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An exploratory method to detect tephras from quantitative XRD scans: examples from Iceland and east Greenland marine sediments

John T. Andrews,[1*] D.D. Eberl[2] and
Greta B. Kristjansdottir[1,3]

([1]INSTAAR and Department of Geological Sciences, University of Colorado, Box 450, Boulder CO 80309, USA; [2]U.S. Geological Survey, 3215 Marine Street, Suite E-127, Boulder CO 80303, USA; [3]The Godwin Laboratory for Palaeoclimate Research, Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK)

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Abstract: Tephras, mainly from Iceland, are becoming increasingly important in interpreting leads and lags in the Holocene climate system across NW Europe. Here we demonstrate that Quantitative Phase Analysis of x-ray diffractograms of the <2 mm of marine sediment fraction (ie, sand, silt and clay) from Iceland and East Greenland can detect peaks in volcanic glass concentrations (weight%) even though discrete tephra layers are not visible; thus it provides a rapid overview of the probable location of volcanic glass within sediment sequences. Experiments in spiking samples from Baffin Bay and an artificial mixture of minerals with known weight% fractions of an Icelandic tephra (Hekla 4) demonstrate a significant correlation ($r^2 = 0.92$ and 0.97) between known and estimated weight percentages, although the slope of the measured to observed weight% is around 0.65 and not 1.0 as expected. In core B997-321PC off North Iceland we identify tephras from point counting in the >150 μm fraction and identify these same peaks in XRD scans – two of these correlate geochemically and chronologically with Hekla 1104 and 3. At a distal site to the WNW of Iceland, on the East Greenland margin (core MD99-2317), the weight% of volcanic glass reaches values of 11% at about the time of the Saksunarvatn tephra. The XRD method identifies the presence of volcanic glass but not its elemental composition; hence it will assist in focusing attention on specific sections of sediment cores for subsequent geochemical fingerprinting of tephras.

Key words: Tephra detection, x-ray diffraction, XRD, marine sediments, Iceland, Greenland, Holocene.

Introduction

In so far as tephras provide potentially unambiguous isochrones, then our understanding of the dynamics of the climate system on Holocene timescales will be greatly improved if we can detect and correlate such events over hundreds to thousands of kilometres (Wastegård *et al.*, 2001; Pilcher *et al.*, 2005). In the last few years numerous studies have indicated that materials from the numerous volcanic eruptions from the Icelandic volcanic system (Figure 1) (Larsen, 2000; Haflidason *et al.*, 2000; Hardardottir *et al.*, 2001) have been widely distributed across NW Europe and broadly across the northern North Atlantic region (Dugmore *et al.*, 1995; Turney *et al.*, 1997; Wastegård, 2002; Jennings *et al.*, 2002, 2005; Pilcher *et al.*, 2005) as macro-, crypto- or microtephra. In most cases these events are not marked by discrete visible layers (macrotephra) (for example, see Andrews *et al.*, 2002a) but can be determined only from point-counting the sand fraction or by density separation techniques (Turney *et al.*, 1997; Bond *et al.*, 2001).

Terminology

We have encountered some difficulty in the selection of an appropriate terminology for the kind of tephra that our method can detect. This is largely because the 'tephra community' is in the midst of debating an acceptable terminology. Our

*Author for correspondence (e-mail: andrewsj@colorado.edu)

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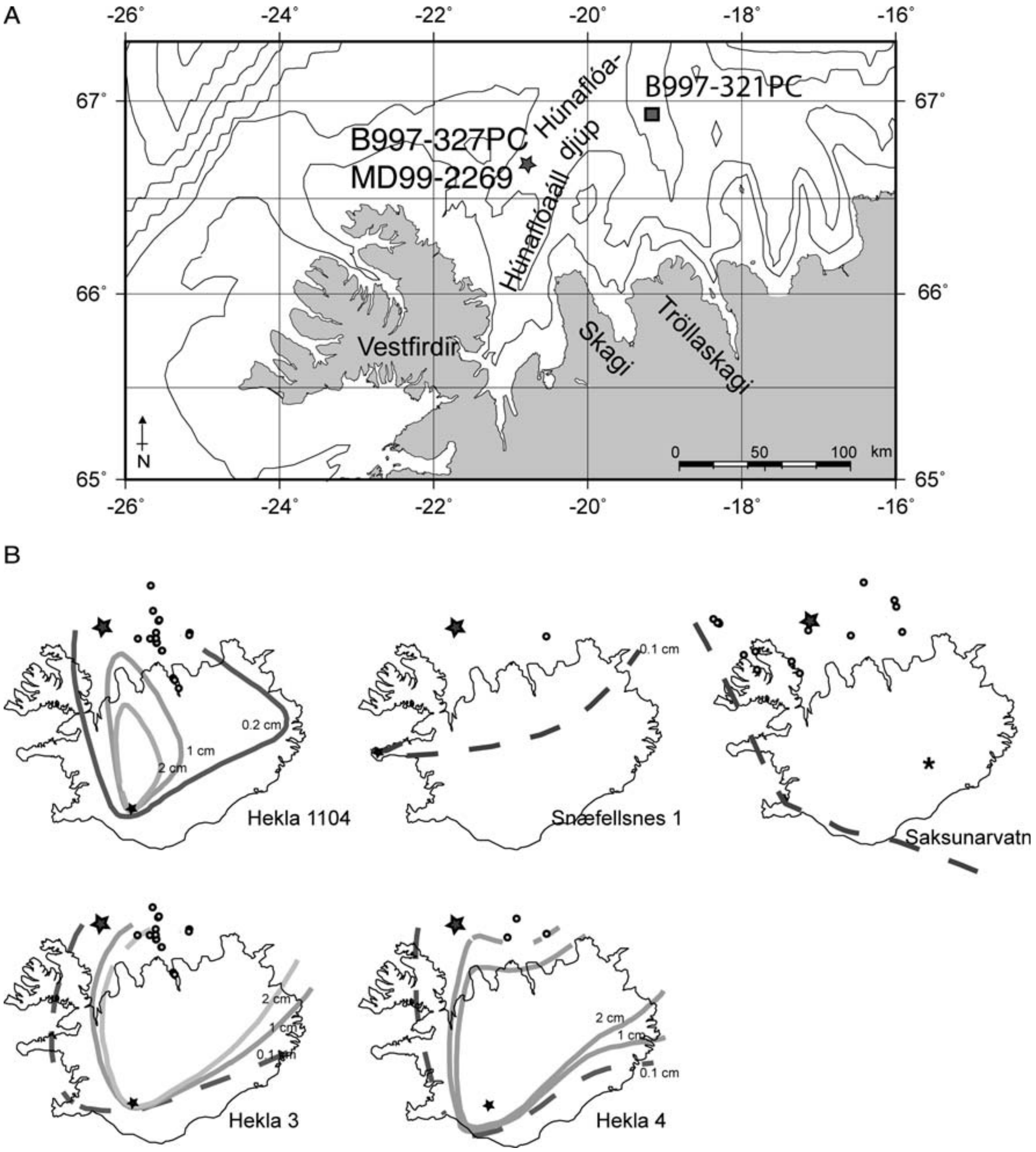

Figure 1 (A) Location map of the core sites off N Iceland (MD99-2269, B997-321PC and B997-327PC, which is at the same location as MD99-2269) and (B) some examples of mapped distributions of tephras around Iceland showing, in open circles, the reported occurrence of each tephra in marine sediment cores on the Iceland shelf. The basaltic Saksunarvatn tephra is a visible layer in the cores while the other tephras, all rhyolitic, are microtephras (see Kristjansdottir, 2005 and Kristjansdottir *et al.*, 2006 for details on sources). The star symbol shows the location of MD99-2269 and B997-327PC

method detects tephra events that are not visible as a discrete sedimentary layer, thus they fall into the category of either cryptotephras or microtephras. In some uses 'cryptotephras' contain sand-size glass shards whereas 'microtephras' consist of grain-sizes < 63 μm. Our method looks at the full range of sediment compositions < 2 mm and hence has the potential to detect both. However, following what we gather is the consensus of the community we will refer to tephras that are not visible as a discrete unit as only microtephras.

Importance

Based on our experience of the marine sediments off North Iceland we propose that x-ray diffraction (XRD) can be used to detect tephras that are not visible by eye or on x-radiographs. The method is 'exploratory' in the sense that it provides evidence for the presence of significant amounts of 'vitreous ash' (volcanic glass finer than 2 mm) – we will use the term 'tephra' (derived from the Greek for 'ash') to describe such material. The method is also rapid, especially when compared with the time taken for density separations or for sieving and point counting, and its attraction is that it will focus attention on specific depths within a core rather than the need to examine every sampled level.

An alternative exploratory method might be magnetic susceptibility scans of sediment cores, but on the Iceland and East Greenland margins the tephras do not stand out as peaks in susceptibility because of the high background readings of the sediment – indeed, the prominent Saksunarvatn tephra is distinguished in Icelandic marine sediments by a magnetic susceptibility low (Andrews *et al.*, 2002a). Rapid x-ray fluoresence (XRF) scanning of sediments is also now possible, although this method is limited to the detection of the major

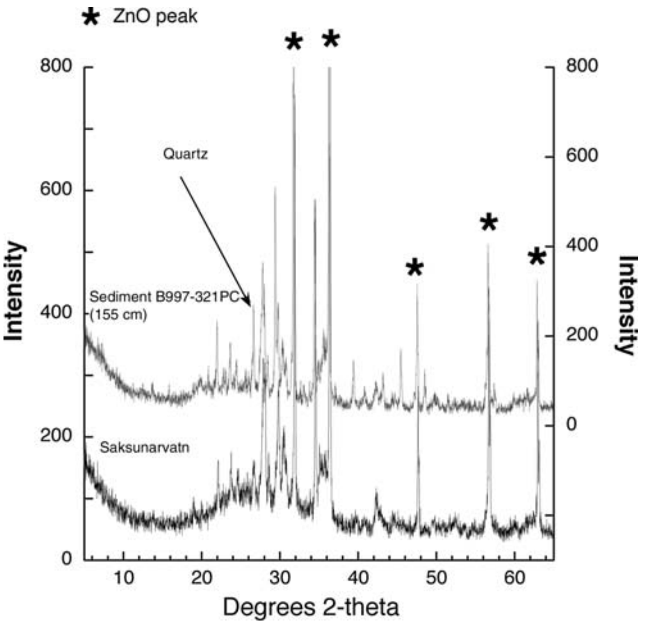

Figure 2 Examples of XRD scans of a sediment sample from B997-321PC at 155 cm depth versus a scan of tephra from the Saksunarvatn event. The peaks for quartz and ZnO are identified. Examples of weight% estimates from RockJock5 are shown in Tables 1 and 2. Intensity is counts per 2 seconds. Note the offset of scale on the right-hand axis designed to separate the two plots

and minor elements and thus does not distinguish mineral species. In reality, studies can benefit from the application of complimentary exploratory methods.

Preparation of samples

As part of an investigation of ice rafting onto the Iceland shelf (Andrews *et al.*, 2005; Moros *et al.*, 2006) we have run ~500 samples from surface and downcore marine sediments using a quantitative x-ray diffraction method (Eberl, 2003). On examining the XRD scans it was noticeable that they frequently contained a broad peak in the scans centred between 20° and 30° 2-θ (Figures 2 and 3). Previous investigations had indicated that this was frequently a measure of volcanic glass, probably associated with the large amount of amorphous materials created by these events (Figure 3). In RockJock5, an Excel macroprogram (Eberl, 2003), the list of mineral species includes a generic rhyolitic volcanic glass as well as the rhyolitic White River tephra of Alaska. The distinction that we make between 'glass' and 'tephra' can be seen by comparing Figure 3 with Figure 2. Based on RockJock, the surface marine sediments on the Iceland shelf contain on average 22 weight% of volcanic glass in the <2 mm sediment fraction (J.T. Andrews, unpublished data, 2006) (Table 1, Figure 4). There are considerable variations in the weight% estimates but they are regionally consistent – for example the area of low weight% in the fjord region of NW Iceland (compare Figures 1B and 4).

Sample preparations for the x-ray diffraction procedures are detailed in Eberl (2003, 2004). This approach was placed third in the international competition for the Reynolds Cup a competition to determine the quantitative composition of 'unknown' mineral mixtures (McCarty, 2002). Briefly, 3 g of sediment <2 mm is weighed and mixed with 0.333 g of zincite (ZnO) (the latest protocols now call for 1 g of sediment and 0.111 g of ZnO). The mixture is placed in a McCrone micronizing mill (O'Connor and Chang, 1986) with 4 ml of methyl alcohol and milled for 5 min. The sample is then oven dried at 80°C, sieved through a 500 μm screen, and about 1 g of the mixture is tapped into a side-mounted holder (Eberl, 2003). The samples are then placed in an x-ray diffraction machine, in this case a Siemens D500, and the sample is scanned between 5° and 65° 2-θ in 0.02° steps at 2 second scans. The sample rotates during the scanning process at 30 rmp, thus ensuring a representative scan of the sample's surface. The specifics of the XRD set-up are detailed in Eberl (2003). The output file is then pasted into RockJock5, a 50 MB Excel program, which evaluates the goodness-of-fit between a calculated mineral assemblage and the observed XRD scan. The output is an estimate of the weight% of non-clay and clay minerals (Table 1). An important point is that the weight% of each mineral is computed independently and hence the closeness of the total sum to 100% is a measure of the appropriateness of the chosen composition. However, the data are frequently presented as normalized to 100% (Table 1). The identification of tephra material is based on electronically cleaned XRD scans, as illustrated in Figure 3 – in RockJock this pattern is called

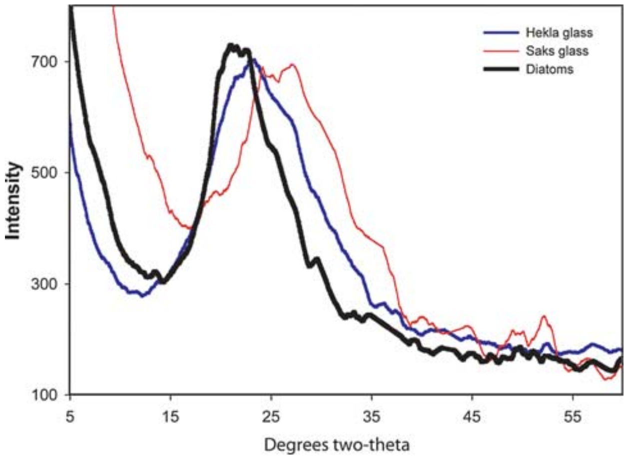

Figure 3 Plots of x-ray diffraction (XRD) intensities for Hekla 4 and Saksunarvatn glass compared with another source (diatoms) of amorphous silica. The various minerals present in XRD scans (Figure 2) have been electronically removed so as to emphasize the broad hump caused by the amorphous materials in the glass versus the amorphous silica (opal) in the sample of diatoms

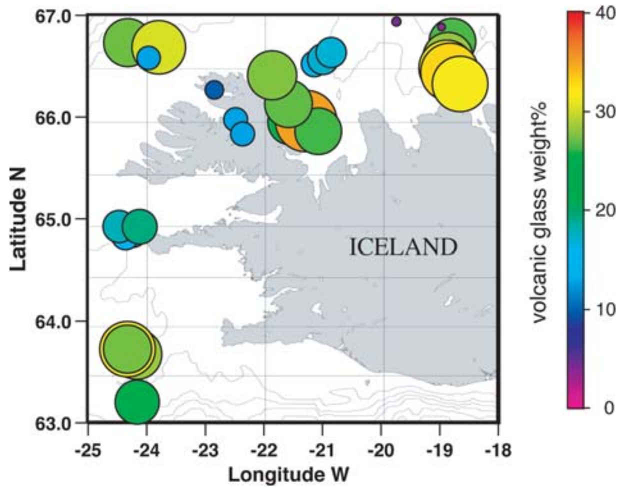

Figure 4 Map showing the weight% of tephra as determined from XRD scans and use of RockJock in the non-clay mineral fraction on sea floor surface sediments from Iceland west of 18° longitude

Table 1 Example of results from B997-321PC as weight%. Sample 12944 is from 155 cm. Sample normalized to sum to 100%

Full pattern degree of fit:	0.106
Quartz	1.3
Intermediate Microcline feldspar	1.0
Labradorite feldspar	11.6
Bytownite feldspar	9.4
Anorthite feldspar	0.6
Calcite	8.5
Mg-calcite	0.0
Aragonite	0.0
Dolomite	0.0
Halite	3.3
Amphibole	0.1
Pyroxene	11.5
Pyrite	0.7
Magnetite	0.9
Hematite	0.5
Maghemite	0.0
Volcanic glass	37.6
Total non-clays	86.8
Kaolinite	0.0
Saponite	5.0
Ferruginous smectite	2.7
1Md illite	0.0
1M Illite	4.2
Chlorite	1.2
Serpentine	0.0
Total clays	13.2
Total	100.0

'volcanic glass' and it constitutes the amorphous phases of the tephra, which is mineralogically more complex (Table 2).

The preparation time per sample is around 15 min spread over 24 h. The XRD scan then takes 100 min per sample, and the calculation of the weight% data on RockJock takes between 15 and 25 min. We have routinely processed 50–70 samples per week using a 40-sample cassette – thus within a week our method could provide information on a 3.5 m core sampled every 5 cm.

Table 2 Comparison between Hekla 4 and Saksunarvatn tephras (two different samples)

Mineral	Hekla 4	Saks 2	Saks 3
Quartz	3.2	0.2	1.2
Ordered Microcline feldspar	0	0	0
Intermediate Microcline feldspar	1.1	0	1.9
Andesine feldspar	1.4	3.2	0
Labradorite feldspar	5.8	7.9	9.5
Bytownite feldspar	0.2	9.1	0.8
Pyroxene	0	0	0
Magnetite	0.3	4.8	5.8
Maghemite	0	13.2	9.7
Volcanic glass (from Hekla)	87.5	58.0	67.9
Total	99.5	96.4	96.8
Normalized to 100%			
Quartz	3.2	0.2	1.2
Ordered Microcline feldspar	0.0	0.0	0.0
Intermediate Microcline feldspar	1.1	0.0	2.0
Andesine feldspar	1.4	3.3	0.0
Labradorite feldspar	5.8	8.2	9.8
Bytownite feldspar	0.2	9.4	0.8
Pyroxene	0.0	0.0	0.0
Magnetite	0.3	5.0	6.0
Maghemite	0.0	13.7	10.0
Volcanic glass (from Hekla)	87.9	60.2	70.1
	100.0	100.0	100.0

Samples processed for this study

We investigated the variations in mineral composition in cores B997-321PC and B997-327PC from the north Iceland Shelf (Figure 1) (Helgadottir, 1997), with the goal of examining the variations in quartz weight% as a proxy for variations in drift ice off the Iceland coast (Koch, 1945; Ogilvie, 1996; Eiriksson *et al.*, 2000; Knudsen *et al.*, 2004; Moros *et al.*, 2006). Core B997-321PC occurs within an area where drift ice has been noted and it is a core where point-counts identified tephras as discrete peaks in fresh, sand-size tephra shards (Kristjansdottir, 1999). Laser-based grain-size measurements (Andrews *et al.*, 2002b) of the tephra units in core B997-321PC at 35 and 135 cm (see below) and other intervals (Figure 5) show that the bulk of the sediment is in the silt-size range with average compositions of 62 samples as ~10% sand, 62% silt and 28% clay. There is nothing distinctive about the grain-size spectra of the two tephras that might warrant inspection and there is no well-defined magnetic susceptibility peak.

To investigate the changes in XRD patterns and prediction capabilities we prepared a small suite of samples for XRD from HU76029-033 from Baffin Bay that had been spiked with 0%, 0.09%, 4.3%, 8.2%, 15% and 20.8% by weight of Hekla 4 tephra. We also prepared an artificial mixture of minerals (labradorite feldspar 50%, calcite 5%, pyroxene 20%, magnetite 10%, ferruginous smectite 10%, 1M illite 5%), intended to reflect an 'Icelandic' mixture, to which we added 0%, 1%, 5%, 10%, 20%, 30% and 40 weight% of Hekla 4 tephra.

We investigated the XRD patterns of the basaltic Saksunarvatn ash and the rhyolitic Hekla 4 tephra (Figures 2 and 3). The Saksunarvatn ash was obtained from a 1 m unit in a lake core from Hvitarvatn, central Iceland (Black *et al.*, 2005), and the Hekla 4 tephra was taken from an outcrop near this lake (A. Geirsdottir, personal communication, 2005).

Counts were made of the composition of the >150 µm sand fraction in B997-321PC (Figure 1) using a binocular microscope (Kristjansdottir, 1999). At least 300 grains were counted and each particle was assigned one of the following categories: fresh dark tephra, fresh silica-rich (light) tephra, lithics – including reworked tephra, biogenic particles (foraminifera, mollusks, diatoms), and others. The data were converted to percentages. At three levels, ~35, 135 and 268 cm, geochemical elemental analyses were performed on tephra shards at the Nordic Volcanological Institute (Kristjansdottir, 1999). An initial chronology for this core is based on four ^{14}C AMS radiocarbon dates on marine mollusks; three were used in Kristjansdottir's (1999) study (Smith and Licht, 2000) and an additional date has been obtained for this study. The dates were calibrated using CALIB 5 with no correction to the ΔR (ocean reservoir) term, although it appears that some correction will be required (Larsen *et al.*, 2002; Eiriksson *et al.*, 2004; G.B. Kristjansdottir, J.S. Stoner, A.J.T. Jull, J.T. Andrews and A.E. Jennings, unpublished data, 2006). The age used in the depth/age calculations is the mid-point between the ±2 sigma estimates. The chronology for B997-327PC (same site as MD99-2269, Figure 1) has been presented previously and is constrained by five AMS radiocarbon dates (Andrews *et al.*, 2003).

Results and discussion

It is clear from our data (Figure 4) that sediments on the Iceland shelf have a high proportion of volcanic glass. However, in places where tephras have been located in NW

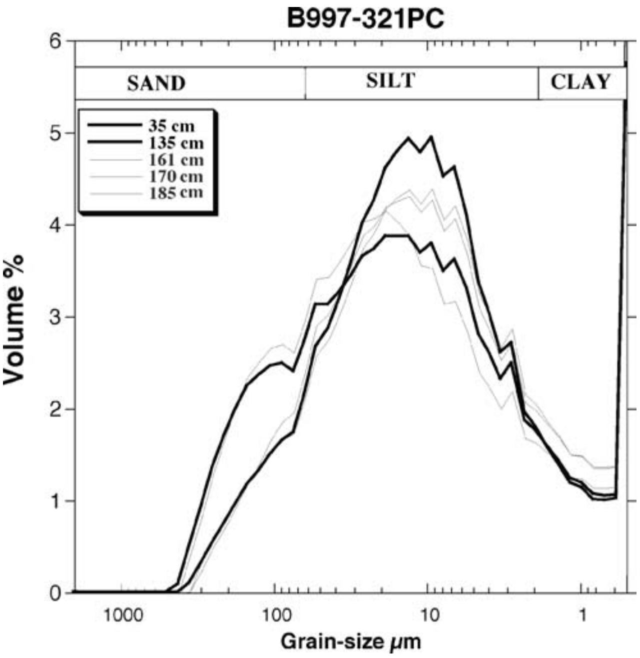

Figure 5 Grain-size spectra of intervals in B997-321PC with identified tephras or no discrete tephra

Europe the bedrock and soils would have little or no tephra to erode. The question is, at what level could quantitative XRD analyses of the <2 mm sediment fraction (the vast bulk of Holocene lake and marine sediments) detect an eruptive event? To investigate this question we took marine sediment from Baffin Bay (core HU76029-033, Hillaire-Marcel *et al.*, 1989) (71° 20′N and 64° 16′W) where the surrounding bedrock is similar to parts of Fennoscandinavia (granites and gneisses and Palaeozoic carbonates). The results from the five XRD scans and analysis in RockJock5 indicated a highly significant association between the weight% of Hekla 4 and that estimated (Figure 6). With $n = 6$, $r^2 = 0.92$ with 95% errors on the regression coefficients of ± 0.14 on the slope and ± 1.7 on the intercept. The slope, which in the ideal case would equal 1.0, has 95% limits of between 0.46 and 0.89.

Artificial sediment was made by mixing together known weights of laboratory minerals (see earlier). The results in terms of estimated weight% of tephra (Figure 6) are similar to those from the previous experiment with $r^2 = 0.97$ ($n = 7$). The intercept is not zero and the least squares regression (Figure 6) has 95% confidence limits on the intercept of between 7.8 and 11.8 with a slope lying between 0.51 and 0.7. The slopes on the two lines (Figure 6) are not statistically different (Till, 1974). Although we have run hundreds of samples where the estimates of volcanic glass were close to zero weight% the samples that we used for the spiking experiments have a moderate background of amorphous material. In the artificial mixture no such material was added. We are presently trying to resolve the cause of this anomaly.

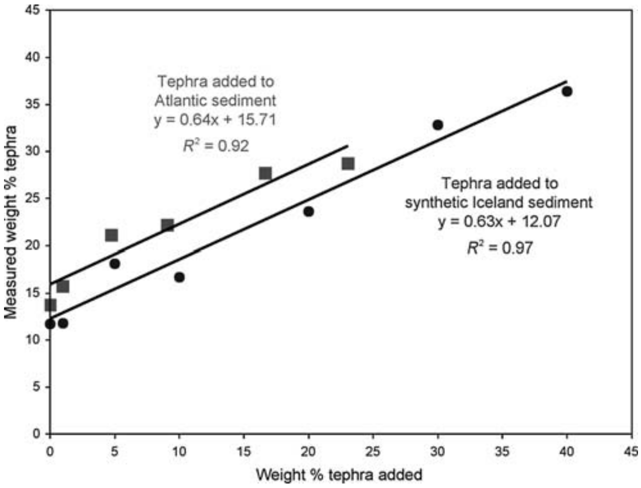

Figure 6 Results of an experiment where various weight% of Hekla 4 tephra were added to mid-Wisconsinan marine sediments from Baffin Bay (core HU76029-033), and where various weight% of Hekla 4 tephra were added to an artificial mixture of 'Icelandic' volcanic composition, showing the regression lines, linear least squares equations and explained variances

Basaltic versus rhyolitic tephra

Initial experiments show that there are, as might be expected, measurable differences in XRD scans between the rhyolitic Hekla 4 tephra and the Saksunarvatn basaltic tephra (Figures 2 and 3). Table 2 shows a comparison of the mineralogy between the Hekla 4 and Saksunarvatn tephras based on the non-clay fraction. There are notable differences between the mineralogies of sediments (Table 1) and the tephras (Table 2). A sample of Hekla 4 tephra has 87.5 weight% of glass compared with 58 and 67.9 weight% of glass in two (not identical) Saksunarvatn samples. These variations are similar, in a relative sense, to determinations of the relative amounts of SiO_2 in rhyolitic versus basaltic tephras (65–75% versus 45–55%), and suggest that the XRD method will, in future, be able to distinguish between basaltic and rhyolitic tephras. Work is on-going on this particular question.

Downcore identification of intervals of high weight% tephra

The sediments we processed are all splits from the samples processed for grain-size and for point counting. We processed samples at 5-cm intervals, which corresponds to a resolution averaging 80 yr/sample in B997-321PC and ~ 50 yr in B997-327PC.

The plots of volcanic glass weight% B997-321PC for the <2 mm size fraction (Figure 7) shows a series of discrete peaks that we compare with Kristjansdottir's (1999) point-counts from the same samples. The grain-counts of silica-rich tephras have background percentages of 2–15%, which is presumably caused by reworking of the sediments, with four peaks rising well above this background noise. The peaks at 35 and 135 cm have interpolated ages of 925 and 3615 cal. yr BP, whereas the peaks at ~ 70 and 150 cm have age estimates of 1550 and 4150 cal. yr BP. The RockJock5 analyses (Figure 7) also identify the 35 and 135 cm peaks as major intervals of tephra accumulation. The background is around 30% volcanic glass, which implies a steady input of air-fall tephras and/or substantial reworking of sediments at the sea floor. Elemental analyses of the glass shards at 35 and 135 cm in core 321 indicate an affiliation with the Hekla 1104 and Hekla 3 eruptions (Kristjansdottir, 1999); these correlations indicate errors in the age/depth interpolations of around -100 and $+500$ yr.

There are correlations between the two methods (Figure 7), but there are also differences. These may be caused by (a) the point counts include only fresh tephra grains, or (b) some volcanic glass peaks (Figure 7) may include only materials <63 µm (Lacasse, 2001) – ie, the microtephras of Great Britain and NW Europe (Turney *et al.*, 1997; Wastegård, 2002; Hall and Pilcher, 2002). A significant fraction of silt and clay-size eruptive materials are definitely deposited on the Iceland shelf; this is borne out by the weight% data on Figure 4, which are substantially greater than the weight% of sand in the surface sediments (Andrews *et al.*, 2002b).

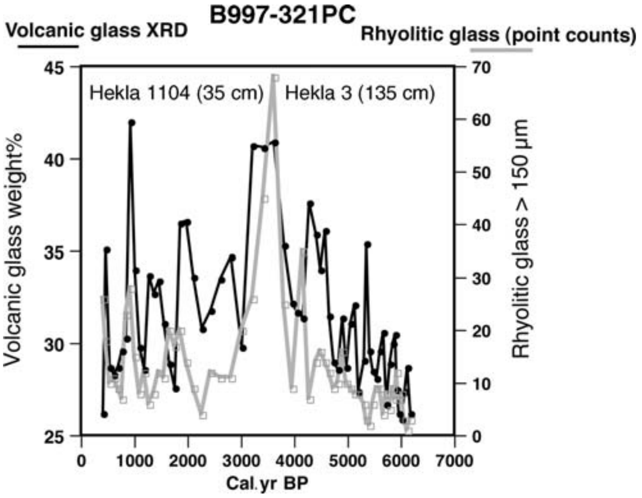

Figure 7 Comparison of the results of counting the >150 µm sand fraction for volcanic shards and the weight% of volcanic glass determined from quantitative XRD analysis on core B997-321PC (Figure 1). The two Hekla tephra layers were geochemically identified as Hekla 1104 and Hekla 3 (Kristjansdottir, 1999)

Because the Holocene marine sediments off Iceland contain substantial amounts of volcanic glass (Figures 4 and 7) we developed a preliminary protocol for identifying discrete tephra events that will warrant further investigation. This protocol may not be necessary for sites hundreds of kilometres removed from Iceland (see later). The protocol is as follows (Figure 8A and B): a low order polynomial is fitted to the weight% volcanic glass data and the residuals (observed − predicted) obtained. The standard deviation of the residuals is calculated and the data are plotted with a cut-off at +1 sigma, thus excluding approximately 86% of the measurements. These residuals are plotted on Figure 8A and B for cores B997-321PC (the chronology for B997-321PC was adjusted to include the ages and depths of Hekla 1104 and Hekla 3) and B997-327PC (Figure 1) and compared with the grain-counts in B997-321PC and with microtephras identified in MD99-2269. In a detailed inspection of the sand-size tephra grains in MD99-2269 (Figure 1) (Kristjansdottir, 2005; Kristjansdottir *et al.*, 2006) basaltic and rhyolitic microtephras were isolated, microprobed and age estimates obtained. The estimated ages of the tephras in MD99-2269 can be matched with temporal equivalent peaks in core B997-321PC (Figure 8A); this would provide a 'first-look' exploratory template for additional sampling and geochemical analyses.

In a pilot study of the application of the method to a more distal region, we ran samples from core MD99-2317 (68.103°N and 27.861°W) (Jennings *et al.*, 2006) some 500 km or so to the WNW of Iceland, off East Greenland. We selected a part of the core that spanned the Saksunarvatn tephra (~ 10.20 cal. ka BP, or 9.0 ^{14}C ka BP) – it is known that the Saksunarvatn tephra reached the summit of the Greenland Ice Sheet (Gronvold *et al.*, 1995). The results (Figure 9) show that values of <1% are estimated on either side of peaks in volcanic glass that date slightly after the time of the Saksunarvatn eruption (Jennings *et al.*, 2006). This is an example of where the XRD method would direct research towards a more focused examination of part of a sediment record. The cleaned XRD pattern of biogenic silica ($\sim$ diatoms) has a pattern not dissimilar to volcanic glass although the peak is offset (Figure 3) and it would not contain the ancillary minerals noted in raw scans (Figure 2). The inputs of tephras into lake and seawater provide a source of nutrients, which may trigger diatom blooms.

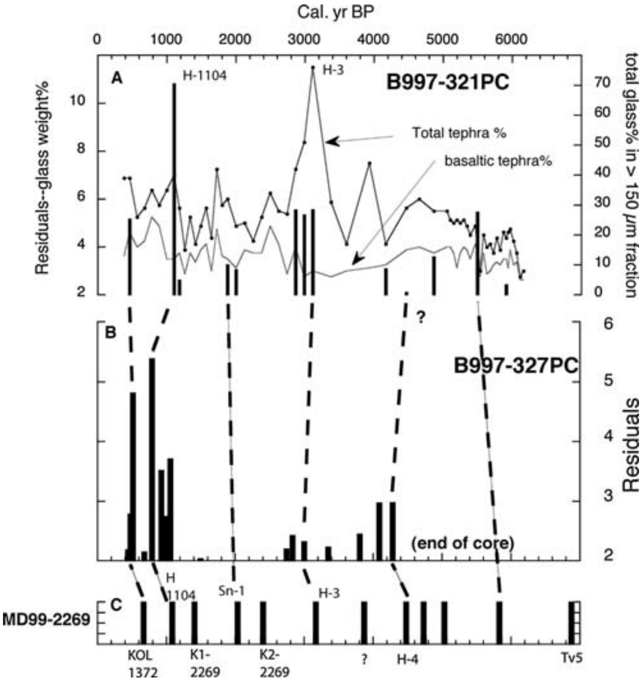

Figure 8 (A) Data from B997-321PC showing the total percentage of glass in the point counts on the >150 µm fraction versus the location of peaks in volcanic glass that exceed the +1 sigma rule (see text). The timescale has been changed by using the two Hekla peaks identified in this core (Figure 7). (B) Peaks in volcanic glass in B997-327PC (Figure 1) that exceed the +1 sigma rule. (C) Geochemically identified microtephras in MD99-2269: KOL, Kolbeinseyridge; H, Hekla; K, Katla; Sn, Snæfeusnes; Tv, Torfadalsvatn (Kristjansdottir, 2005; Kristjansdottir *et al.*, 2006). The chronology of this core is very well constrained with 44 AMS ^{14}C dates (Stoner *et al.*, 2006); 23 tephras were identified from point counts and were probed for major elemental composition of which 11 lie within the time range of core B997-321PC (Figure 8C)

What cannot be done

Our results to date show that sediment intervals with high glass content can be identified (Figures 6–8). However, the method does not provide a precise geochemical fingerprint (but see Table 2), and it cannot distinguish between fresh or reworked tephras. Thus, the strength of the method will be to isolate sections in core where either point counting of the sand fraction, or geochemical separations of the fine-grained tephra fraction can be undertaken for geochemical fingerprinting. The XRD-method should thus be considered as an exploratory tool that will focus attention on specific sediment intervals. As the current sample size for the sample loader is ~ 1 g, then it is technically possible to evaluate variations in tephra occurrence for a slab of sediment 4 cm × 4 cm × 1 mm thick (assuming a density of 0.8 g/cm^3).

Conclusions

In our use of quantitative XRD analyses to distinguish intervals of ice-rafted sediment along the North Iceland shelf we serendipitously noted that volcanic glass constitutes a substantial (as to be expected) weight% fraction of sand/silt and clay (Figure 4). Experiments with spiking samples with known weight% of Hekla 4 tephra demonstrate that the

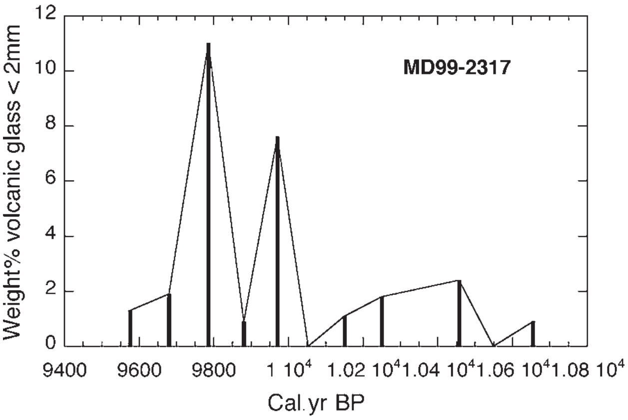

Figure 9 Volcanic glass weight% data from core MD99-2317 off East Greenland (Jennings *et al.*, 2006) in an interval of the core where we might expect to find Saksunarvatn tephra

method can detect the addition of a tephra although the slope of the relation is < 1 (Figure 6). Because the intercepts are > 0 and the slopes < 1, the estimates of absolute abundance are imperfect. Further experiments are planned but our conclusion is that values of > 10–15% by weight of tephra can probably be detected (Figure 9).

Standing above an overall background we noted several peaks in weight% of volcanic glass that correlate with point counts of glass shards in core B997-321PC. In addition, peaks in weight% of volcanic glass appear coeval with tephras identified geochemically in MD99-2269 and with peaks in the weight% of volcanic glass in B997-327PC from the same site (Figure 8).

The method provides an initial exploratory approach to detecting the presence of tephra materials in the sand/silt/clay size fractions of sediments, but it does not provide *a priori* a geochemical fingerprint to distinguish between tephra sources. The results in Table 2 show that there are mineralogical variations between basaltic and rhyolitic tephras, but how consistent these are remains to be evaluated.

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