significantly extended the tephrostratigraphy, from 32 to 62 layers and allowed for the integration of tephra isotrons from volcanic sources further afield (Fig. 1; McLean et al., 2018, 2020b). In general, this work revealed four times as many cryptotephra layers relative to the visible layers that were preserved, providing an unprecedented record of eruptions that dispersed ash to the populated regions of central Honshu. Moreover, this work has helped generate more complete eruptive records; for instance, where only one visible ash layer was identified from Aso caldera, this has been supplemented by eight additional cryptotephra layers within the sediments dating between 50 and 30 ka (McLean et al., 2020b). In the investigated sediments, at least one significant cryptotephra
Table 1. Overview of the investigated Lake Suigetsu sediments, the (crypto-)tephrostratigraphy and any ITRAX detection of tephra. Visible ash layers are shaded grey, and the cryptotephra layers that can be positively identified using compositional variations detected using a µXRF core scanner are shaded in green. Changes (above or below the baseline for the sediments) are typically observed in one of the following: Ca/Ti, K and/or Fe

| Tephra Label | SUQD Composite Sampling Depth | Tephra (name, volume) | Glass Shard Morphology | Glass Shard Concentration on (g/dl) | Visible Thickness (cm) | Glass composition | ITRAX detection of tephra? | Elements for detection in Suigetsu sediments | Increase | Decrease | Single elements for detection | Useful element ratios | Position of ITRAX Peak | identification and Geochemical Reference |
|--------------|-------------------------------|-----------------------|-----------------------|-----------------------------------|-----------------------|----------------------|--------------------------|-----------------------------------------------|---------|---------|----------------------------|----------------------|------------------------|-----------------------------------------------|
| LO-098       | TPL, MV, M                   | 1.475                 | Low                    | Rhyolite                          | No, no signal         | Potential peak 304    | K, Ca, Ti, Fe, Zn, Rb (minor) |                                |         |         |                            |                      |                        |                                |
| LO-2021      | 220.5 - 221.4               | Ow, O. M, MV          | 2.985                 | Low                               | Rhyolite              | No, no signal         | Subtle peak at Ca/Ti |                                |         |         |                            |                      |                        |                                |
| SUQD16-0726  | 225.5                         | L, M, Changdoshan     | 0.1                   | High                              | Rhyolite              | No                   | None                     |                                |         |         |                            |                      |                        |                                |
| SUQD16-0529  | 213.5 - 240.1               | G, H., Katsuno       | 0.1                   | Medium                            | Rhyolite              | No                   | None                     |                                |         |         |                            |                      |                        |                                |
| SUQD16-0638  | 422.0 - 430.0               | P, 21, Ungak          | 1.300                 | High                              | Rhyolite              | No                   | None                     |                                |         |         |                            |                      |                        |                                |
| SUQD16-0648  | 418.0 - 409.0               | P, 21, Ungak          | 1.300                 | High                              | Rhyolite              | No                   | None                     |                                |         |         |                            |                      |                        |                                |
| SUQD16-0658  | 587.0                         | Tep, Sambu           | 0.3                   | Medium                            | Rhyolite              | Yes                  | K, Ca, Sr            |                                |         |         |                            |                      |                        |                                |
| SUQD16-0750  | 595.0 - 610.0               | P, 21, Ungak          | 0.3                   | Medium                            | Rhyolite              | No                   | None                     |                                |         |         |                            |                      |                        |                                |
| SUQD16-0751  | 775.0                         | P, 21, Ungak          | 0.3                   | Medium                            | Rhyolite              | Yes                  | K, Ca, Sr            |                                |         |         |                            |                      |                        |                                |
| SUQD16-0803  | 837.0 - 854.0               | P, 21, Ungak          | 0.3                   | Medium                            | Rhyolite              | Yes                  | K, Ca, Sr            |                                |         |         |                            |                      |                        |                                |
| SUQD16-0977  | 997.0                         | P, 21, Ungak          | 0.3                   | Medium                            | Rhyolite              | Yes                  | K, Ca, Sr            |                                |         |         |                            |                      |                        |                                |

References: 1) McLean et al. 2018; 2) McLean et al. 2016; 3) Smith et al. 2013; 4) Albert et al. 2018; 5) McLean et al. 2020a;6) Smith et al. 2011; 7) Mclean et al. 2020b;8) Albert et al. 2019.

The correlation model used for the depth is version 24 August 2009. The exact master core positioning of the ash layers are published in the attached references.

PU = Pumiceous, PL = Platy, C = Cuspate, F = Fluted, V = Vesicular, MV = Microvesicular, MI = Microlite inclusions, G = Green.
layer is detected in each metre of sediment (an event approximately every 500 years), although there are periods that contain very high concentrations of background glass shards, reflecting reworking events, which are likely to mask other important cryptotephra layers (Fig. 1). Critically, detailed density separation work also identified numerous fine visible ash layers (~1 mm in thickness) that were not picked up by visual examinations of the cores, such as the B-Trm Changbaishan ash (McLean et al., 2016). In summary, the tephra layers utilised in the time periods here vary in their glass concentrations (from 1000 to >20 000 shards per gram) and originate from at least 16 different volcanic centres across east Asia (reflected in their geochemical composition) (Table 1).

Materials and methods

Cryptotephra identification

As highlighted, high-resolution density separation techniques were employed throughout the 12 m of Holocene sediments (≤10 ka; McLean et al., 2016, 2018) and more recently the 14 m of annually laminated (varved) sediments dating to between ca. 50 and 30 ka (McLean et al., 2020a, b). The master SG14 core (composite sequence) was contiguously subsampled at a 5 cm resolution avoiding the known high-energy event layers (e.g. flood horizons). If elevated shard concentrations were observed in the ca. 5 cm sample, the sediment was resampled at a 1 cm resolution to determine the precise stratigraphic positioning of the peak. The extracted glass shards were counted via microscopic examination to quantify the number of shards per gram of dried sediment (shards/gram). Glass shards were extracted from samples chosen for geochemical analysis and handpicked from a wellled slide using a micromanipulator (see Lane et al., 2014 for details). These shards were mounted in epoxy resin stubs, which were sectioned and polished to expose a flat surface, and carbon coated for electron microprobe analysis. Major and minor element compositions of individual glass shards were measured using a JEOL-8600 wavelength-dispersive electron microprobe at the Research Laboratory for Archaeology and History of Art, University of Oxford. These geochemical datasets can be found in the supplementary material of the references indicated in Table 1. Identified tephra layers in the Suigetsu sediments are named, and are referred to using their SG06 (correlation model 6 June 2017) or SG14 (correlation model 30 May 2016) core CD(s) in centimetres.

High-resolution µXRF elemental scanning

SG06 LL-channel core sections were scanned using the ITRAX core scanning facility at Aberystwyth University and was operated following the standard methodology outlined in Croudace et al. (2006). Rather than using a single spot X-ray beam, the ITRAX is equipped with a flat X-ray beam, measuring a rectangular window. In this way, grain-to-grain variances are averaged across the horizontal core axis, ensuring a stronger signal and predominance of the environmental signal through depth. This is particularly useful for the identification of cryptotephra layers, which may be patchy and/or of low concentration. For the analyses used here a 20 x 0.1 mm rectangular beam was used, with a step size of 60 μm, a count time of 4 s, a voltage of 30 kV, a current of 30 mA and a Mo X-ray tube. A more detailed description of the settings used is given by Marshall et al. (2012). To avoid spurious patterns and relationships between elements caused by the effects of organic matter and water content, all data are normalised to the incoherent plus coherent (inc + coh) scattering.

As an initial step, we utilise baselines across the µXRF core scanning data to determine typical variability in the host sediment composition across the Holocene and varved MIS 3 sediments. These baselines were adopted to help quantify significant peaks (i.e. elemental counts significantly above the known paleoenvironmental and varve signal), and provide an assessment of which tephra layers are distinctive when regarded in context (i.e. within periods of sedimentation spanning several metres). For instance, within the Holocene sediments (1290 to 20 cm SG06 CD) a baseline of 0.01 cps/inc + coh scattering for Ca was used (dotted red line marked on Fig. 2a), where 23 exceeding peaks are identified through the 11.7 m of sedimentation. For the varved sediments dated between 50 and 30 ka, a higher baseline of 0.02 cps for Ca was used until 3095.9 cm SG06 CD, and 0.15 cps from 3095.9 to 2650.0 cm SG06 CD (Fig. 2b). This accounts for the known sedimentological change, likely caused by the redirection of the River Hasu. Here, Ca and Sr were used as key denominator elements as they yielded strong intensities, and showed the highest contrast between the visible volcanic layers and background lacustrine sediments. Relative peaks in Mn, Fe, Ti, K and Ba were also used as possible proxies for ash, as these elements are found in high concentrations in the glass and minerals of volcanic material. Significant peaks in elemental counts (i.e. those above positive baselines) were compared with the known ash concentration (e.g. shards per gram of dried sediment as published in McLean et al., 2018, 2020b) to determine whether these coincided with known, or potentially undetected, event layers (i.e. tephra or high-energy flood/earthquake events). In several instances, glass preserved in peaks that did not coincide with known cryptotephra layers were geochemically analysed as part of this study using the methodology outlined in McLean et al. (2018) to check for other compositionally unique ash horizons, but they were not found to be new cryptotephra layers.

As a second step, a 30 cm interval across the position of all tephra (10 visible and 30 cryptotephra layers) was assessed to utilise the high-resolution core scanning data (at both 60 μm and averaged 1 mm) and decipher potentially muted signals. This interval uses the same scanning parameters as listed above and is used to provide a more thorough investigation across all single, or ratios of elemental counts, and the opportunity to locate the precise stratigraphic positioning of the cryptotephra. The µXRF elemental responses for visible ash layers were used to help determine useful elements for cryptotephra identification, specifically those erupted from the same volcanic source and have similar glass compositions.

Thin section microscopy

In order to further investigate the stratigraphic preservation of cryptotephra layers within the Suigetsu varved sediments, we microscopically examined a thin section taken from core section B-17, known to contain the trachytic cryptotephra layer erupted from Changbaishan (SG14-3380; ca. 42 ka). Thin sections of the sediments were prepared previously for microanalytical and varve analysis at Lake Suigetsu (see Schlollaut et al., 2014). Sediments from the LL-channels were cut into 10 cm long segments and freeze-dried and then impregnated with synthetic resin under vacuum. These blocks were then glued to glass slides and cut, ground and polished to produce a 20 μm thin slice suitable for microscopic analysis as shown here (Brauer and Casanova, 2001).
Figure 2. Overview of the ITRAX µXRF elemental compositions (in cps normalised to incoherent plus coherent) through the (a) Holocene and (b) MIS 3 Lake Suigetsu sediments. Significant peaks above these baselines (red dotted/bold horizontal lines) were compared with the ash concentrations (e.g. shards per gram of dried sediment) to determine whether these coincided with known or potentially undetected event layers (i.e. tephra or high-energy events). Tephra layers are delineated using a bold (visible) and dotted (cryptotephra) grey line, elemental responses of key tephra layers are capped with a red T. In order to only capture the geochemical enrichment caused by ash layers, the threshold for the Holocene and MIS 3 sediments needs to be >0.03 (cps) for Ca. [Color figure can be viewed at wileyonlinelibrary.com]
Results

Overview and baselines for tephra detection

Key elemental counts obtained by µXRF core scanning across the two sedimentary periods (i.e. the Holocene and MIS 3) are illustrated in Fig. 2. The studied sediments comprise different proportions of autochthonous (e.g. calcite precipitates, siderite, pyrite, diatoms) and allochthonous components (e.g. epiclastic, terrestrial plant remains, benthic diatoms) as reflected in the downcore data. For both periods, there is inherent variability throughout, as well as frequent and rapid deviation from baseline levels, particularly for Ti, Ca, K and Mn. As highlighted, the typical elemental counts of the host sediments change in MIS 3, with a relative drop in Ca, Ti and Sr stratigraphically above 3095.9 cm SG06 CD, followed by a greater sensitivity of Mn that frequently overprints the varve compositional baselines. In general, the µXRF core scanning counts throughout the Holocene are typically half those through the MIS 3 sediments. The most significant relative downcore compositional changes are positioned at visible
tephra (typically with relative enrichment in K, Ca, Sr and Ba; marked by a red ‘T’ on Fig. 2), reflecting the abundance of volcanic material, as well as other event layers caused by high-energy events such as floods/earthquakes (typically with relative increases in K, Ti, Fe).

In order to only capture the geochemical responses caused by ash layers, the threshold for the MIS 3 sediments needs to be >0.03 (cps) for Ca, which records five of the 30 ash layers (three visible and two cryptotephra; Fig. 2). A threshold of >2.0 (cps) for Ca/Ti incorporates three of these layers. For the Holocene sediments, count thresholds also need to be greater than >0.03 (cps) for Ca, which captures the position of four of the six visible ash layers, but none of the 30 cryptotephra layers. Lowering the baselines for these and other elements (e.g. Si, Al, Fe, K, Ti and Ba) in order to capture the peaks only attributed to tephra is not possible. For instance, a marginally lower Holocene baseline of 0.01 cps for Ca (red dashed line on Fig. 2a) incorporates 23 relative peaks, only one of which coincides with an additional cryptotephra layer (SG14-0490; KGP tephra).

In general, assessing the presence of ash layers in their broader stratigraphic context (i.e. across several metres of sedimentation) is challenging and requires a detailed understanding of the host sediment matrix and the possible palaeoclimatic influences through time. Detailed assessments using a more constrained stratigraphic interval (i.e. 30 cm), as well as utilising a range of single and/or ratios of two elements is often essential to identify elemental enrichment/depletion caused by the ash, and to rule out which peaks are attributed to other depositional processes. These specific elemental profiles are explored in more detail for all 10 visible and 30 cryptotephra layers in the following sections.

Elemental profiles across visible event layers

As highlighted, the most significant elemental peaks through the core occur at the position of visible ash (Figs 2 and 3) and delineate the position of seven of the 10 layers within the stratigraphic sequences of study (Table 1). Of these relative changes, the µXRF Ca/Ti profile across the basaltic–andesite tephra SG06-3485 (0.5 cm thick) is one of the most distinct, peaking at 10 times greater than the normal background/baseline variations at 5.5. This is to be expected as the glass shard compositions of this tephra are up to 10 times higher in CaO (8.5–10.6 wt.%) compared with the other layers in this study (Figs 2b and 3c). Its positioning also coincides with a relative decrease in K (Fig. 3c), not observed for other ash layers detected using µXRF core scanning, and must also relate to the glass compositions which contain 0.33–0.67 wt.% K₂O and are the lowest of the deposits investigated here. The three tephra layers erupted from Sambe volcano (central Japan) are also very clearly distinguishable within the host sediment compositions, with sharp enrichments in K, Ca, Ca/Ti, Sr and Sr/Ti, and relative depletions in Ti, Fe and Mn (Figs 2 and 3b; Table 1). These elemental responses clearly and precisely distinguish the tephra positions, despite their thicknesses being ≤0.3 cm.

Other fine ash visible layers (i.e. ranging in thickness between 0.1 and 0.2 cm) were not as easily identifiable in the µXRF core profiles, falling below the baseline Ca of 0.3 (cps), and also indicate the importance of glass compositions in their detection against the host sediment. These include the high-K (>4 wt.% K₂O) rhyolitic tephra layers erupted from Changbaishan and Aso (n= 2; 0.1 cm thick) and the phonolitic/trachytic tephra layers that erupted from Ulleungdo. Glasses erupted from Ulleungdo and Changbaishan show pronounced negative feldspar-related anomalies in Ba, Sr and Eu (McLean et al., 2020a) and are abundant in major element contents that are already high in the host sediments and eroded rocks from the catchment (e.g. Al₂O₃, K₂O and CaO).

Elemental peaks for these visible ash layers are therefore relatively subtle, but can be more easily recognised within a 30 cm-stratigraphic interval, using Ti/K or Ca/Ti for Changbaishan, and K/Ti or Zr/Ti for Ulleungdo (Fig. 6; Table 1). The thin visible (0.1 cm) tephra that erupted from Aso (SG06-3912) contains glass with some of the highest K₂O content (4.46–4.90 wt.%) and also coincides with the largest K peak count. However, due to the significant downcore variability of this element, the SG06-3912 is not easily distinguished within a broader stratigraphic context (i.e. over several metres of sedimentation; Fig. 2b), and thus could easily be overlooked as a palaeoenvironmental or hydrological signal (Fig. 2).

A strong upcore signal/profile is observed within some of the thickest layers, this is most clearly demonstrated for SG06-0967 (K-Ah tephra), as shown in Fig. 3a. Since no chemo-stratigraphic variation occurs through this eruptive unit, it is interpreted that this strengthening must relate to the upwards fining (decreasing grain size, increased compaction) of the ash particles, which is also visible in the split cores. Interestingly, following the visible ash unit, the elemental spikes associated with the ash rapidly drops, even though the cryptotephra investigations show the sediment still contains very high concentrations of ash. For instance, baseline µXRF concentrations are reached almost immediately above the upper boundary of the K-Ah ash, whereas over 5000 shards per gram of sediment persist in the overlying 2 m (McLean et al., 2018). A significant element response was observed for this rhyolitic tephra (e.g. enrichment in Si, K, Ca, Ti, Mn, Zn and Sr, and depletion in Fe; Fig. 2a) which replicates the 2.8 cm thickness of the visible deposit.

Other key fluctuations were observed in the µXRF data at the positions of known high-energy event layers defined previously in the core by Schloulart et al. (2014). Several of these peaked over the baseline levels and concentrations observed associated with visible ash layers, for instance at 2923.4 cm SG06 CD (as marked on Fig. 2b), a position where no peak in glass shards was identified within the sediments. The visual characteristics and structure of the µXRF profiles for the significant high-energy events (see Schloulart et al., 2012) mean it is generally straightforward to discriminate between signals caused by ash or reworking deposits. Many event layers also coincide with significant increases in Ti, which is not typically observed for visible ash layers. However, the thick K-Ah ash unit is an exception to this, likely due to the considerable input of tephra and relatively high TiO₂ (ca. 0.54 wt.%) content of these rhyolitic glasses (Fig. 3a). Several of the thinner remobilisation events (i.e. <0.5 cm units that are visible in the core) are also newly identified by µXRF fluctuations, as highlighted on Figs 2 and 3.

Elemental profiles across positions of known cryptotephra layers

Overview

Just two of the 30 cryptotephra layers (SG14-0490 (Fig. 2a) and SG14-3605 (Fig. 2b)) could be clearly identified when plotting µXRF profiles for both study periods (e.g. Holocene or 50–30 ka; Fig. 2). These are recognised by significant elevations above baseline levels in K, Ca, Ti and Sr. When the known stratigraphic positioning of the cryptotephra layer is used, it is possible to detect muted responses for other layers.
across a defined 30 cm stratigraphic interval (SG14-0840; SG14-3316; SG14-3380; Table 1). Unlike that for the visible ash layers, there is no clear relationship with the elemental response and glass compositions. Furthermore, elemental baselines for detecting cryptotephra are not useful, as responses frequently fall below, or occur within, environmental transitions.

In cases where peaks in single or elemental ratio profiles are able to clearly delineate the cryptotephra marker, the stratigraphic position can be resolved at a greater level of precision, to between 0.1 and 0.2 cm, compared with the typical cryptotephra sampling resolution of 1 cm, which has been previously used for the Suigetsu sediments (McLean et al. 2018, 2020b; Table 1; Fig. 4a). This fine tuning of the ash layers’ stratigraphic position is relevant for high-resolution correlation of records, which would better allow for spatial variations in proxy responses to climate to be identified. Furthermore, better stratigraphic resolution enables greater chronological age precision, and could potentially resolve eruptions to individual seasons.

Aso cryptotephra layers

During the varved MIS 3 sediments (i.e. 50–30 ka), three cryptotephra layers erupted from within the Aso caldera coincide with significant fluctuations observed in the µXRF profiles (Fig. 5). These cryptotephra layers include the andesitic/trachy-andesitic SG14-2625 (~61.8 wt.% SiO₂; 7.0 wt.% TAS), the andesitic SG14-3085 (dominant population ~57.3 wt.% SiO₂; 6.3 wt.% TAS) and the dacitic SG14-3605

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**Figure 4.** Selected µXRF elemental profiles over the positioning of several key visible and cryptotephra layers preserved in the Lake Suigetsu sediments. These examples highlight the ability of µXRF to assist in the identification and interpretation of the glass concentrations by: (a) refining the precision of the stratigraphic position of the peak; (b) the ability to identify primary cryptotephra layers during periods of high background glass concentrations (>5000 shard per gram), i.e. the To-Cu tephra at 836.3 cm CD (the compositional spike at 875.1 cm CD was investigated and it does not correspond to a tephra layer); and (c) the opportunity to track cryptotephra tails, renewed inwash events (using Ti) and determine the initial input/eruption position. The blue shading shows the position of the cryptotephra as determined by density separation techniques where the resolution is 1 cm. The grey bars show the position of crypto-event layers defined using the µXRF elemental responses shown. [Color figure can be viewed at wileyonlinelibrary.com]
The glass concentrations for these layers range from 2200 (SG14-3605) to 9838 shards per gram (SG14-2625; Fig. 5). The most diagnostic µXRF elemental shifts for SG14-3085 and SG14-3605 are K, Ca, Ti, Fe, Zn, Rb, Sr and Zr (in cps normalised to incoherent plus coherent) across the known cryptotephra layers that have been correlated to eruptions of Aso (SG14-3085, SG14-2625, SG14-3605, SG14-2739 and SG14-2752). The cryptotephra counts are from McLean et al. (2020b). Horizontal lines indicate the positioning of the cryptotephra peak as determined using density separation techniques. The position of SG14-3605 (dacite; ~64.5 wt.% SiO$_2$; 7.8 wt.% TAS) is clearly determined using the µXRF core scanning data, even when assessing the values across the entire interval (e.g. 50–30 ka). Interestingly, this cryptotephra layer contains one of the lowest concentrations of glass shards (2200 shards per gram) and masked any possible µXRF response to the ash deposit. This interpretation is strengthened by similar levels of fluctuations stratigraphically below where no peaks in ash are present (shown on Fig. 5b). The position of SG14-3605 (dacite; ~64.5 wt.% SiO$_2$; 7.8 wt.% TAS) is clearly determined using the µXRF core scanning data, even when assessing the values across the entire interval (e.g. 50–30 ka). Interestingly, this cryptotephra layer contains one of the lowest concentrations of glass shards (2200 shards per gram).
yet has a µXRF signal seemingly as strong as many of the visible ash layers (Fig. 2).

The core scanning elemental data show two significant peaks at the position of SG14-3085, which occur within 0.8 cm of sedimentation (Fig. 5a). This cryptotephra is positioned immediately following a thick event layer. This event layer was most likely deposited following a subaqueous slump, and is known to contain low concentrations of glass shards (Fig. 5a; McLean et al., 2020b). The upper of the two µXRF peaks is defined by a significant increase in Ca and coincides with the position of the cryptotephra layer in the sediments. Further investigations using thin sections captured from these sediments revealed that both µXRF peaks coincide with fine-grained laminations, which may be caused by the formation of siderite or calcium carbonate. This sedimentological information gleaned using the thin sections highlight that other lake hydrological processes can cause very similar µXRF responses to the presence of glass shards.

The position of four other silicic tephra layers erupted from Aso (ranging from andesitic to rhyolitic in glass composition; Table 1) could not be identified using any single element profiles, or ratios including those that help accentuate the rhyolitic visible Aso tephra (ACP4; Ti/K, Ca/Ti or Ca/Ba). These rhyolitic cryptotephra lack a clear µXRF response, despite glass concentrations exceeding 20 000 shards per gram in some cases.

Other rhyolitic cryptotephra layers

No significant µXRF responses were observed for the rhyolitic cryptotephra layers erupted from Aso caldera (SG14-2814, SG14-2856, SG14-2873, and SG14-3844), and others from undefined sources along the Ryukyu-Kyushu arc, all of which ranged in glass concentrations from 1550 shards per gram to over 16 000 shards per gram in the varved lake sediments. A single elemental spike in Sr is recognisable at the positioning of the rhyolitic cryptotephra SG14-3336, despite glass concentrations falling below 6000 shards per gram. Of the eight rhyolitic cryptotephra layers preserved in the non-varved Holocene sediments, only the high-K cryptotephra layer from Kawagodaira volcano (SG14-0490) with shard concentrations >8000 shards per gram was clearly identifiable (Table 1; Fig. 4c). The most diagnostic single element and element ratio signals relate to Si, K, Ca, Ti, Fe, Zn, Rb, Pb, Ca/Ti and Sr/Ca. The µXRF profile suggests that the cryptotephra peak occurred at 485.2 cm CD, with a later inwashing event occurring at 484.4 cm CD with peaks in several other diagnostic elements including Ti (Fig. 4c). This is in close agreement with glass concentration counts (1 cm scan) which showed that the cryptotephra position fell between 484.0 and 485.0 cm SG06 CD (McLean et al., 2018).

Ulleungdo and Changbaishan cryptotephra layers

Ratios of elements that were useful for the detection of the visible ash (U-3/SIG14-1091; U-Oki/SIG06-1288 and U-Ym/ SIG14-3216) deposits from Ulleungdo (i.e. K/Ti, Zr/Ti) were not able to detect a compositionally identical cryptotephra layer (SG14-0803), despite containing >20 000 shards per gram in the Suigetsu sediments (Fig. 6). A possible peak was observed for the U-2 tephra (SG014-0803) using Ca/Ba (Fig. 6d) but this is not particularly distinctive, and within the range of the sediments, and is not diagnostic. The trachytic cryptotephra erupted from Changbaishan (SG14-3380) can only be identified using Ca/Ba at 3396.3 cm SG06 CD, which is consistent with the low Ba concentrations in the SG14-3380 glass shards caused by K-feldspar fractionation.

Cryptotephra layers in high-background sediments

An elemental response (relative peak in Ca/Ti) for cryptotephra layer SG14-0840 (To-Cu) tephra was identified in the sediments following the thick K-Ah tephra (SG06-0967; Fig. 4b). These sediments contain very high concentrations of glass (18 750 shards per gram) that are predominantly derived from remobilisation or inwash of the K-Ah ash. The To-Cu eruption could be identified microscopically by a sharp change in the morphology of the glass shards (McLean et al., 2018), which was confirmed by geochemical analysis. Other Ca/Ti peaks within this high background interval were investigated as part of this study to determine whether these positions also contained other primary ashfall deposits (i.e. at 875.1 cm CD). However, glass shard compositions from these positions were consistent with those for the K-Ah. Across this period other high-energy events and renewed inwash of the K-Ah tephra can be delineated using a K/Ca plot (Fig. 4b).

Refining the stratigraphic positioning of cryptotephra using µXRF core scanning

To further investigate the µXRF elemental responses across the cryptotephra layers, we examined a thin section taken from core section B-17, known to contain the trachytic cryptotephra layer erupted from Changbaishan (SG14-3380; ca. 42 ka). Density separation techniques showed that the cryptotephra marker contained 18 383 shards per gram and was therefore a likely candidate for identification in the µXRF core scanning data. Nonetheless, it was only possible to detect a compositional change in Ca/Ba across the 1 cm stratigraphic interval known to contain the Changbaishan glass (Fig. 6d).

Using the thin section, and the precise stratigraphic positioning determined by the Ca/Ba peak (i.e. 3396.3 cm SG06 CD), it was possible to microscopically locate the positioning of glass shards within the varved sediments (Fig. 7). The glass shards are situated along a small crack that was likely caused via freeze-drying when generating the thin section. As shown in Fig. 7, the shards are remarkably well constrained, forming a layer <200 µm thick within the sediments. These findings are significant, showing the excellent stratigraphic preservation of the glass shards in the varved sediments, which is not always the case for cryptotephra in other archives. Although this stratigraphic preservation is very useful for ultra-precise correlations between different records, as well as for precise chronological age modelling (perhaps here down to a seasonal resolution), this may not be ideal for detection via µXRF core scanning. The glass shards make up <20% of the total analysis, and without very distinctive glass compositions, a pronounced elemental signal is not likely.

Discussion

µXRF core scanning for the detection of cryptotephra layers

This investigation demonstrated that in this geological setting, the ITRAX core scanning data were not able to independently establish a detailed crypto-tephrostratigraphy. While distinct and recognisable elemental responses were evident for 7 out of 10 visible tephra layers in the investigated time window, only 2 of the 30 cryptotephra layers were clearly resolved (Table 1; Fig. 2). Relative enrichments in K, Ca, Sr, Ca/Ti, Sr/Ti and sometimes Ca/Ba could be used to locate these ash layers, but there is no single element or ratio that can be used to unequivocally identify just the tephra layers. Due to the significant downcore variability of the sediment matrix,
Figure 6. Comparison of the glass shard concentrations and elemental profiles across the positioning of known cryptotephra layers erupted from (a–d) Ulleungdo (SG06-1288, SG14-3216, SG14-1288 and SG14-1091) and (e) Changbaishan (SG14-3380). Horizontal blue lines indicate the positions of the cryptotephra peak as determined using density separation techniques (McLean et al., 2020b). K/Ti and Zr/Ti elemental profiles were effective in identifying the position of the fine (1 mm thick) layers from Ulleungdo, but were not able to identify the high-concentration cryptotephra layer (U2 eruption). Ca/Ba was effective in positively locating the position of SG14-3380. [Color figure can be viewed at wileyonlinelibrary.com]
baselines for tephra detection are not very useful. For instance, more than 50 additional peaks would require assessment using the lower Ca threshold level shown in Fig. 2 (dotted line), and over 80% of the cryptotephra layers would remain undetected. Since each investigated peak would contain a significant proportion of ash (especially those caused by remobilisation events), further density separation work using traditional extraction methods would be required to establish their shard profiles and geochemical distinctness. Establishing the eruptive history record for a single compositionally heterogeneous centre such as the Aso caldera, would mean that, at best, only three of the eight eruptions would be identified if µXRF core scanning was used as a first-order method for detection (Table 1). As outlined above, even when the precise stratigraphic interval is known, in many instances no clear geochemical signal could be detected, despite ash concentrations reaching over >20 000 shards per gram. This may be caused by the tight stratigraphic preservation of the glass shards, shown to be constrained to <200 µm in thickness in the varved sediments, and contributing to <20% of the total analysis (Fig. 7). In general, establishing just 10% of the cryptotephrostratigraphy will not be useful for the vast majority of studies aiming to generate comprehensive eruptive records and isochrons for stratigraphic correlation. It is likely that studies that use µXRF core scanning will be missing other key ash layers, especially those that contain low glass concentrations and thus offer the most valuable and broadest chronostratigraphic tie-points.

We illustrate here that despite these findings, µXRF core scanning can work alongside traditional cryptotephra identification methods to provide new insight into the stratigraphic positioning, and assessment of glass reworking events. In several instances it is possible to use K/Ca and Ti peaks to locate ‘cryptic’ high-energy events that have remobilised glass from older eruptions. Moreover, for cryptotephra layers that were positively identified, µXRF core scanning allowed their stratigraphic position to be significantly constrained, to less than a millimetre, which allows an improvement in the chronological age modelling (which currently uses the full 1 cm age uncertainty). In the varved sediments of Lake Suigetsu, constraining the position of these layers helps to reduce the age uncertainty. It was also possible to locate the precise varve position using the µXRF core scanning data in conjunction with thin section microscopy, offering significant potential to assign the eruption to a seasonal resolution.

Another advantage of µXRF core scanning is that the compositional signal associated with a tephra is only pronounced over the layer, and the high background shards that occur after the layer often do not affect the signal. This means that µXRF core scanning could be used to detect and verify new, compositionally distinct ash layers in sediments that contain

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Figure 7. Thin section energy-dispersive X-ray spectroscopy (EDS) composition (a, b) and backscattered electron (BSE) (c) image showing the glass shards of SG14-3380 in core section B-17. This trachytic tephra that erupted from Changbaishan volcano (B-SG-42) is not visible in core sections but contains concentrations of 18 383 shards per gram (McLean et al., 2020b). The glass shards are located in a small crack in the sediment and constrained to <200 µm in thickness. Even though numerous shards (tens to 50 µm in diameter) are observed across the 250 µm section scanned, the µXRF response is limited to a peak in Ca/Ba (see Fig. 6d). [Color figure can be viewed at wileyonlinelibrary.com]
high background concentrations of glass shards, where density separation methods are not suitable. For instance, we utilised the µXRF data to look for layers in the sediments following the very thick AT tephra that erupted at 30 ka (>50 cm thick) where glass shards from this are reworked through the catchment for over 10 km. Although the visible layers that are in the sediments following the AT tephra are clearly identified, no further cryptotephra layers can be distinguished. Finally, for visible ash layers it may be possible to infer general glass compositions for the layers, if less evolved tephra layers show distinct elemental responses (e.g. key depletions in K, Ti, Fe for Fuji- derived ash), but these characteristics are not comparable to, or a substitute for, single shard geochemical datasets generated using the electron microprobe (see Peti et al., 2020). We are not able to present reliable and universal guidelines for such applications of µXRF core scanning within tephrachronology. While we are able to refine the stratigraphic positioning of ash layers and identify reworking events in the sediments of Lake Suigetsu, these signatures and opportunities will not be universally applicable across other records; for instance, within the marine realm where cryptotephra layers are not as perfectly preserved or sedimentation rates are lower. Moreover, remobilisation signatures will be unique to each archive and are dependent on the setting, sediment composition and volcanic input. Such applications require further detailed investigations using both datasets (µXRF and density separation techniques) in each specific archive.

Factors affecting tephra identification using µXRF core scanning

We find the likelihood of detecting visible and cryptotephra layers using µXRF core scanning depends on three key factors: 1) the host sediment composition and contrast with the composition of the deposited tephra; 2) the palaeoenvironmental sensitivity of the archive (and overprinting of the signals); and 3) the stratigraphic preservation of the glass shards (e.g. concentration, positioning and grain size). The vast majority of tephrostratigraphic studies will use a climatically sensitive archive, and hope to integrate multiple eruption sources through time, meaning conditions to detect cryptotephra layers using µXRF core scanning are likely to be unfavourable at the outset. Perhaps the most critical aspect faced in this example is the geochemical distinction between the tephra and the sediment matrix. The catchment geology surrounding Lake Suigetsu includes granite, dolerite, basalt and chert which forms the host sediments, which are high in Si, Al and Fe and many of the other elements that are abundant in the tephra. Since the compositional baseline is made up of these eroded Si-bearing rocks, the composition of the silicate tephra layers are not radically different and it is impossible to distinguish a signal from the background noise.

Since we used an existing high-resolution µXRF dataset for the Lake Suigetsu sediment cores and do not have data obtained with different analytical settings we can only make some inferences on the scanning parameters. Other analytical changes (e.g. comparing a Cr vs. Mo-tube, increasing the exposure times to >4 s, and the 20 µm step size) could be the focus of future work in different archives and may prove useful, especially if a narrow range of volcanic compositions are expected and can be optimised for. It is unlikely that multiple scanning positions (i.e. offsetting the core centre) see Peti et al., 2020) would improve the success rate in identifying the cryptotephra layers. This is because we do not typically see patchy deposits of ash, and even fine layers remain well constrained and uniform, most clearly observed within the varved structure.

In certain volcanic settings µXRF core scanning may prove to be more useful in delineating tephra positions, especially if less evolved products dominate the record, or are likely to receive tephra from highly potassic sources, which often comprise tephra with high levels of trace element enrichment which exceed host sediment baseline levels (e.g. Zr and Sr). This was demonstrated more successfully in the karstic system at Lake Ohrid (Albania/Macedonia) where peaks in K, Sr and Zr have been used to identify cryptotephra deposits from the Campanian volcanoes (Somma-Vesuvius and Campi Flegrei) (Vogel et al., 2010). Due to the exceptional climatic sensitivity of the Suigetsu sedimentary archive, the lake sediments often show pronounced fine laminations recording both local and regional hydrological and environmental change, which often overprint muted responses caused by tephra. Again, this contrasts with studies using other sedimentary records, like those from the marine environment, where a smaller proportion of the µXRF signal may form peaks, and therefore warrant further investigation for the presence of tephra (e.g. cores analysed from the coast of Montserrat; Cassidy et al. 2014).

Conclusions

This study finds that cryptotephra identification by µXRF core scanning is not a suitable standalone technique to establish a comprehensive cryptotephra stratigraphy for a particular sequence. However, it shows that the technique offers a useful tool to accompany more rigorous tephrostratigraphic investigations. For the cryptotephra layers that were identified in the µXRF core scanning, it was possible to refine their stratigraphic position from 1 cm to below a millimetre, thus improving their modelled eruptive age and precision as isochrons. Indeed, in the varved Suigetsu sediments, we show for the first time that cryptotephra shards can be very precisely constrained, spanning just <200 µm in thickness, offering opportunities for ultra-high resolution correlations. Since high concentrations of rhyolitic glass are required to elicit a change in the µXRF elemental signals, core scanning can help identify compositionally distinct tephra layers in sediments that contain high background concentrations of glass shards, and can also help discriminate remobilisation (e.g. reworking) events, which can be notoriously difficult to decipher in cryptotephra stratigraphies. This example using the Suigetsu sediments reveals that µXRF core scanning is useful for the identification of visible tephras, but only recognises 10% of the cryptotephra layers that were identified using density separation techniques. As µXRF data are routinely acquired to provide sedimentological information for key palaeoclimate archives, these data should be investigated for tephra studies but they need to be used in conjunction with standard cryptotephra investigations to generate more complete eruptive records.

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Table 1. Additional datasets can be accessed through the project website (http://www.suigetsu.org). We thank Dr Leonie Peti and another anonymous reviewer for their constructive comments which helped us to improve the manuscript, and Professor Rewi Newnham for editorial handling.

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Supporting information
Additional supporting information can be found in the online version of this article. The glass geochemical data referred to in this study can be located in the supplementary materials of references listed in Table 1. Additional Suigetsu publications and datasets can be accessed through the project website (http://www.suigetsu.org/publications.html).

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