Trace element analysis of Late Holocene tephras from Greenland ice cores

TRACE ELEMENT ANALYSIS OF LATE HOLOCENE TEPHRAS FROM GREENLAND ICE CORES

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Abstract

Locating and geochemically characterising cryptotephra in polar ice cores is critical for identifying the sources of volcanic markers that the ice cores contain. Trace element analysis of tephras is an important compliment to major element analysis as trace element composition can help differentiate volcanic sources and provide insights into the processes that generated the tephra. Here, we examine the trace element composition of selected tephras from Greenland ice cores using laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) in an attempt to verify their sources. Our results support the attribution of the ~1641 BCE acid layer in Greenland ice to Aniakchak, but we demonstrate that an eruption from an unidentified source was coeval with the Millennium Eruption of Changbaishan in 946 CE. We find that small shard size and the presence of multiple tephra populations pose particular challenges to the successful analysis of sparse tephra layers in the ice.

Introduction

Polar ice cores provide important records of palaeovolcanism that are critical for evaluating the role of volcanic forcing of climate. Sulphur dioxide and other aerosols from volcanic eruptions, potential contributors to past climate change, form acid layers within the ice which can be used in climate models to account for volcanically-induced changes in the Earth's radiative balance (e.g. Gao et al., 2008). Acid layers cannot reveal their source, however, nor can they reliably differentiate between high-, mid- or low-latitude eruptions, and the potential to examine the likely palaeoenvironmental impacts of the eruptions is therefore limited. The identification and characterisation of tephra in the ice cores can significantly improve the understanding of the source, impact and timing of volcanic activity, and tephra studies can thus contribute enormously to the evaluation of volcano-climate processes.

Over the last two decades, efforts to identify tephras in the Greenland ice cores have intensified (see review in Abbott and Davies, 2012). Much of the attention has been focused on Last Glacial ice, where a large number of tephras have been found, most of which have major element compositions that compare mainly with sources in Iceland (Abbott et al., 2012; Bourne et al., 2015), although some sources around the North Pacific Rim have also been reported (Bourne et al., 2016). In contrast, mid- to Late Holocene tephras appear to derive *mainly* from non-Icelandic sources, including Alaska and China (Coulter et al., 2012; Jensen et al., 2014; Sun et al., 2014; Sigl et al., 2015). While these apparent discrepancies may be due to differences in sampling strategies employed to each of the intervals (continuous sampling of Last Glacial ice *versus* focused sampling on events of interest in the Holocene), it is notable that non-Icelandic sources are comparatively rare in the continuous Last Glacial records, whereas sampling of some centuries-long Late Holocene sections (e.g. ~845–953 CE in NGRIP; Coulter et al. 2012) did not detect *any* of the many tephras erupted in Iceland during this time, despite targeting specific Icelandic events. An alternative explanation for the greater frequency of non-Icelandic tephras in the later period may that the predominantly easterly flow of air masses in the northern high-latitudes emerged in the Holocene. The precise origins of many tephras remain unidentified, however, mainly due to a dearth of published comparative glass data from potential volcanic regions. This apparently greater potential source area for mid- to Late Holocene tephras in Greenland ice cores raises the possibility that major element data alone may be insufficient to discriminate tephras from different volcanic regions that share similar major element compositions.

Here we attempt to verify the source of selected Greenland tephras by analysing their trace element compositions using laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS). We highlight the difficulties of obtaining successful datasets on sparse, fine tephra shards, and demonstrate the need to match major and trace element data from discrete shards to ensure a more complete characterisation of the sample and the reliable distinction of heterogeneous populations, particularly for small and analytically-challenging shards.

Sample selection and methods

We selected three ice core tephra samples whose major element geochemistries have previously been analysed by electron probe micro-analysis (EPMA) and for which either reference sample material or published trace element data were available for their suggested correlatives (Table 1). QUB-1819 is a bimodal tephra from the NEEM-2011-S1 ice core, both of whose major element populations correlate with the mid-9th century CE "Millennium Eruption" of Tianchi, Changbaishan, on the North Korea-China border (Sun et al., 2014). A similar tephra has been identified in NGRIP (Coulter et al., 2012). QUB-1819 contains a mixture of fine (~30 μm) and very fine (~10 μm) shards, and the presence of a third population (QUB-1819c) was suggested by one dissimilar major element analysis that is not characteristic of Changbaishan tephra (Sun et al., 2014). For comparison, reference samples (rhyolitic component, K02017; dacitic component, K02065) whose major element compositions were previously established by Zhao (2010; Sun et al., 2014; Zhao et al. 2017) were analysed.

Table 1. Ice core and comparative samples selected for LA-ICP-MS analysis. *Age based on NS1-2011 timescale (Sigl et al. 2015) **Age based on GICC05 chronology (Vinther et al. 2006)

	Age	Sample origin	Suspected source/correlation
ICE CORE SAMPLES			
QUB-1819	946-7 CE*	NEEM-2011-S1, Greenland	Millennium Eruption (Changbaishan)
QUB-1528	853±1 CE*	NGRIP, Greenland	AD860B/WRAe (Mount Churchill)
QUB-1198	1641 BCE**	NGRIP, Greenland	Aniakchak caldera eruption 3.6 ka

COMPARATIVES		
K02017	Changbaishan crater	Millennium Eruption (Changbaishan)
K02065	Changbaishan crater	Millennium Eruption (Changbaishan)
QUB-109	Sluggan Bog, N. Ireland	AD860B/WRAe (Mount Churchill)

QUB-1528 has been matched on major element composition to the AD860B tephra found widely in Europe (Pilcher et al., 1996; Hall & Pilcher, 2002; Lawson et al., 2012) and recently correlated with the White River Ash Eastern Lobe (WRAe) from Mount Churchill, Alaska (Jensen et al., 2014). An extensive major, minor and trace element dataset for this tephra has been published by Preece et al. (2014). For comparison, we analysed QUB-109 from Sluggan Bog, the first sample in which the AD860B tephra was found in Europe, though it is mixed with a second population, AD860A, of presumed Icelandic origin.

A major acid spike in the Greenland ice cores at 1641 BCE (GICC05 chronology) has been attributed to Thera (Hammer et al., 2003), but the correlation of its associated tephra in the GRIP core (A1340-7) has been questioned on the basis of its major and trace element composition (Pearce et al., 2004; Denton & Pearce, 2008). Coulter et al. (2012) identified a tephra (QUB-1198) in the NGRIP ice core whose major element geochemistry more closely resembles the rhyolitic component of the Aniakchak caldera eruption of 3.6 ka. A single dacitic shard was recorded within this sample that is distinct from Aniakchak rhyolitic and andesitic end-members. Here we examine the trace element composition of QUB-1198 to compare with the composition of the A1340-7 tephra determined by Hammer et al. (2003) using ion microprobe analysis, and of Aniakchak (Kaufman et al., 2012) and Thera ash (Pearce et al., 2002) determined by LA-ICP-MS data.

All samples had been mounted on glass slides in Buehler epoxy resin, ground, polished and carbon-coated prior to EPMA. The same mounts were used for trace element analyses, but slide co-ordinates for the analysed shards were not available to allow the same shards to be analysed for their trace composition. LA-ICP-MS analysis on single shards was performed using a Coherent GeoLas 193-nm Excimer laser with a Thermo Finnigan Element 2 high-resolution sector field mass spectrometer at the Department of Geography and Earth Sciences, Aberystwyth University. Data were collected using a 10 μm ablation crater, employing ^{29}Si as an internal standard and NIST SRM 612 silicate glass as a calibration standard (Pearce et al., 1997; 2007; Pearce, 2014). Instrument operating conditions and corrections for fractionation effects followed Pearce et al. (2011).

Results

QUB-1819 (Millennium Eruption target)

The two components (K02017, K02065) of the Millennium Eruption reference material show a strong relationship with each other and indicate a highly differentiated product depleted in Ba and Sr and enriched in Y, Zr and rare earth elements (Fig. 1). The comparable Ba:Y ratio between the two components suggests a fractionation trend between them. Both populations correlate with proximal tephra from Changbaishan recently published by Chen et al. (2016). Analysis of QUB-1819 was complicated by the small size of the shards both in terms of locating and distinguishing tephra from non-tephra, and of obtaining a large enough target for analysis (Fig. 2). Twenty points were analysed, of which only eleven produced results consistent with volcanic glass. With an ablation crater size of 10 µm, however, several of the elements lie close to or below the lower limit of detection. Determining the correct ^{29}Si value to employ as an internal standard was not possible given the presence of three populations whose SiO_2 content ranged from 67.63 wt% to 76.53 wt%, and therefore the mean SiO_2 content of the total dataset (71.03 wt%) was used. This will have only a modest impact on the results, underestimating some analyses by about 5%, overestimating others by a similar amount. The results indicate particles that are clearly less evolved than the Millennium Eruption reference samples, and the analysed material is evidently not from this source. The trace element composition is transitional with adakite-like characteristics (Castillo 2012), suggesting an origin at a subduction zone. Comparable trace element compositions have been reported for Japanese tephras (Marayama et al., 2016), some of whom have major element geochemistries similar to QUB-1819c (SiO_2 >76 wt%, FeO and CaO < 1 wt %). In view of these data, we tentatively suggest that a second eruption coeval with the Millennium eruption and possibly in the Japan arc or neighbouring region, may have simultaneously dispersed tephra towards Greenland in 946 CE.

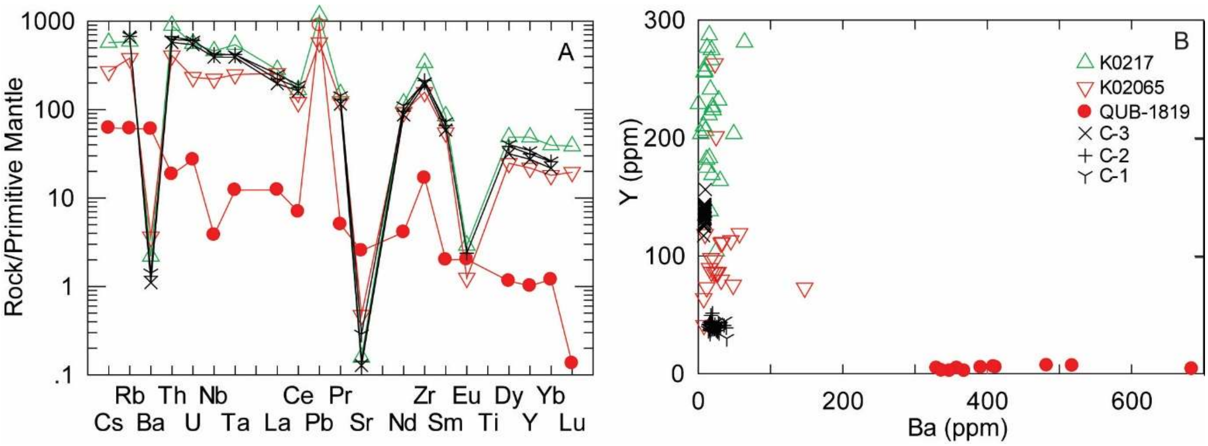

Fig. 1. Glass trace element characteristics of the Millennium Eruption tephra (K02017, K02065) and one component of QUB-1819, compared with published proximal Changbaishan (C-1, C-2, C-3) tephra (Chen et al., 2016). A) Primitive mantle normalised elements (based on averaged data) showing a clear difference between QUB-1819 and the Millennium Eruption/Changbaishan data (primitive mantle values from Sun and McDonough 1989). B) Biplot illustrating Ba depletion and Y enrichment of the Millennium Eruption/Changbaishan samples in contrast to the less evolved shards in QUB-1819.

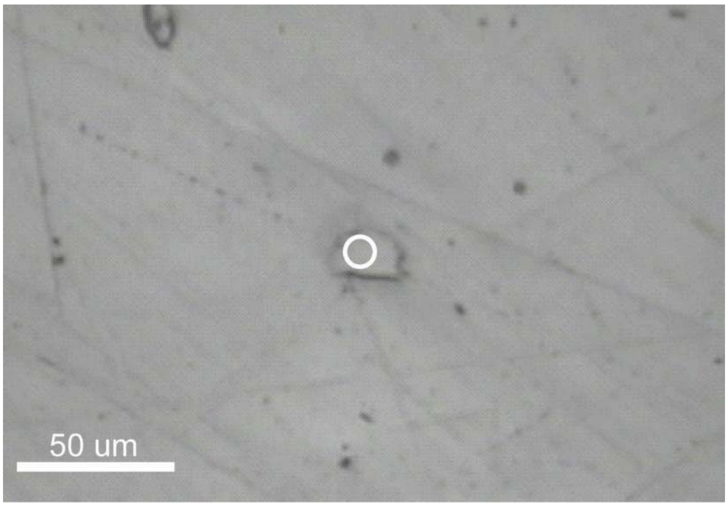

Fig. 2. Example of an exposed surface of a QUB-1819 shard (beneath circle, which is 10 μm in diameter). The very small size of the shard renders it difficult to obtain a complete and accurate analysis. Scale bar: 50 μm.

QUB-1528 (AD860B/WRAe target)

Of the 25 points that were analysed from QUB-1528, and 28 from QUB-109, no reliable datapoints that were clearly consistent with volcanic glass were obtained. Low signals were returned from a large proportion of targets, possibly due to the small size and vesicular nature of these shards, and other analyses were influenced by the presence of zircon, feldspar and quartz inclusions. We cannot therefore evaluate the correlation between these two tephras and WRAe.

QUB-1198 (Aniakchak target)

Tephra shards were easily recognisable in the QUB-1198 sample, and in some instances an impression from the rastered beam used during major element analysis was evident (Fig. 3). In total, 21 targets were analysed from QUB-1528, of which only three yielded results that were considered acceptable. Notwithstanding the small size of the population, the results are consistent with data from the mid-Holocene Aniakchak eruption (Kaufman et al., 2012; Fig. 4) and support the attribution of this tephra to Aniakchak (Coulter et al., 2012). They also reveal a strong similarity to the A1340-7 tephra from GRIP.

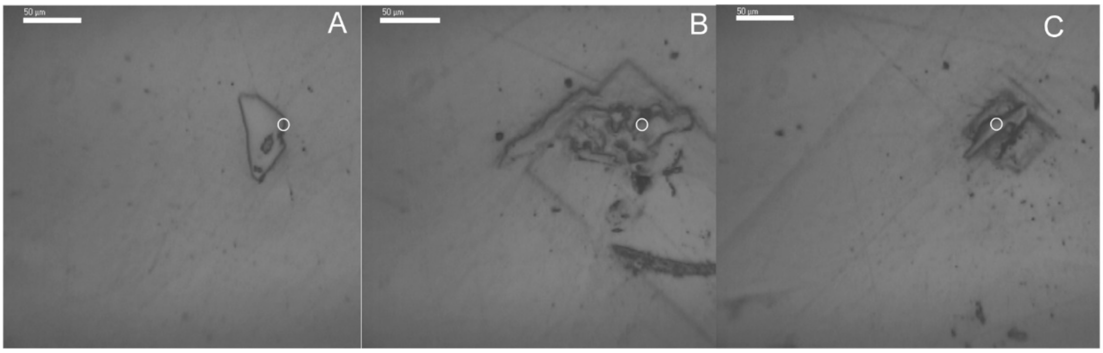

Fig. 3. Exposed surfaces of shards from QUB-1198. Oblique rectangular outline of rastered beam (demagnified) following major element analysis is visible in B and C. Scale bars = 50 μm; circle diameters = 10 μm.

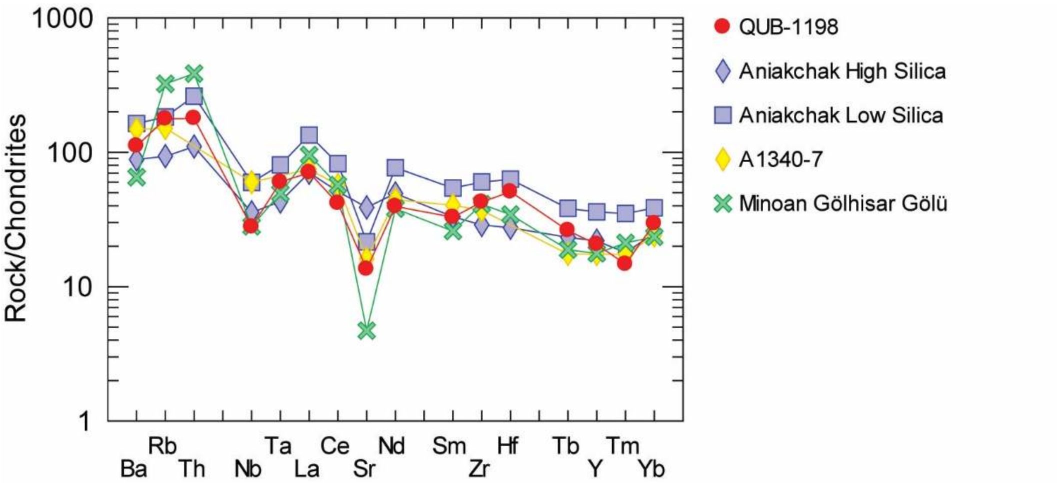

Fig. 4. Chondrite normalised spider plot (based on averaged data) showing similarities between QUB-1198, the Aniakchak caldera eruption (Kaufman et al., 2012) and A1340-7 in the GRIP ice core (Hammer et al., 2003). The Minoan (Thera) tephra from Gölhisar Gölü (Pearce et al., 2002) is distinguishable by its notably lower Sr and higher Rb and Th composition. Chondrite normalisation is based on Thompson (1982).

Discussion

In this investigation, an attempt to characterise the trace element composition of selected Late Holocene ice core tephra samples has met with limited success. A major limiting factor has been the small shard size that prevents sufficient counts from being acquired before shards are entirely ablated. As a result, it was not possible to obtain reliable data for QUB-1528 or QUB-109, both of which feature mainly small, vesicular shards. Furthermore, because slide co-ordinates were not available for those shards whose major element compositions had previously been determined, analysis was complicated by difficulties in locating glass shards of known geochemical composition and in determining the correct internal standard (^{29}Si content) to apply to the trace element data where multiple populations are present. We strongly recommend, therefore, that the recording of coordinates for shards analysed by EPMA should be standard practice in order to facilitate trace element characterisation of those same shards.

Our trace element results do not provide support for the correlation of QUB-1819 with the Millennium Eruption of Tianchi. We do not, however, reject this correlation as the major element data provide compelling evidence for a strong match with both the rhyolitic and dacitic end-members of this event. Furthermore, recent independent dating of the eruption (Oppenheimer et al., 2017) is consistent with the NS1-2011 ice core age for the QUB-1819 tephra. One possible explanation for the disparity in our results may be that we have inadvertently analysed glass from a third population. QUB-1819 is known to contain a population whose source has not yet been determined, and it is possible that the trace element data relate to this component. Subsequent examination of the specimen indicates that many of the shards analysed by LA-ICP-MS were obliterated, and we are therefore unable to determine if this component is morphologically distinct in any way that would have made it more prominent during LA-ICP-MS analysis. Furthermore, many of those shards from which we had obtained major element data remain intact, demonstrating that we have not obtained trace element data from them; further research may therefore be possible to verify their correlation with the Millennium Eruption.

Although only three datapoints were obtained from QUB-1198, the results are consistent with tephra from Aniakchak, as well as the GRIP tephra A1340-7 previously attributed to Thera (Hammer et al., 2003). Our trace element data from QUB-1198 support, therefore, the contention that the tephras in the ice cores at this time instead correlate with Aniakchak (Pearce et al., 2004).

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