Holocene tephras highlight complexity of volcanic signals in Greenland ice cores

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[1] Acidity peaks in Greenland ice cores have been used as critical reference horizons for synchronizing ice core records, aiding the construction of a single Greenland Ice Core Chronology (GICC05) for the Holocene. Guided by GICC05, we examined sub-sections of three Greenland cores in the search for tephra from specific eruptions that might facilitate the linkage of ice core records, the dating of prehistoric tephras and the understanding of the eruptions. Here we report the identification of 14 horizons with tephra particles, including 11 that have not previously been reported from the North Atlantic region and that have the potential to be valuable isochrons. The positions of tephras whose major element data are consistent with ash from the Katmai AD 1912 and Öraefajökull AD 1362 eruptions confirm the annually resolved ice core chronology for the last 700 years. We provide a more refined date for the so-called "AD860B" tephra, a widespread isochron found across NW Europe, and present new evidence relating to the 17th century BC Thera/Aniakchak debate that shows N. American eruptions likely contributed to the acid signals at this time. Our results emphasize the variable spatial and temporal distributions of volcanic products in Greenland ice that call for a more cautious approach in the attribution of acid signals to specific eruptive events.

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1. Introduction

[2] The Greenland ice cores provide among the most detailed records of past environmental change that can be reconstructed through the study of various chemical and isotopic signatures within the ice [e.g., *Lamb*, 1970; *Hammer*, 1977; *Alley*, 2000; *Stuiver and Grootes*, 2000; *NGRIP Members*, 2004; *Rasmussen et al.*, 2007]. Much of the value of these archives is associated with their highly resolved timescale [*Andersen et al.*, 2006; *Rasmussen et al.*, 2006; *Svensson et al.*, 2006, 2008; *Vinther et al.*, 2006], the superior precision of which has improved the understanding of the timing and duration of major palaeoenvironmental changes [e.g., *Rasmussen et al.*, 2006]. This is particularly true at times when the precise dating of other terrestrial and marine sediments by methods such as ^{14}C dating have been hampered by varying levels of uncertainty [e.g., *Davies et al.*, 2008].

[3] Research since the early 1990s has demonstrated that numerous far-traveled tephras can be detected in the southern and central Greenland ice cores [*Ram and Gayley*, 1991; *Palais et al.*, 1991, 1992; *Fiacco et al.*, 1993; *Grönvold et al.*, 1995; *Zielinski et al.*, 1997; *Mortensen et al.*, 2005; *Davies et al.*, 2008]. Establishing the presence of tephras in the ice cores aids chronology construction in two respects. First, where historical tephras (i.e., the source eruption is historically documented) are found, these can be used to validate the precise chronology of the ice cores [e.g., *Vinther et al.*, 2006]. Second, where non-historical tephras occur, the age estimate of these tephras can be greatly improved beyond the level of precision offered by most other dating methods through the assignation of the ice core date to the tephra [e.g., *Grönvold et al.*, 1995]. As isochrons, both historical and non-historical tephras enable the direct linkage of ice, terrestrial and marine sediments wherever a given tephra is identified, and can aid the reconstruction of the wider environmental impacts of a given eruption. In this work, we target several well-documented tephras to fulfill several main objectives: first, to test the ice core chronology using the following historical eruptions: Katmai AD 1912, Laki AD 1783–4, Öraefajökull AD 1362, Hekla AD 1104, Eldgjá ~AD 930s, the Settlement Layer ~AD 870s and Vesuvius AD 79; second, to use the ice core chronology to ascertain precise ages for Thera ~17th century BC and Hekla 4 ~2300 BC; third, to look for tephra that would establish the source of

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Table 1. Sections of the Greenland Ice Cores Investigated in This Study and the Tephra Layers Recorded in Each Section

Depth (m)	Section Age AD/BC[a]	Target Tephra	Tephras Found
		DYE-3	
325.6–327.8	AD 1360.2–1365.4	Öraefajökull AD 1362	QUB-1303/1304
427.35–430.1	AD 1103.6–1110.6	Hekla AD 1104	none
492.8–495.55	AD 929.4–936.0	Eldgjá ~AD 930s & Settlement ~AD 870s	QUB-1212/1213
1352.45–1367.3	2381.3–2287.5 BC	Hekla 4 ~2300 BC	QUB-1539
		GRIP	
67.1–67.65	AD 1782.5–1784.7	Laki AD 1783–1784	none
164.45–165.55	AD 1360.4–1365.8	Öraefajökull AD 1362	QUB-1052
218.35–222.75	AD 1091–1111.5	Hekla AD 1104	none
830.5–837.1	2277.9–2232.8 BC	Hekla 4 ~2300 BC	none
849.75–850.85	2368.9–2361.8 BC	Hekla 4 ~2300 BC	none
		NGRIP	
27.5–28.6	AD 1910.8–1915.0	Katmai AD 1912	QUB-1004
141.9–143.55	AD 1358–1367.0	Öraefajökull AD 1362	none
159.5–164.45	AD 1243.5–1270.1	AD 1259	QUB-1360
187–197.45	AD 1059.4–1117.6	Hekla AD 1104	QUB-1186
216.15–235.4	AD 845.5–953.6	Eldgjá ~AD 930s & Settlement ~AD 870s	QUB-1425; QUB-1437 (2 populations, -1437a, -1437b); QUB-1470; QUB-1528
364.1–369.6	AD 67.8–101.4	Vesuvius AD 79	QUB-1328
634.7–647.35	1682.6–1598.6 BC	Santorini – Thera ~17th century BC	QUB-1188; QUB-1198; QUB-1201
746.9–748	2368.8–2362.1 BC	Hekla 4 ~2300 BC	none

[a]According to GICC05 [*Vinther et al.*, 2006].

an acid spike at AD 1259; and finally, to examine the relationship between the positions of tephra layers and peaks in the electrical conductivity (ECM) and sulfate records in the ice cores.

2. Methods

[4] Our research has focused on the Dye-3, GRIP and NGRIP ice cores, collected from southern, central and northern Greenland respectively. While the GRIP and NGRIP cores provide high resolution records of the Last Glacial, the Dye-3 core is characterized by a high accumulation rate that enables the distinction of seasonal cycles for the Mid- to Late Holocene. A common timescale has been developed for the three ice cores based upon linkages between volcanic signals and ECM measurements in their records [*Vinther et al.*, 2006]. There is a heavy reliance on the Dye-3 oxygen isotope record for annual layer counting during the Holocene as it provides the most complete and highly resolved data set for this time period. This is especially true for the period between ~AD 187–5903 BC in NGRIP and between ~1846–5903 BC in GRIP when the oxygen isotope record of the respective cores is insufficiently resolved to allow annual counting, and Dye-3 dating is exclusively imposed onto them [*Vinther et al.*, 2006]. Counting errors between the ice cores have been intermittently "zeroed" using the positions of acid signals attributed to specific eruptions, in some cases supported by the presence of associated tephra. As a result of this procedure, and of relevance to this investigation, the precision of the GICC05 is estimated to be within 1–2 yr for the late first millennium AD, within 1 yr for the period between AD 79 and 252 BC, within 5 yr in the 17th century BC and within 11 yr from the 17th century BC back to 2933 BC.

[5] The likely positions of the tephras targeted by this study were determined with the aid of the GICC05. The samples mainly spanned periods in which one or more acidity spikes had been recorded in the ice, some of which had an inferred association with a specific eruption. Our sampling strategy initially focused on ice immediately next to targeted acid spikes. Where we failed to find tephras associated with these features, we expanded our sampling to encompass longer time intervals and sometimes other acid spikes. As chronological resolution decreases with depth, our sampled intervals typically span more time in older ice. The subsampled sections from each core are detailed in Table 1.

[6] The ice cores were sub-sampled in the cold work area adjacent to the main cold store at the Niels Bohr Institute in Copenhagen. The 55 cm-long core sections were sliced on a band-saw, the slices divided into 10, 15 or 20 cm-long samples according to how much ice was available (see Table 2 for sample volume information). The subsamples were put into individual Nalgene bottles with screw lids and allowed to melt outside the cold room. At Queen's University Belfast, the water samples were centrifuged and the solids transferred via pipettes onto pre-ground glass slides in a laminar flow work area. Once fully dry, the residues were covered in Buehler or EpoxiCure epoxy resin and the samples were examined using light microscopy. Each slide was scanned at ×100 magnification and potential tephra shards examined at ×400 with polarized light. Slides with tephra were prepared for microprobe analysis by grinding and polishing using 12 μm alumina powder and 1 μm diamond paste until the surfaces of tephra shards were exposed through the resin.

[7] Three systems were used for microprobe analysis of single shard major element composition: a Cameca SX-100 electron microprobe at the Tephrochronology Analytical Unit, Edinburgh University; a Jeol 733 Superprobe and the Jeol FEG SEM 6500F (both at Queen's University, Belfast). Details on these systems and their operating conditions are given in Table S1 in the auxiliary material.[1] Consistency in

[1]Auxiliary materials are available in the HTML. doi:10.1029/2012JD017698.

Table 2. Number of Tephra Shards Identified Optically in Each Sample in This Study, Their Principle Composition (Following Nomenclature of *Le Bas et al.* [1986]), and Their Relationship to Other Volcanic Proxies in the Corresponding Ice Cores

Tephra Code	Depth in Ice (m)	GICC05 Age of Sample	Volume of Sample (cm^3)	Number of Shards	Number of Analyses	Composition	Association With Other Volcanic Proxies
			Dye-3				
QUB-1303/1304	325.80–326.15	AD 1364	85.9	>11	9	Rhyolitic	Coincident with small peak in ECM
QUB-1212/1213	494.45–494.85	AD 931	76.6	12	11	Rhyolitic	Coincident with low ECM peak
QUB-1539	1354.10–1354.30	2300–2298 BC	55.6	12	12	Rhyolitic	Follows small increase in ECM
			GRIP				
QUB-1052	165.20–165.40	AD 1362–1363	not recorded	>200	31	Rhyolitic	None
			NGRIP				
QUB-1004	28.25–28.45	AD 1912–1913	not recorded	26	13	Rhyolitic	Precedes peak in ECM and then SO_4^{--}
QUB-1360	162.45–162.65	AD 1254	58.6	1	1	Rhyolitic	Precedes and follows elevated ECM but coincides with acid neutralization event?
QUB-1186	189.95–190.15	AD 1101–1102	55.8	4	2	Rhyolitic	Immediately follows ECM peak
QUB-1425	216.15–216.35	AD 953–954	57.0	6	3	Rhyolitic	Follows small peak in ECM
QUB-1437	218.35–218.55	AD 941–942	59.6	32	16	a. Trachytic-trachydacitic b. Rhyolitic	Coincident with narrow SO_4^{--} peak
QUB-1470	224.40–224.60	AD 907–908	59.9	6	1	Trachydacitic	None
QUB-1528	235.05–235.25	AD 846–847	49.7	>1,000	25	Rhyolitic	Coincides with peak in ECM
QUB-1328	366.70–366.85	AD 85–87	not recorded	1	1	Basaltic	None (ECM data only)
QUB-1188	639.10–639.30	1629–1628 BC	41.8	6	4	Rhyolitic	None (ECM data only)
QUB-1198	640.95–641.15	1641–1639 BC	49.4	>15	11	Trachydacitic to rhyolitic	Coincides with large peak in SO_4^{--}, then in ECM
QUB-1201	641.50–641.70	1644–1643 BC	41.1	4	3	Rhyolitic	None

their data output has been demonstrated by *Coulter et al.* [2009]. Secondary glass standards were measured at each analytical run to ensure operating conditions were within acceptable limits of precision (see Table S1 for available data). Analyses were obtained from all shards that were sufficiently large and whose surfaces were exposed through the resin at the time of probing. All analyses are presented in Table S1 as both raw and normalized data sets. Often analytical totals were below 95% that may in some cases be due to the overlap of the beam with the epoxy resin. In other instances, however, normalization of the data indicates homogeneity in the composition that suggests variable water content in the tephras (e.g., QUB-1303/1304). To examine the correlation of our results with tephras of similar age (including reference material for targeted tephras or other, broadly contemporary tephras reported from Greenland ice cores), similarity co-efficients were calculated using the major element analyses that comprised >1% concentration of the tephras, following *Borchardt et al.* [1972]. Values ≥0.95 are accepted as indicating compositional correspondence (Table S2).

3. Results

[8] Of the 695 Holocene samples examined (representing 92.95 m of ice, and corresponding to 470 ice core years), 17 were found to contain tephra (Tables 1 and 2). In two samples, only isolated shards were observed (QUB-1360, QUB-1328) and, although geochemical analyses were obtained (Table S1), their significance as tephra isochrons is, for the time being, ambiguous. In two other instances (QUB-1303/1304, QUB-1212/1213), individual tephras were spread across two contiguous samples, and one layer (QUB-1437) contained a bimodal population representing what appear to be two coeval but distinct eruptive events, rendering a total of 14 discrete tephras. For these layers, shard abundance varied from as few as four shards up to more than 1,000 glass particles at one level, but in general, tephra concentrations were very low. The ECM and SO_4^{--} peaks attributed to Laki AD 1783–4, Hekla AD 1104, Eldgjá ~AD 930s, Settlement eruption ~AD 870s, an unidentified but presumed low-latitude event at AD 1259, and Vesuvius AD 79 were not associated with tephras detectable in the ice and their correlations with specific eruptions cannot therefore be confirmed by our tephra analysis. The majority of the tephra populations (n = 12) analyzed are rhyolitic in composition, and only one basaltic tephra (QUB-1328), an isolated shard in NGRIP dating to ~AD 85–87, was recorded. These tephra populations are discussed below.

3.1. QUB-1004 (GICC05 Age AD 1912–1913)

[9] Twenty-six tephra shards were detected by light microscopy at a depth of 28.25–28.45 m in NGRIP, equating to an age of AD 1912 (QUB-1004). Geochemical analyses are predominantly consistent with the initial, high silica phase of the Katmai eruption (similarity co-efficient = 0.97), with one shard correlating with the transitional rhyolite identified by *Federman and Scheidegger* [1984]; another shard is evidently an outlier (Figure 1 and Table S1). Rhyolitic Katmai tephra has previously been reported from the GISP2 ice core (quoted as 'unpublished finding' in *Zielinski and Germani* [1998, p. 285]), and our major element data indicate that the tephra reached Greenland, highlighting the potential to find this tephra in sedimentary sequences across N. American high latitudes.

3.2. QUB-1052 (GICC05 Age AD 1362–1363) and QUB-1303/1304 (GICC05 Age AD 1364)

[10] Over 200 shards were found in the GRIP core at a depth of 165.05–165.25 m in ice dated by GICC05 to

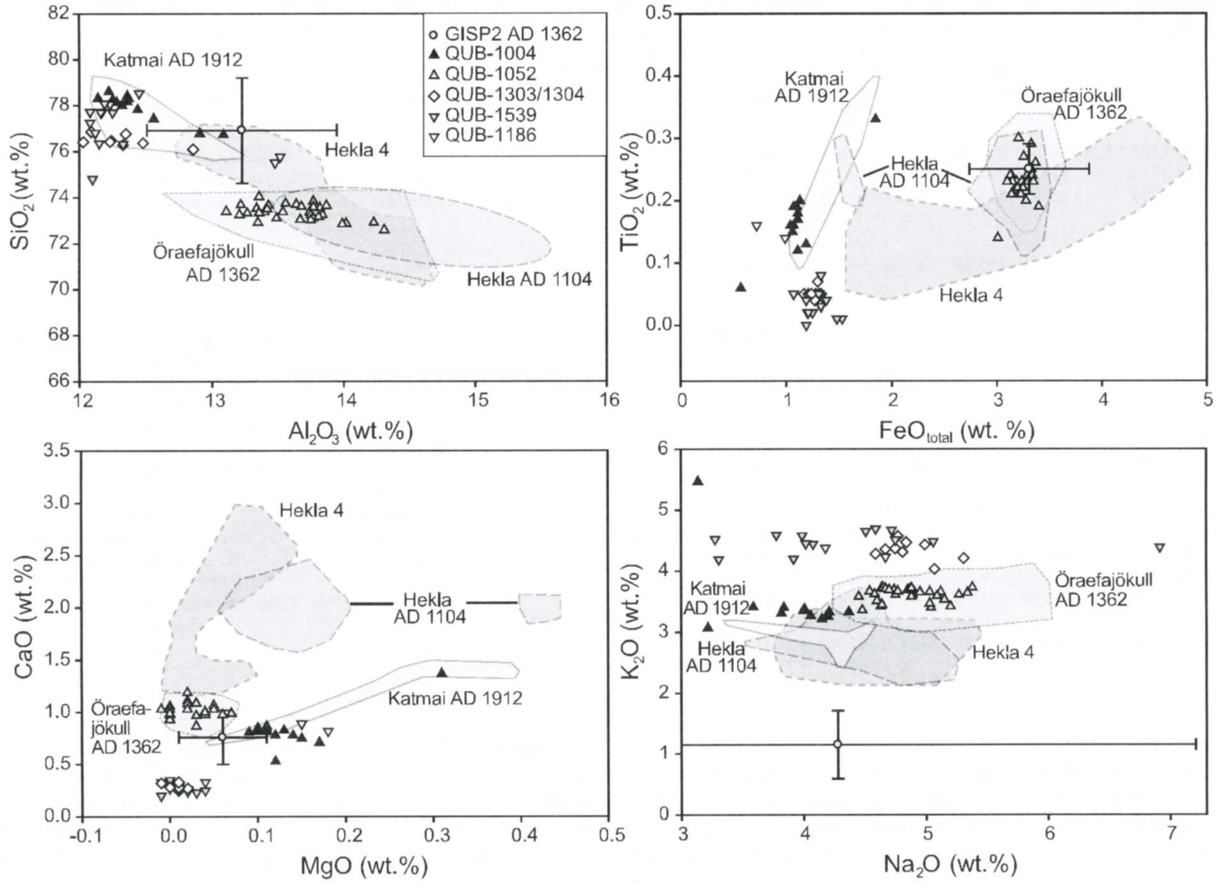

Figure 1. Binary plots illustrating the geochemical comparisons of tephras (excluding layers dating to ~AD 850–950 and 17th century BC) found in the Greenland ice cores. Data have been normalized for presentation. Each datapoint represents a single analysis except in the case of the AD 1362 tephra in GISP2, for which the mean and standard deviation (from eight analyses) have been plotted. Geochemical ranges of comparative material (excluding outliers) for Katmai AD 1912, Öraefajökull AD 1362, Hekla AD 1104 and Hekla 4 (rhyolitic component) are represented by gray envelopes. The following data sets have been used for comparison: Katmai AD 1912 matrix glass [*Palais and Sigurdsson*, 1989; *Federman and Scheidegger*, 1984; *Fierstein and Hildreth*, 1992]; Öraefajökull AD 1362 in Iceland [*Larsen et al.*, 1999] and Ireland [*Pilcher et al.*, 1995]; GISP2 AD 1362 tephra [*Palais et al.*, 1991]; Hekla AD 1104 in Iceland [*Larsen et al.*, 1999] and Ireland [*Pilcher et al.*, 1995, 1996; *Hall and Pilcher*, 2002]; Hekla 4 in Iceland, Scotland [*Dugmore et al.*, 1992, 1995] and Ireland [*Pilcher et al.*, 1996].

AD 1362–1363 (QUB-1052). The major element data indicate that this rhyolitic tephra derives from the Öraefajökull eruption (Figure 1 and Table S1; similarity co-efficient = 0.97). In Dye-3, an acid spike at 326.7 m (corresponding to a GICC05 date of AD 1362–63 based on annual layer counting in this core) has been attributed to the Öraefajökull eruption. We found no tephra at this position, and cannot therefore confirm this designation. We did, however, identify tephra (QUB-1303/1304) in ice ~2 years after the acid signal whose chemistry is distinct from that of Öraefajökull (Figure 1 and Table S1); its source eruption is at present unknown. The chemistry of a tephra dating to AD 1362 in the GISP2 and attributed to the Öraefajökull eruption [*Palais et al.*, 1991] correlates poorly with both QUB-1052 and QUB-1303/1304.

3.3. Tephras Dating to ~AD 850–950

[11] We examined an extended section (~AD 850–950) of NGRIP ice for which frequent ECM spikes are recorded representing a period of considerable volcanic activity, and ice spanning a shorter time interval (~AD 929–936) from Dye-3. In total, five tephra layers, one of which contained a bimodal population, were found (Table S1); the two most prominent horizons are discussed below. While Eldgjá has been consistently cited as part of the AD 930s ice acid story [*Hammer*, 1984; *Zielinski et al.*, 1995] and the Settlement tephra has been identified in the GISP2 and GRIP ice cores [*Grönvold et al.*, 1995; *Zielinski et al.*, 1997], none of our findings compares with either of these ashes nor to any other Icelandic source (G. Larsen, personal communication, 2010).

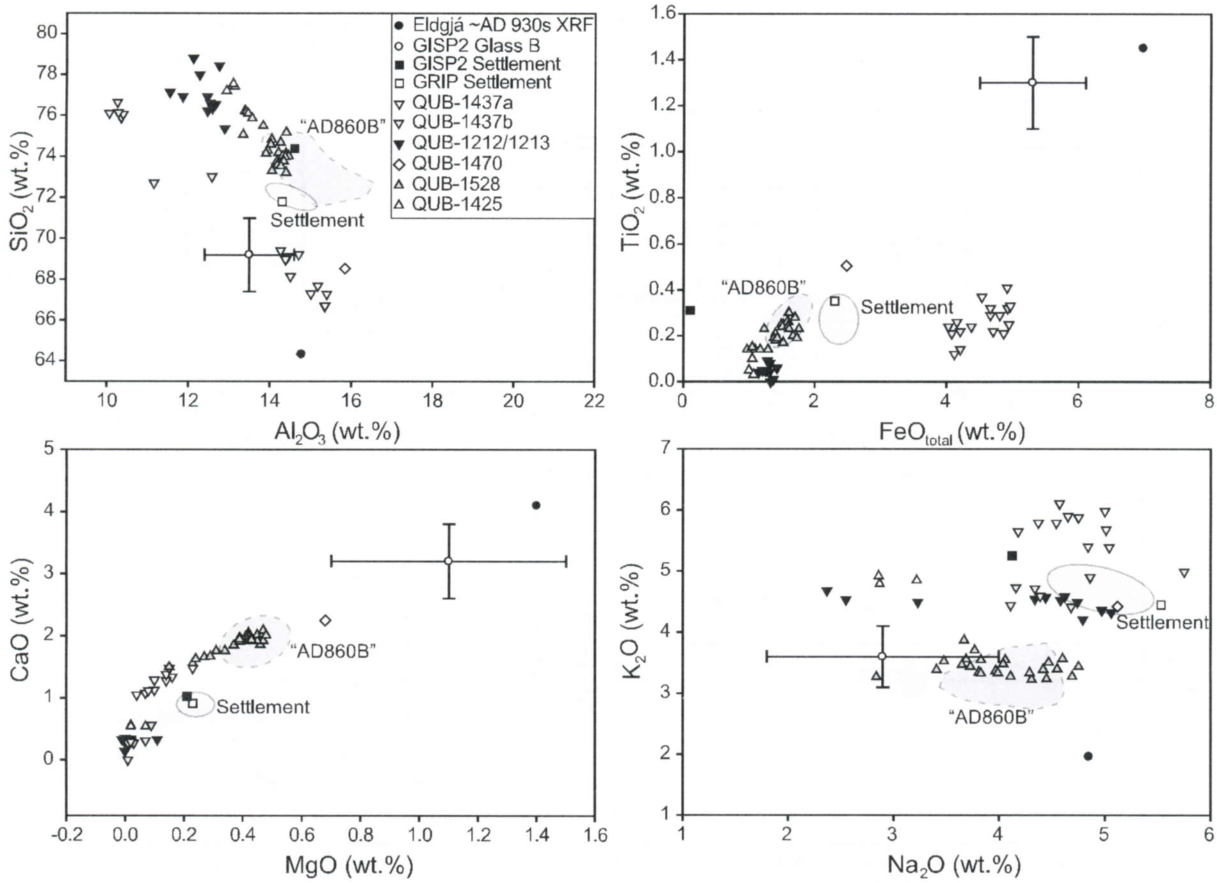

Figure 2. Binary plots illustrating comparison of tephras found in the Greenland ice cores between ~AD 850–950. Data have been normalized for presentation. Each datapoint represents a single analysis except in the case of Glass B for which a mean and standard deviation (based on nine analyses) is shown, and the Settlement Layer rhyolitic component in GISP2 for which the mean of six analyses is shown. The geochemical ranges of reference material for the rhyolitic component of the Settlement Layer in Iceland and the "AD860B" tephra (excluding outliers) in NW Europe are represented by gray envelopes. The following data sets have been used for comparison: Eldgjá ~AD 930s XRF analysis of silicic component (G. Larsen, personal communication, 2010); Glass B in GISP2 [*Zielinski et al.*, 1995]; silicic component of Settlement Layer in Iceland [*Larsen et al.*, 1999], GRIP [*Grönvold et al.*, 1995] and GISP2 [*Zielinski et al.*, 1997]; "AD860B" in Ireland [*Pilcher et al.*, 1995; *Hall and Pilcher*, 2002] and Norway [*Pilcher et al.*, 2005].

3.4. QUB-1437 (GICC05 Age AD 941–942)

[12] Thirty colorless and two brown shards were seen in light microscopy. Geochemical analyses fell into two distinct populations (similarity co-efficient = 0.90), one trachytic-trachydacitic (QUB-1437a) and the other rhyolitic (QUB-1437b), that are possibly from two different sources, the provenances of which have not been identified (Figure 2 and Table S1). The tephras can be given a GICC05 age of ~AD 940–941.

3.5. QUB-1528 (GICC05 Age AD 846–847)

[13] Over 1,000 tephra particles were seen in light microscopy making this the most abundant tephra recorded in this study. Geochemical analyses indicate a composition (Table S1; similarity co-efficient = 0.96) that correlates with the rhyolitic "AD860B" tephra found in Ireland, Scotland, Germany and northern Norway [*Pilcher et al.*, 1995, 2005; *Langdon and Barber*, 2002; *van den Bogaard and Schmincke*, 2002]. The "AD860B" tephra has been dated in Ireland by high precision ^{14}C wiggle-match dating of ombrogenous peat containing the ash to AD 776–887, though more frequently reported as AD 860 ± 20 [*Pilcher et al.*, 1996]. More precise dating of this marker horizon can now be based on the GICC05 chronology [*Vinther et al.*, 2006] which places it at ~AD 846–847.

3.6. QUB-1188 (GICC05 Age 1629–1628 BC), QUB-1198 (GICC05 Age 1641–1639 BC) and QUB-1201 (GICC05 Age 1644–1643 BC)

[14] The Minoan eruption of Santorini, often referred to as "Thera," has received a lot of attention because of its

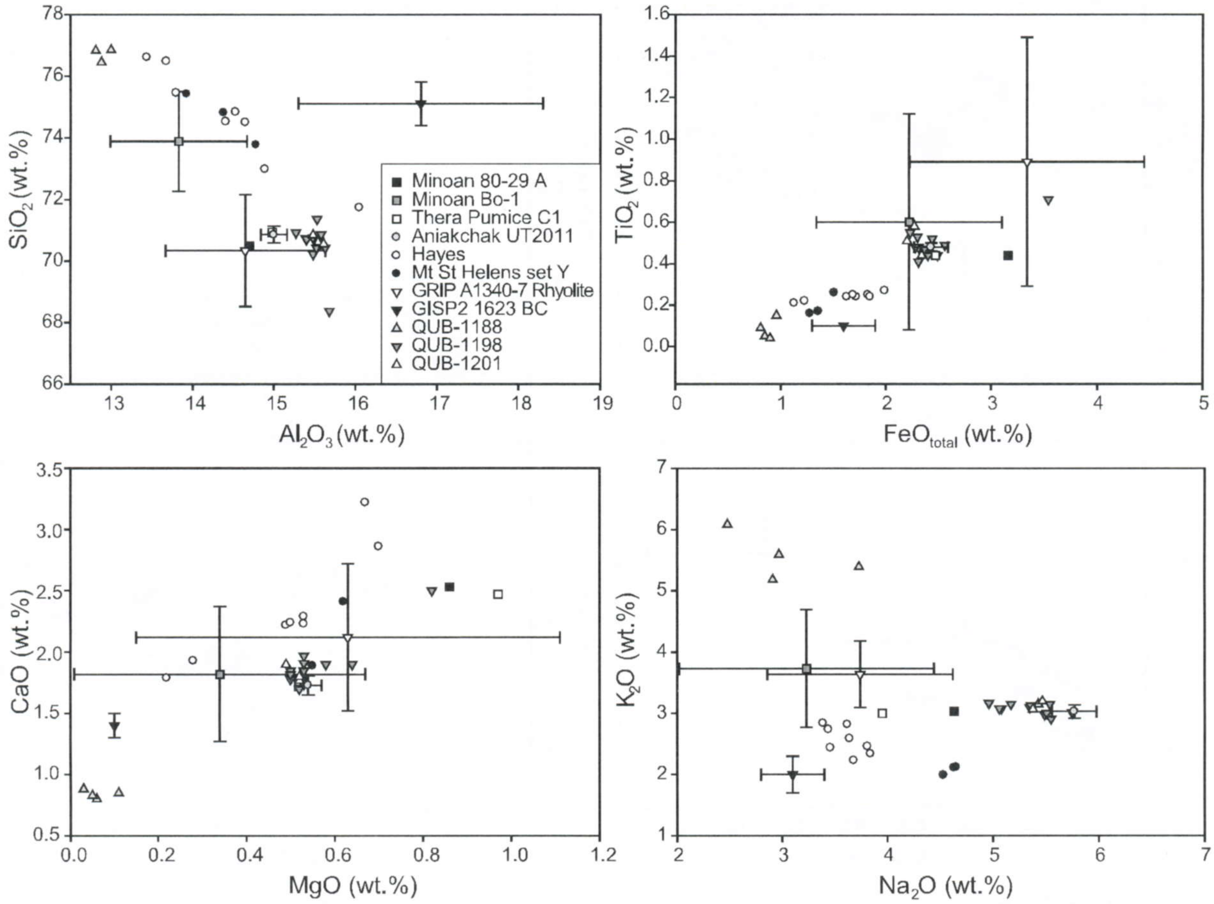

Figure 3. Binary plots illustrating the geochemical comparisons of tephras found in NGRIP between ~1680–1600 BC and other tephras of similar date. Data have been normalized for presentation. Each data-point represents a single analysis, except in the case of Minoan Bo-1 glass, A1340–7 from GRIP, the GISP2 1623 BC tephra and Aniakchak UT-2011, for which means and standard deviations are shown (standard deviations for TiO_2 or MgO in the GISP2 1623 BC tephra are not published), for Thera for which only mean values are available, and for Hayes for which mean values from several data sets are presented. The following data sets have been used for comparison: Minoan rhyolite 80–29 A [*Druitt et al.*, 1989]; Thera pumice C1 [*Vitaliano et al.*, 1990]; Minoan Bo-1 glass and A1340–7 (GRIP) [*Pearce et al.*, 2004, after *Hammer et al.*, 2003]; GISP2 1623 BC [*Zielinski and Germani*, 1998]; Aniakchak UT-2011 [*Denton and Pearce*, 2008]; Mt St Helens Set Y [*Westgate*, 1977]; Hayes [*Riehle*, 1994].

importance to Near Eastern archeology [e.g., *Manning*, 1999]. Resolving a precise age for this eruption is integral for an understanding of cultural developments in the Bronze Age of the eastern Mediterranean. Tephra was found in NGRIP layers dated by GICC05 to ~1629–1628 BC (QUB-1188), ~1641–1639 BC (QUB-1198) and ~1644–1643 BC (QUB-1201) (Tables 2 and S1). The major element geochemistries of the three tephras are plotted in Figure 3 against published analyses from Santorini [*Druitt et al.*, 1989; *Vitaliano et al.*, 1990; *Pearce et al.*, 2004] and Aniakchak [*Pearce et al.*, 2004], as well as analyses from eruptions of Hayes, Alaska [*Riehle*, 1994], and Mount St Helens, Washington [*Westgate*, 1977] which are known to have occurred around this time. QUB-1198 and QUB-1201 are similar to each other in their major element composition (similarity co-efficient = 0.97) and seem to represent two closely timed eruptions of the same volcanic system. The geochemistries of the two tephras compare well with that of Aniakchak (similarity co-efficients = 0.96 for both tephras) and appear to be distinct from any published analyses of tephra from Thera or other N. American eruptions of this period. QUB-1188 has a low FeO and high K_2O composition that is unlike tephra from either Santorini or Aniakchak and its source presently remains unidentified.

3.7. Other Tephras

[15] In addition to the tephras described above, five other layers (QUB-1212/1213; QUB-1539; QUB-1186; QUB-1425; QUB-1470) have been recorded which have not yet been linked to a source eruption or volcanic system (Tables 2 and S1). Although represented by few shards in the ice samples and small numbers of analyses, QUB-1186 and QUB-1425 occur in close association with acid peaks in the ice cores, and the normalized data for each level indicate

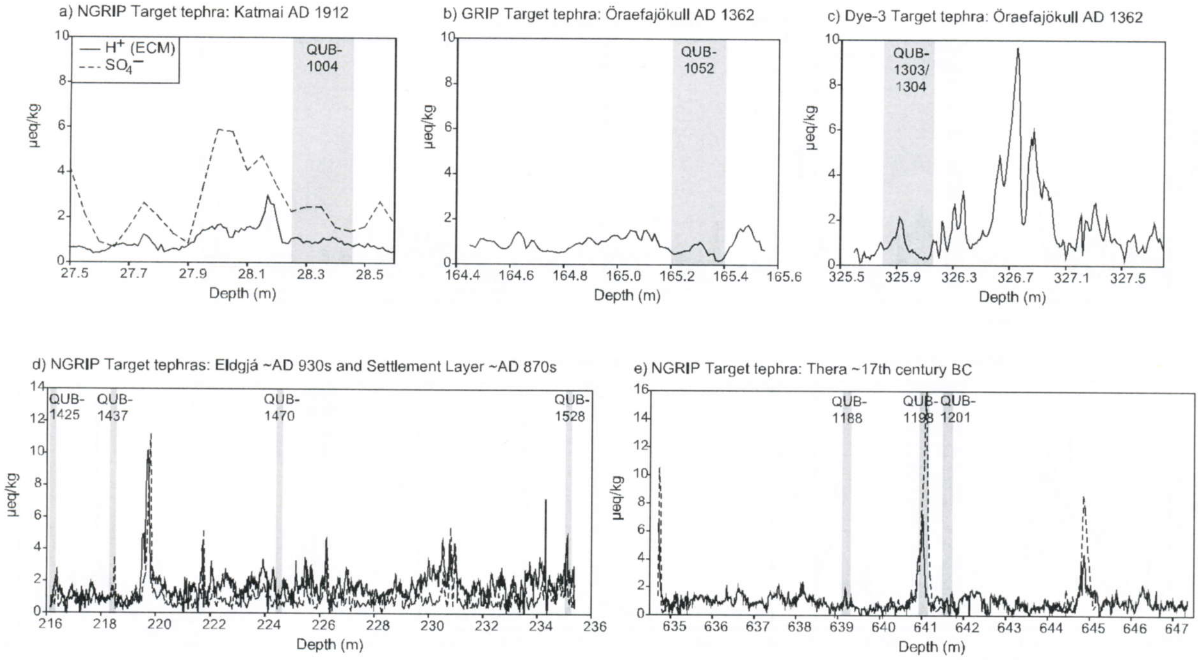

Figure 4. Graphs displaying the position of the samples containing tephra in sections of Greenland ice cores spanning the acid signals attributed to the Katmai AD 1912, Öraefajökull AD 1362, Eldgjá ~AD 930s, Settlement Layer ~AD 870s and Thera 17th century BC eruptions. ECM and sulfate data are provided in Table S3.

homogenous compositions. These layers likely represent, therefore, discrete eruptive events. Only one analysis was obtained from the sparse layer QUB-1470, on the other hand, and additional geochemical analyses are needed to determine its reliability. QUB-1212/1213 and QUB-1539 share major element compositional affinity with QUB-1303/1304 (similarity co-efficients = 0.96–0.99). All three tephras were found in Dye-3 where they are associated with small peaks in ECM, but are absent in ice of the same age from the central and north Greenland cores. These tephras have the potential to be valuable isochrons if found in terrestrial, marine or other ice cores, but further work is required to ascertain their provenance and the likely extent of the respective ashfalls.

3.8. Tephra and Volcanic Proxies in the Ice Cores

[16] Our findings illustrate variable relationships between the positions of tephra horizons and other volcanic signals in the ice cores (Table 2 and Figures 4 and 5). The deposition of the Katmai AD 1912 tephra precedes the peak levels in ECM and subsequently SO_4^{--} that have been associated with this eruption. The Öraefajökull AD 1362 tephra in GRIP is not associated with any rise in ECM, although this is perhaps not surprising as the eruption is estimated to have produced little sulfate aerosol [*Sharma et al.*, 2008]. QUB-1303/1304, on the other hand, coincides with a small peak in ECM, as do QUB-1188, QUB-1212/1213 and QUB-1539. QUB-1528, the most abundant tephra layer in this study, is coeval with a peak in ECM whereas QUB-1437 is associated with a narrow but highly prominent SO_4^{--} peak only, and QUB-1198 coincides with pronounced increases in both proxies. QUB-1186 and QUB-1425 immediately follow relatively small peaks in ECM. Although QUB-1360 comprises an isolated shard, its position correlates with a drop in otherwise elevated ECM values which may correspond to an acid neutralization event in the ice [cf. *Palais et al.*, 1991]. QUB-1470 and QUB-1201, as well as QUB-1328, an isolated basaltic shard, are not associated with volcanic proxies. Most of the prominent volcanic signals in the ice we have examined, on the other hand, have no associated tephra.

4. Discussion

4.1. The Holocene GICC05

[17] Volcanic signals in Greenland ice have been pivotal in the construction of the GICC05, as major acidity signals seen all across Greenland have been used to cross-date the ice core records [*Clausen et al.*, 1997; *Vinther et al.*, 2006]. The sampling strategy adopted for this work aimed to locate tephras that might verify the suggested relationship of certain acid layers with specific eruptions [*Vinther et al.*, 2006]. Although we have succeeded in corroborating the historical precision of the chronology back to AD 1362 with identification of tephras whose major element chemistries match those of the Katmai and Öraefajökull eruptions (QUB-1004 and QUB-1052, respectively), the absence of other targeted tephras means that we cannot substantiate the attribution of certain acid signals to specific events or the cross-correlation of the various ice core records beyond this date.

[18] We have, on the other hand, identified 12 other tephras that, if found in other sedimentary records, may prove to be highly refined chronological marker horizons. Discovery of the "AD860B" tephra in NGRIP (QUB-1528), already a valuable isochron in NW Europe [cf. *Lawson*

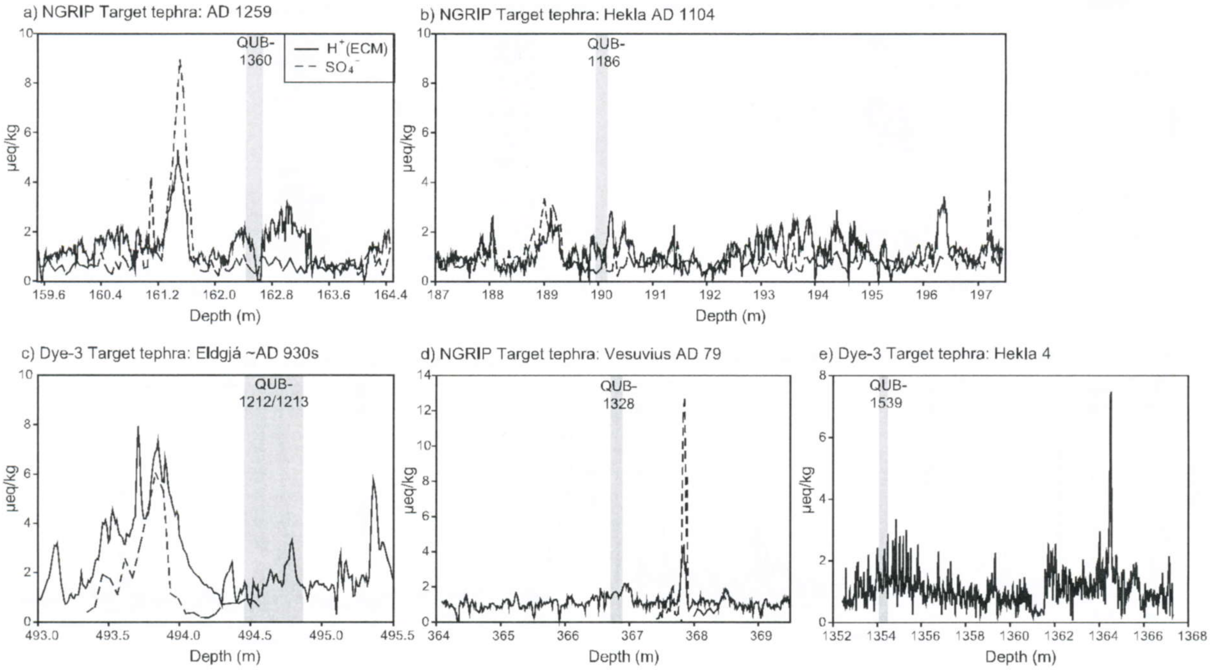

Figure 5. Graphs displaying the position of samples containing tephra in sections of 635 Greenland ice cores spanning the period of the AD 1259 acid peak, and the acid signals attributed to the Hekla AD 1104, Eldgjá ~AD 930s, Vesuvius AD 79 and Hekla 4 eruptions. ECM and sulfate data are provided in Table S3.

et al., 2012], has provided a significant advance in ice core tephra work. This tephra can now be ascribed a more precise GICC05 age of ~AD 846–847.

4.2. Deposition of Volcanic Constituents

[19] This study illustrates the variable relationship between tephras and volcanic proxies in the ice (Table 2 and Figures 4 and 5). In previous studies, chemical constituents have been found "offset" from the occurrence of tephra shards in the ice. This phenomenon is not restricted to far-distant volcanic events, but is also observed for Icelandic eruptions. For instance, tephra from the Laki 1783–4 eruption has been observed to lead the main sulfate deposition in GISP2 [*Fiacco et al.*, 1994] and on Svalbard [*Kekonen et al.*, 2005], in contrast to the apparently synchronous tephra and sulfate deposition in western Greenland [*Wei et al.*, 2008]; we found no tephra associated with the acid layer of this date in GRIP. QUB-1004 from Katmai AD 1912 was found in NGRIP ice a few months prior to the main aerosol fallout, implying rapid tropospheric transport of the ash to Greenland. On the other hand, QUB-1198, probably also of Alaskan origin, seems synchronous with the main acid deposition in NGRIP, suggesting stratospheric or tropospheric fallout of both components, assuming they are derived from the same source. It should be noted, however, that the sampling resolution in this part of the NGRIP core is not sufficient to quantify small time differences between the various volcanic products.

[20] Our work also highlights the spatial complexity of volcanic records in the ice cores. Despite sampling some common time periods in the Dye-3, GRIP and NGRIP cores in search of specific tephras, we have been unable to replicate their tephrostratigraphical sequences. It is not surprising that the distribution of tephra shards over an area the size of Greenland is patchy as this is a common finding all over Europe throughout the Holocene [e.g., *Wastegård et al.*, 2003; *Lawson et al.*, 2012] and has been noted in Greenland ice [e.g., *Abbott et al.*, 2012], but here we can also firmly demonstrate differences in aerosol and particle distributions in the ice cores. The Öraefajökull AD 1362 eruption is represented in northern Greenland only by high concentrations of tephra (QUB-1052). Chemical signals around this time are evident in southern Greenland but cannot be attributed to Öraefajökull with absolute certainty as no tephra is recorded, though the precise parallel annual layer counting in the GRIP and Dye-3 ice cores shows that the chemical signal dates to the same year as the Öraefajökull eruption. This implies that the acid signals can, like the tephra, be erratic in their distribution. The present findings highlight the need for a more cautious approach in the attribution of acid signals to specific volcanic events if timing and environmental impacts of the eruptions are to be investigated. Furthermore, multiple eruptions can potentially contribute to acid signals and may hinder estimates of stratospheric loading from specific events [cf. *Zielinski et al.*, 1995].

[21] The volcanic events represented by seven other tephras (QUB-1303/1304, QUB-1470, QUB-1188, QUB-1201, QUB-1212/1213, QUB-1186, QUB-1539) do not stand out strongly in their corresponding acid record. Our findings support the suggestion that silicic eruptions are under-represented in ice cores by acidity peaks due to their low content of associated acidic volatiles [*Palais and Sigurdsson*, 1989]. *Davies et al.* [2010] and *Abbott et al.* [2012] similarly found poor correspondence between the positions of basaltic tephras and sulfates in Last Glacial ice from Greenland, however, and it seems that many eruptions may only therefore be detectable

through tephra studies. Basaltic eruptions are very much under-represented in the tephra record of the ice cores during the periods we have examined. Indeed, the prevalence of rhyolitic tephras in our study, only one of which can be certainly correlated with an Icelandic source, stands in contrast to the dominance of basaltic tephras of mainly Icelandic origin found in Last Glacial sections of Greenland ice cores [*Grönvold et al.*, 1995; *Davies et al.*, 2010; *Abbott et al.*, 2012]. Intermediate and rhyolitic tephras are nonetheless recorded in Last Glacial ice in Greenland, but are also of Icelandic origin [*Grönvold et al.*, 1995; *Ram et al.*, 1996; *Zielinski et al.*, 1997; *Mortensen et al.*, 2005]. This apparent discrepancy in the main volcanic sources of tephra in Greenland ice between Glacial and Holocene times may be indicative of variance in atmospheric circulation patterns [cf. *Lacasse*, 2001].

4.3. The Thera Debate

[22] The relationship between volcanic episodes and evidence in the ice is more difficult to tease out in sections of the record containing multiple ECM and sulfate peaks. This is most evident in NGRIP ice spanning 1682–1598 BC, the section containing a strong sulfate signal argued as having derived from the Thera eruption [*Hammer et al.*, 2003; *Vinther et al.*, 2006, 2008]. Debate over the timing of this event has continued for several years [*Hammer et al.*, 1987; *Baillie and Munro*, 1988; *Manning*, 1999; *Friedrich et al.*, 2006]. *Hammer et al.* [2003] reported finding numerous small tephra particles from this eruption in the GRIP core and proposed an age of 1645 $\pm$ 4 BC. This claim has, however, been challenged by other researchers [*Pearce et al.*, 2004; *Denton and Pearce*, 2008] who suggest that the tephra derives instead from an eruption of Aniakchak. In GISP2, *Zielinski et al.* [1994] highlighted an acidity peak which they date to 1627–1623 BC (corresponding to $\sim$1600 BC in GICC05) but more recently, tephra from this layer has been shown to have a geochemical composition that does not match any documented eruption, including Thera [*Zielinski and Germani*, 1998].

[23] Our results from NGRIP show that at least three tephras occur in the "Thera timeframe" dated by GICC05 to $\sim$1629–1628 BC, $\sim$1641–1639 BC and $\sim$1644–1643 BC. Their chemistries do not compare well with tephra data reported from Thera, GRIP or GISP2 around this time but QUB-1198 and QUB-1201 have chemistries that match that of Aniakchak, more so than the disputed tephra in GRIP [*Hammer et al.*, 1987, 2003; *Pearce et al.*, 2004; *Denton and Pearce*, 2008]. Given the coeval deposition of the QUB-1198 and the aerosol in NGRIP, it must be accepted that the link between the acid signal at this time in the Greenland ice cores and the Aniakchak eruption proposed by *Pearce et al.* [2004] is just as likely as the link of this signal to the Santorini eruption as proposed by *Hammer et al.* [1987, 2003]. If the acid signal is indeed the result solely of the Aniakchak event, it should be noted, however, that no other major acidity signals in the Greenland ice cores conform with the ^{14}C dating of the Minoan eruption [*Vinther et al.*, 2008]. Given this and the dissimilarity between tephras observed at GRIP and NGRIP, we must also consider the possibility that multiple eruptions contributed to the acid signal in the Greenland ice cores. Our study thus highlights the difficulty in attributing ECM peaks in ice cores to particular volcanic events without unambiguous tephra geochemical evidence.

5. Conclusion

[24] Positively identifying tephras from ice cores through geochemical analysis can provide crucial support for attributing ECM and acid peaks to specific volcanic eruptions. Such verification is a requisite for establishing the wider environmental significance of a given event, including the dating of non-historic eruptions, the reconstruction of volcanic processes and atmospheric conditions at the time of the eruption, and palaeoenvironmental impact of the event. Our results underscore some of the issues relating to this procedure, namely that 1) expected tephras can be absent from the ice, 2) there are many eruptions which are poorly or not at all evident in the ice core volcanic proxy records, 3) there is erratic distribution of both tephra and aerosols across Greenland that hinders the potential to achieve precise chronological tie-points between the ice cores, and ultimately 4), in view of the variable relationship in the positions of tephras and acid signals, there is no reliable, *a priori* means of inferring the source of an acid signal in the ice. A more cautious approach in interpreting the origin of volcanic signals in the ice and environmental impact of volcanic events is therefore warranted.

[25] Our study has also found that the acidity layer in the NGRIP ice core dated to 1641–1639 BC and previously attributed to the Minoan Thera eruption [*Hammer et al.*, 2003; *Vinther et al.*, 2006, 2008] is coeval with a tephra layer (QUB-1198) most likely from Aniakchak, Alaska, suggesting that this eruption at least contributed to the pan-Greenland 1642 $\pm$ 4 BC acid signal as proposed by *Pearce et al.* [2004] and *Denton and Pearce* [2008]. Tephras with major element chemistry consistent with ash from Katmai (QUB-1004) and Öraefajökull (QUB-1052) have been identified in Greenland ice cores confirming the accuracy of the GICC05 time scale back to AD 1362. Despite the apparent absence of some key tephras, this research, like that of other workers [*Grönvold et al.*, 1995; *Mortensen et al.*, 2005], has revealed more tephras in the selected sections of ice than at present can be linked to known eruptions, and not of all of which are represented in the volcanic aerosol records. So far we have only examined ice representing about 470 years of the Holocene. As we have found evidence for 14 volcanic events, the potential for valuable isochrons in the 11,700 years of the Holocene is considerable.

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