Reinterpretation of Greenland Ice-Core Data Recognises the Presence of the Late Holocene Aniakchak Tephra (Alaska), not the Minoan Tephra (Santorini), at 1645 BC

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Abstract

The precise age of the Minoan eruption of Santorini (Thera) volcano, which erupted some time during the Second Millennium BC, is in debate. A range of dates between 1600–1650 BC has been proposed and the relative merits of these estimates have been widely argued. Recently, chemical analyses of small glass shards recovered from the GRIP ice-core from Greenland have been used to confirm a 1645±4 BC date for the Minoan eruption of Santorini (Hammer et al., 2003), but marked differences in the concentrations of Si, Ti, Mg, Ba, Sr, Nb, REE (particularly La/Sm) deny this correlation. Instead, glass shards from the GRIP ice-core have a composition which is indistinguishable from glass shards from the late Holocene Aniakchak tephra, Alaska, which is proposed as the source for the material in the GRIP ice-core. This provides a precise date of 1645 BC for the caldera-forming eruption of Aniakchak, but leaves the issue of the precise age of the Minoan eruption of Santorini unresolved.

Introduction

The date of the Minoan eruption of the Santorini (Thera) volcano which erupted some time during the Second Millennium BC is of major importance in placing time constraints on the evolution of civilisations in the Eastern Mediterranean. In attempts to derive precise dates for the Minoan eruption, several proxy records have been linked to this event, including accurate dates derived from studies of acid spikes in ice-cores or anomalous growth recorded in tree rings (Hammer et al., 1987; Kuniholm et al., 1996; Manning et al., 2002; Manning et al., 2001). These proxy records often correlate over large distances (Manning and Sewell, 2002), and must reflect major and widespread environmental impacts. These proxies, however-

er, do not identify unequivocally the cause of a particular environmental disturbance. The combination of various proxy records with ^{14}C dating, has seen a range of dates between 1600–1650 BC proposed for the Minoan eruption of Santorini, and the relative errors/merits of these ages have been widely argued (Hammer et al., 1987; Manning, 1998; Manning and Sewell, 2002; Zelinski and Germani, 1998). While the acid spikes in the ice cores record an atmospheric response to a volcanic eruption, they do not record which eruption. Similarly, the tree ring records are equally uncertain. Thus, to be certain of linking a particular eruption with the ice-core record requires the presence within the ice of juvenile volcanic materials which can be chemically correlated with a particular source (e.g. Zelinski and Germani, 1998). Recently, analyses have been published for a suite of minute (~ 5μm) glass shards recovered from the GRIP ice-core from Greenland (Hammer et al., 2003). These analyses are claimed to confirm a 1645 ± 4 BC age for the Minoan eruption of Santorini. However there are serious problems with the correlations suggested by Hammer et al. (2003). Indeed, their interpretations have already been challenged on statistical grounds (Keenan, 2003). Here, the analytical data of Hammer et al. (2003) are evaluated and compared to data from other large eruptions from the early-mid Second Millennium BC, including new analyses of tephra from the Aniakchak volcano on the Alaska Peninsula, which is proposed as the source for the glass shards from this layer of the GRIP ice-core.

Volcanic glass shards from the GRIP ice-core

Hammer et al. (2003) recovered hundreds of microscopic particles from the 1645 BC acid spike layer of the GRIP ice-core (sample A1340-7). Analyses of these particles revealed 174 to be silica-rich volcanic glass. Major element analyses were performed by

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	5Rj125 B	5Rj126 B	5Rj126 C	Hayes A	Hayes B	Hayes C	Hayes D	Hayes E1	Hayes E2	Hayes F	Hayes G	MSH Yb	MSH Yn	MSH Ye
SiO_2	63.44	62.82	59.19	75.45	76.61	74.49	72.98	74.52	71.74	76.48	74.83	73.77	74.81	75.42
TiO_2	1.23	1.21	1.36	0.24	0.22	0.24	0.27	0.25	0.24	0.21	0.25	0.26	0.17	0.16
Al_2O_3	15.50	16.51	16.52	13.80	13.44	14.65	14.89	14.41	16.05	13.68	14.53	14.78	14.38	13.93
FeOt	6.69	6.23	8.04	1.72	1.23	1.63	1.99	1.83	1.85	1.13	1.69	1.51	1.36	1.28
MnO				0.06	0.05	0.04	0.05	0.06	0.06	0.04	0.04			
MgO	1.86	1.92	2.87	0.53	0.28	0.49	0.70	0.53	0.67	0.22	0.50	0.62	0.55	0.53
CaO	4.29	4.84	6.32	2.29	1.93	2.22	2.86	2.23	3.22	1.79	2.24	2.41	1.89	1.79
Na_2O	4.87	4.67	4.11	3.46	3.39	3.64	3.81	3.44	3.84	3.62	3.68	4.53	4.63	4.65
K_2O	2.13	1.79	1.59	2.44	2.84	2.59	2.46	2.74	2.34	2.82	2.23	1.99	2.11	2.12
Cl												0.13	0.10	0.12
F														
O=F,Cl														
Cr_2O_3														
Total	100	100	100	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
H_2Od	3.6	1.9	1.9	3.65	3.28	4.42	3.94	7.00	4.65	2.06	7.79	2.20	1.88	0.96

	A1340-7 (n=174)	Bo-1 (n=38)	Relative difference A1340-7/ Bo-1	Minoan tephra Gölhisar Gölü (n=67)	Minoan Bo, Basal surge, Vitaliano et al 1990	Aniakchak UT2011 (n=14)	A1340-7 calibrated and normalised	Aniakchak normalised	Relative difference A1340-7/ Aniakchak
SiO_2	70.34 (1.82)	73.88 (1.62)	−5%	73.62 (0.59)	73.9	71.23 (0.19)	70.53	71.37	−1%
TiO_2	0.89 (0.60)	0.60 (0.52)	49%	0.29 (0.06)	0.2	0.47 (0.08)	0.44	0.47	−7%
Al_2O_3	14.65 (0.98)	13.83 (0.84)	6%	14.02 (0.18)	13.9	15.21 (0.11)	14.95	15.24	−2%
FeOt	3.34 (1.11)	2.22 (0.88)	50%	2.04 (0.12)	2.2	2.45 (0.08)	3.08	2.46	25%
MnO	0.36 (0.40)	0.18 (0.29)	100%	0.07 (0.04)		0.13 (0.05)	0.13	0.13	3%
MgO	0.63 (0.48)	0.34 (0.33)	83%	0.28 (0.04)	0.29	0.52 (0.02)	0.51	0.52	−2%
CaO	2.12 (0.60)	1.82 (0.55)	17%	1.40 (0.10)	1.4	1.74 (0.09)	1.65	1.75	−6%
Na_2O	3.74 (0.88)	3.23 (1.21)	16%	4.76 (0.64)	4.7	5.13 (0.13)	5.54	5.14	8%
K_2O	3.64 (0.54)	3.73 (0.96)	−3%	3.24 (0.12)	3.4	2.93 (0.10)	3.17	2.94	8%
Cl				0.31 (0.04)		0.20 (0.03)			
F				0.07 (0.09)					
O=F,Cl				−0.09 (0.04)					
Cr_2O_3	0.29 (0.46)	0.17 (0.24)							
Total	100.00	100.00		100.00	100	100.00	100.00	100.00	
H_2Od	1.05	0.92		2.36 (1.53)		0.89			

Table 1 Major element data for tephra deposits considered in this study: Units A–G from Hayes volcano (RIEHLE, 1994); Mount St Helens (MSH) Y tephra set (WESTGATE, 1977); Bo-1 glass from Santorini (HAMMER *et al.*, 2003); Minoan tephra from Gölhisar Gölü, SW Turkey (EASTWOOD *et al.*, 1998; EASTWOOD *et al.*, 1999; PEARCE *et al.*, 2002); A1340-7 from the GRIP ice-core (HAMMER *et al.*, 2003); Veniaminof (samples "5Rj…") (RIEHLE *et al.*, 1999); and Aniakchak (UT2011, this study). All analyses have been recalculated to 100% excluding H_2Od. H_2Od is water by difference. The A1340-7 analyses have also been recalibrated using the reported Bo-1 analyses (HAMMER *et al.*, 2003) and the analyses for the Minoan tephra (EASTWOOD *et al.*, 1999) for those elements common to both data sets, and the UT2011 analyses have then been recalculated to 100% for the same elements for comparison. Numbers in parentheses are 1 standard deviation. Concentrations in wt%

analytical scanning electron microscope (ASEM), for which no details are given, although HAMMER *et al.* (2003) state that the "small sizes and irregularity of the particles prevents ideal calibration". ASEM analyses are less precise than conventional electron probe microanalyses, although, when calibrated correctly have the potential to be accurate (www.cameca.fr). HAMMER *et al.* (2003) also determined the trace element composition of 8 larger (about 10 µm) shards from the ice-core sample by secondary ion mass spectrometry (SIMS) using a Cameca ion microprobe. For comparison, HAMMER *et al.* (2003) determined the major element composition of 38 grains of glass from a comminuted sample of the Upper Pumice layer of the Minoan eruption (Bo-1) collected from Santorini, but only 3 grains of this material were analysed for their trace elements. These data are presented in Table 1.

Silica-rich (rhyolitic) magmas have high viscosities which, when combined with high dissolved

Source volcano	^{14}C age	Calibrated ^{14}C age (2σ) or suggested age	Age Sources	Comments and sources of compositional data
Veniamin of Alaska Peninsula	3700±100 BP	2460–1780 BC	(MILLER & SMITH, 1987)	Eruption >50 km^3 magma (RIEHLE et al., 1999)
Aniakchak, Alaska Peninsula	3430±100 BP 3380±80 BP	2012–1515 BC 1889–1449 BC	(MILLER & SMITH, 1987) (VOGEL et al., 1990)	Eruption >50 km^3 magma, tephra NE of source (BEGÉT et al., 1992)
Hayes volcano, Alaska		1850–1550 BC	(RIEHLE et al., 1990)	7 or 8 tephra beds, totalling ~10 km^3 magma, tephra NE of source (RIEHLE, 1994; RIEHLE et al., 1990)
Mount St Helens Yb, Yn and Ye tephras	3410±80 BP	1917–1518 BC 1560 BC	(LUCKMAN et al., 1986) (PRINGLE, 1993)	Eruptions total ~4 km^3 of magma. Yn tephra NE of source, deposits in NW Canada (WESTGATE, 1977)

Table 2 Sources, ages and comments on large North American volcanic eruptions from the early–mid Second Millennium BC. Calibrated ^{14}C ages calculated after STUIVER and REIMER (1993) and STUIVER et al. (1998)

volatiles in the magma, give rise to violent eruptions. From these eruptions widespread tephra deposits may be produced which commonly have similar major element compositions (WESTGATE et al., 1994). Broad or general similarities in the composition of glass from separate deposits are thus insufficient to erect robust correlations: by virtue of their origins, rhyolitic tephras are often broadly similar in composition. Instead, for correlation purposes in tephrochronological studies, the major element chemistry must be essentially identical between widely separated deposits, and as such, acceptable variations are ~1–2% relative for SiO_2 and Al_2O_3, (i.e. SiO_2 within around ±1 wt%, Al_2O_3 within about ±0.25 wt%) and in the 5–10% relative range for the remaining, less abundant elements (PEARCE et al., 2004). Variations of this scale can readily be produced in large single eruptions that drain voluminous, chemically differentiated magma chambers.

Table 1 shows that large differences exist in major element chemistry between the ice-core glass (A1340-7) and the Bo-1 Minoan (HAMMER et al., 2003). Differences of 3.6 wt% SiO_2 (~5% relative) and 0.8wt% Al_2O_3 (~6% relative) are reported between these two deposits, and these are unacceptably large to propose a correlation between these samples. Additionally, HAMMER et al. (2003) report FeOt (total Fe represented as FeO) and TiO_2 as being 50% higher in A1340-7 than Bo-1, MgO is almost twice as high in A1340-7 than Bo-1. K_2O and CaO are similar, and Na_2O is marginally higher in A1340-7, although because of the small sample size and irregular shape, Na is

unlikely to have been determined accurately (HUNT and HILL, 2001). Considering the analyses presented by HAMMER et al. (2003), it is clear that the relative differences are too great to allow a correlation to be proposed between the GRIP ice-core glass and the Minoan Bo-1 deposit. Recently, KEENAN (2003) employed t-tests on the standard errors of the analyses of HAMMER et al. (2003) (standard error = standard deviation / number of analyses) to show that the Minoan Bo-1 sample and the A1340-7 glass cannot be the same. This approach, where the numbers of analyses are large (i.e. n=174 for the ASEM analyses of the ice-core glass) may however reduce the errors to unattainably small values, far less that the true analytical reproducibility attainable by multiple analyses of homogeneous materials (PEARCE et al., 1997). In doing so, when comparing different materials, the standard error approach may enhance the apparent differences between samples. Nonetheless, the conclusions of KEENAN (2003) agree with those here based on acceptable variations in composition between comparable tephra beds, i.e. the glass from the GRIP ice-core is not the same as the glass from the Minoan eruption of Santorini.

CORRELATION OF THE GRIP ICE-CORE GLASS

Many major element analyses of glass from the Minoan eruption (EASTWOOD et al., 1998; EASTWOOD et al., 1999; VINCI, 1984; VITALIANO et al., 1990; WARREN and PUCHELT, 1990) compare favourably with the Bo-1 major element analyses of HAMMER et al. (2003), i.e. similar SiO_2, Al_2O_3, FeOt, MgO, K_2O and

CaO (see Table 1). However, the analyses in HAMMER *et al.* (2003) are generally higher in the minor components TiO_2 and MnO (see Table 1). These differences probably result from calibration problems in ASEM analyses where irregular shard geometry may give rise to problems in the corrections for mass absorption, fluorescence etc. These errors will also be incorporated into the analyses of the GRIP ice-core glass. Thus, to enable a more accurate comparison of the ice-core glass with other possible sources for this material, the ASEM analyses need to be recalibrated. In analysing 38 shards of Bo-1 glass, HAMMER *et al.* (2003) analysed a compositionally well know material (in essence a "standard") and this can be used to recalibrate their analyses. A correction factor can be calculated for the ASEM analyses, taking the average of the ASEM analyses of the Bo-1 glass and comparing this with published analyses of the Minoan tephra (EASTWOOD *et al.*, 1999; VINCI, 1984; VITALIANO *et al.*, 1990). Here, this correction has been made using the average of 59 glass shards by EPMA from EASTWOOD *et al.* (1999) to give a recalibrated analysis of the glass in A1340-7. This has then been further normalised to 100% for those elements common to both data sets (i.e. excluding F, Cl and Cr_2O_3, see Table 1). Normalisation to different published analyses makes only a minute difference to the corrected A1340-7 data. This recalibrated analysis can now be compared with known volcanic sources active at the time of deposition of the ice-core glass.

Several large volcanic eruptions occurred in North America in the mid-Second Millennium BC, their ages making them candidates for correlation with the glass from the GRIP ice-core. Details of these are summarised in Table 2, and include caldera-forming eruptions from Veniaminof and Aniakchak volcanoes, both on the Alaska Peninsula and smaller eruptions of Hayes volcano Alaska and Mount St Helens, Washington. Major element analyses of tephras from these eruptions are listed for comparison in Table 1. All the Hayes volcano and Mount St Helens tephra beds of the appropriate age are too siliceous, and the analyses from Veniaminof are all too silica-poor, to correlate with A1340-7. Differences in FeOt, alkalis and Al_2O_3 likewise exclude the possibility of correlation. It is clear that the Aniakchak tephra (UT2011) and the recalibrated ice-core glass (A1340-7) are extremely similar, showing only minor differences for all elements except FeOt. FeOt has the worst precision of the major elements determined by ASEM, with a relative standard deviation of around ±40% in Bo-1 (HAMMER *et al.*, 2003). This may in part be responsible for the larger difference in FeOt between

A1340-7 and UT2011. The major element chemistry thus strongly suggests that the glass in the ice-core is derived from Aniakchak.

COMPARISONS OF TRACE ELEMENT ANALYSES

HAMMER *et al.* (2003) produced ion microprobe (SIMS) trace element analyses of 8 glass shards from the A1340-7 ice-core sample and compared these with 3 analyses of glass from Bo-1. In samples that are only a few microns in diameter this is a remarkable achievement. These analyses are listed in Table 3. PEARCE *et al.* (2002) have recently defined the extent of trace element variation within the glass from the Minoan tephra using laser ablation LA-ICP-MS analyses, showing a remarkable compositional range between individual glass shards (see Table 3). This reflects small-scale heterogeneity within the magma caused by the combined effects of fractional crystallisation and diffusion giving rise to compositional gradients around crystallising phases (PEARCE *et al.*, 2002). The average of the singe-shard analyses compare extremely well with published bulk analyses, and provide compositional fields as defined on bivariate plots. Unfortunately, with their known range of compositions, the analysis of only 3 grains of Minoan glass by HAMMER *et al.* (2003) is statistically insufficient to gain an impression of the accuracy of the SIMS analyses. Despite this observation, the analyses of many trace elements in the Bo-1 glass (HAMMER *et al.*, 2003) comparable favourably with other published analyses of Minoan material for many elements (EASTWOOD *et al.*, 1999; PEARCE *et al.*, 2002; VINCI, 1984; VITALIANO *et al.*, 1990; WARREN and PUCHELT, 1990), although some elements fall above the range of single shard compositions, e.g. Nb, Ba which may reflect calibration problems (see Table 3). Additionally, the SIMS Rb data fall at the lower end of the range of single shard compositions, and Sr is at the upper end of the range, indicating that the SIMS analyses may not be truly representative. There are considerable differences between the trace element analyses of Bo-1 and A1340-7 given by HAMMER *et al.* (2003), with factors of up to 2.6 for the difference in Sr, ~1.5 for Ba, Sm, Nb and Rb and ~1.2 for La, Ce and Nd. The La/Sm ratio (defining the slope of the LREE) also differs by a factor of ~2 between the two samples. Differences in trace element concentrations of this magnitude cannot be generated by any realistic magmatic process within a single eruption, and in single grain analyses are not a result of contamination of the sample by detrital material. The differences unequivocally rule out a correlation. At the reported concentrations (a few tens to a few hundred
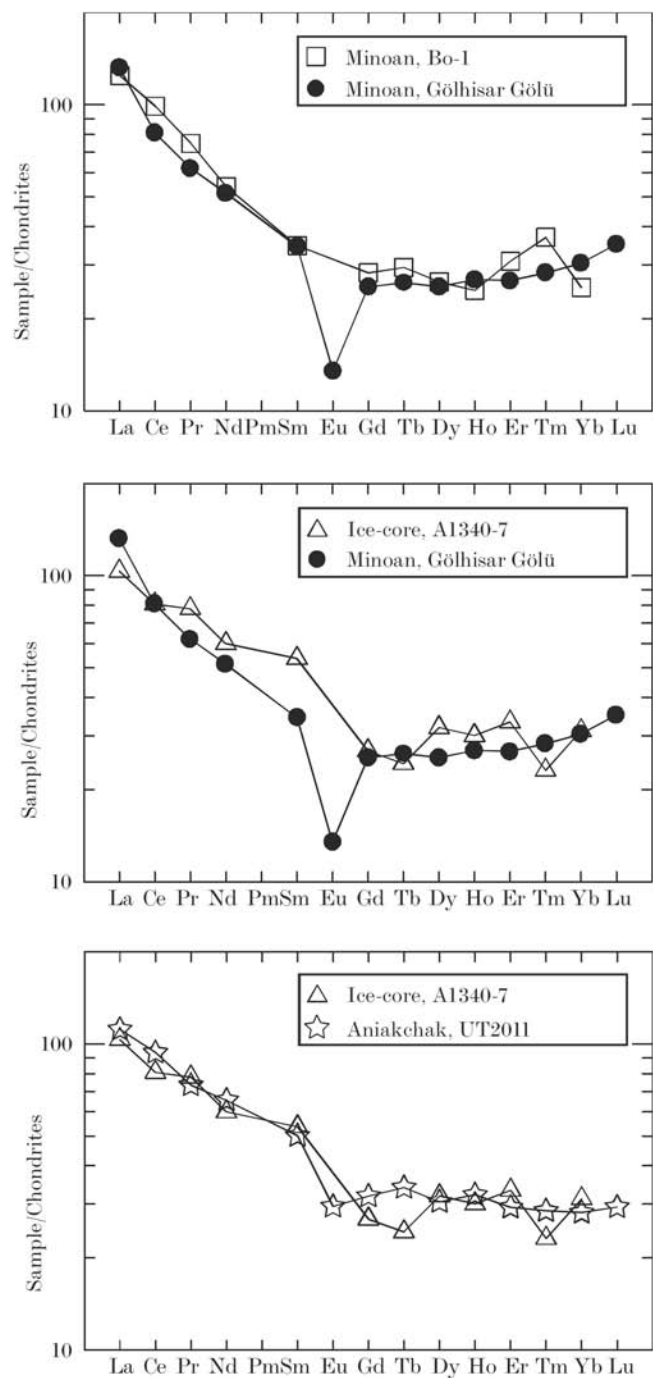
Fig. 1 Chondrite normalised REE spidergrams for glass from A1340-7 from the GRIP ice-core (HAMMER *et al.*, 2003), the Minoan Bo-1 deposit on Santorini (HAMMER *et al.*, 2003), the Minoan tephra deposited at Gölhisar Gölü, Turkey (PEARCE *et al.*, 2002) and tephra from the caldera-forming eruption of Aniakchak (UT2011, this study). Normalisation factors from SUN and McDONOUGH (1989)
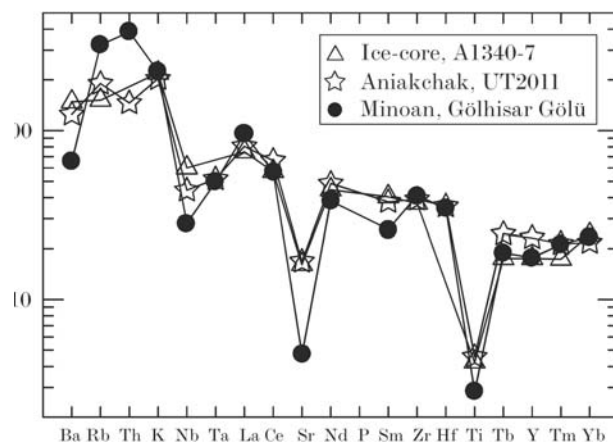

Fig. 2 Chondrite normalised incompatible element spidergram for glass from the GRIP ice-core (A1340-7)(HAMMER *et al.*, 2003), the Minoan tephra deposited at Gölhisar Gölü, Turkey (PEARCE *et al.*, 2002) and Aniakchak (UT2011, this study). Normalisation factors from THOMPSON (1982).

ppm), elements such as Ba, Sr, Rb and the LREE should be determined with good accuracy and precision by SIMS (perhaps ±10%) even in such small and difficult materials, but the differences between the Bo-1 and A1340-7 analyses are also well beyond any

realistic estimates of analytical error, and again are far too great for these deposits to be considered the same. The differences between A1340-7 and the Bo-1 Minoan ash are further highlighted when compared with the single shard LA-ICP-MS analyses from PEARCE *et al.* (2002) (Table 3). The most apparent differences are in the concentrations of Ba, Sr, Rb and the LREE. It is clear that the SIMS and LA-ICP-MS REE concentrations for the Minoan deposit are similar (Fig. 1), but both data sets differ markedly from the ice-core glass, the latter having a much lower La/Sm ratio (see above). Unfortunately, HAMMER *et al.* (2003) did not report Eu, which may have helped in comparisons of the two samples. Despite the large difference in these data sets, HAMMER *et al.* (2003) believed the Bo-1 and A1340-7 analyses show "a remarkable resemblance" and that it is "hard to believe that this resemblance should be coincidental". Unfortunately, any broad similarity which may exist for some elements in the SIMS analyses (but notably this is only *some* elements) is indeed coincidental. This is illustrated by KEENAN (2003) who shows that analyses of the 75ka Toba eruption (WESTGATE *et al.*, 1998) compare well for many elements with both the Minoan and A1340-7 samples (equally as well as the A1340-7 data are claimed by HAMMER *et al.* (2003) to compare with the Bo-1 data), where clearly these cannot be correlatives. For a robust correlation *all* elements (not just some) must compare extremely well, with the only permissible differences, outside analytical variation, being relatively small-scale variations which are caused and explained by magmatic process-

	Aniakchak, UT2011, solution ICP-MS (n=4)	A1340-7 (n=8), SIMS	Bo-1 (n=3), SIMS	Minoan tephra, Gölhisar Gölü (n=56), LA-ICP-MS	Minoan tephra, Gölhisar Gölü, range LA-ICP-MS (min–max)	Minoan tephra, Gölhisar Gölü, solution ICP-MS	Knossos, solution ICP-MS	QLO-1 accepted conc.	QLO-1 Solution ICP-MS (this study) Jun. 2003	QLO-1 Solution ICP-MS (this study) Oct. 2003	RGM-1 accepted conc.	RGM-1 Solution ICP-MS (this study) Jun. 2003	RGM-1 Solution ICP-MS (this study) Oct. 2003
Sc	10.8 (0.65)			13.9 (6.8)	2.57–34.3	6.76		**8.9**	8.43	8.75	**4.4**	4.71	4.62
V	12.2 (0.20)	12 (2)	13 (2)			39.4		**54**	43.3	49.0	**13**	14.4	14.2
Cr	2.02 (0.16)	9.6 (1.7)	1.7 (0.5)			6.20		3.2	3.40	3.43	3.7	3.50	3.46
Rb	66.5 (2.29)	53 (9)	77 (12)	113 (21.9)	56.4–173	91.4	94.8	**74**	73.3	71.1	**149**	150	154
Sr	199 (3.62)	190 (29)	72 (11)	55.5 (9.17)	37.1–76	77.4	103	**336**	340	316	**108**	112	110
Y	46.3 (2.54)	35 (5)	32.5 (5)	35.4 (6.33)	24.3–48.3	35.4	35.1	**24**	23.1	24.6	25	22.9	24.5
Zr	267 (3.92)	253 (39)	292 (44)	281 (48.8)	201–401	260	258	**185**	176	178	**219**	222	227
Nb	15.5 (0.15)	21 (4)	15 (3)	9.85 (1.91)	6.58–14.4	11.2	8.33	**10.3**	10.3	10.2	**8.9**	9.13	9.06
Cs	3.11 (0.11)	3.8 (0.9)	4 (0.9)	3.46 (0.81)	1.87–5.36	2.41	2.71	**1.75**	1.61	1.68	**9.6**	9.67	10.1
Ba	861 (12.5)	1020 (150)	690 (100)	450 (79.6)	297–658	504	489	**1370**	1334	1357	**807**	829	820
La	26.4 (0.19)	24.5 (3.8)	29.5 (4.5)	31.3 (6.24)	20.2–46.0	28.6	26.3	**27**	26.4	26.8	**24**	23.3	23.8
Ce	57.4 (1.96)	49.4 (7.5)	60.5 (9.2)	49.3 (8.40)	32.4–68.5	55.0	55.9	**54.6**	53.5	53.7	**47**	46.4	49.1
Pr	6.96 (0.19)	7.4 (1.2)	7.1 (1.2)	5.88 (1.24)	3.28–9.16	6.62	6.17	**6**	6.01	5.59	4.7	4.86	5.11
Nd	30.6 (0.09)	28 (4)	25.2 (3.9)	24.0 (4.91)	15.5–36.8	25.1	23.2	26	21.7	22.0	**19**	18.8	18.9
Sm	7.66 (0.24)	8.2 (1.6)	5.3 (1.2)	5.26 (1.37)	2.49–8.90	5.58	5.06	**4.88**	4.60	4.87	**4.3**	4.17	4.32
Eu	1.71 (0.10)			0.78 (0.28)	0.00–1.47	1.07	1.02	**1.43**	1.29	1.39	**0.66**	0.67	0.69
Gd	6.54 (0.20)	5.5 (1.6)	5.8 (1.4)	5.22 (1.73)	2.43–9.60	6.48	5.76	4.7	4.49	4.11	**3.7**	3.75	3.70
Tb	1.27 (0.06)	0.91 (0.31)	1.1 (0.3)	0.98 (0.32)	0.00–1.82	0.98	1.02	**0.71**	0.69	0.70	**0.66**	0.63	0.67
Dy	7.74 (0.19)	8.1 (1.4)	6.7 (1.2)	6.46 (1.61)	3.31–10.1	6.79	5.98	**3.8**	3.88	4.04	**4.08**	3.78	3.91
Ho	1.82 (0.08)	1.7 (0.4)	1.4 (0.3)	1.52 (0.32)	0.99–2.31	1.55	1.37	0.86	0.88	0.92	0.95	0.89	0.91
Er	4.84 (0.08)	5.5 (1)	5.1 (0.9)	4.41 (1.21)	2.53–7.99	4.53	4.23	**2.3**	2.38	2.44	**2.6**	2.42	2.55
Tm	0.73 (0.03)	0.59 (0.2)	0.94 (0.24)	0.72 (0.28)	0.30–1.40	0.72	0.75	**0.37**	0.33	0.37	**0.37**	0.37	0.37
Yb	4.78 (0.19)	5.3 (1.1)	4.3 (0.9)	5.17 (1.75)	1.59–8.76	5.00	4.48	**2.32**	2.41	2.41	**2.6**	2.35	2.59
Lu	0.74 (0.02)			0.89 (0.34)	0.30–1.61	0.80	0.79	**0.37**	0.37	0.38	**0.41**	0.38	0.41
Hf	7.12 (0.20)			6.88 (2.34)	3.39–13.3	7.20	6.73	**4.6**	4.59	4.59	**6.2**	6.14	6.36
Ta	1.03 (0.01)			0.99 (0.87)	0.24–5.52	1.25		**0.82**	0.86	0.90	**0.95**	1.01	0.97
Th	6.13 (0.07)			16.2 (3.79)	8.73–26.5	16.5	16.0	**4.5**	4.51	4.52	**15.1**	14.5	14.2
U	2.84 (0.12)			5.39 (1.05)	3.30–7.60	5.16	4.64	**1.94**	1.83	1.88	**5.8**	5.77	5.87
Ba/Rb	12.94	19.25	8.96	3.98		5.51							
Ba/Sr	4.32	5.37	9.58	8.11		6.31							
Rb/Sr	0.33	0.28	1.07	2.04		1.18							
La/Nb	1.70	1.17	1.97	3.18		2.55							
La/Sm	3.45	2.99	5.57	5.95		5.13							

Table 3 Trace element analyses of A1340-7 from the GRIP ice-core and Bo-1 glass from Santorini (HAMMER *et al.*, 2003), the Minoan ash from Gölhisar Gölü, SW Turkey (EASTWOOD *et al.*, 1998; EASTWOOD *et al.*, 1999; PEARCE *et al.*, 2002), Minoan ash from Knossos (WARREN and PUCHELT, 1990) and Aniakchak (UT2011, this study). Figures in parentheses for the data of HAMMER *et al.* (2003) are errors at ±1 standard deviation, and for the LA-ICP-MS data of PEARCE *et al.* (2002) are ±1 standard deviation of the individual glass shard analyses. The latter represents the range of compositions of the individual shards and is not a measure of the analytical precision, which would be approximately ±5% for Ba and Zr; ±20% for Tb, Ho, Tm, Lu and Ta; and ± 10% for the remaining elements. Also included are analyses of the USGS rhyolitic reference materials QLO-1 and RGM-1, which were analysed alongside the Aniakchak tephra (UT2011), with accepted concentrations for comparison (bold = certified, normal = suggested (GOVINDARAJU, 1994)). All concentrations in ppm

es such as fractional crystallisation (PEARCE *et al.*, 2002; PEARCE *et al.*, 2004).

Table 3 also presents new trace element analyses of a sample Aniakchak volcano (UT2011). This analysis has almost identical Sr, Rb, Zr, REE to A1340-7, as well as very similar Ba, Nb, Y and Cs. Any differences between the two data sets can be related in part to the possible accuracy of the SIMS analyses, particularly when allowance is made for the differences between the SIMS analyses of Bo-1 and other analyses of Minoan tephra (e.g. Ba, Nb, see above). The Aniakchak REE analyses are compared with the A1340-7 analyses in Figure 1, where it is evident that the 2 data sets have an indistinguishable

Comparison of samples...		$D^2_{calculated}$	Accept/ reject Ho (D^2 critical 99% = 26.22)
Bo-1 (HAMMER *et al.*)	Minoan tephra, Gölhisar Gölü, (PEARCE *et al.*)	10.78 (17.46)	Accept, samples are possible correlatives
Bo-1 (HAMMER *et al.*)	A1340-7 (HAMMER *et al.*)	26.39	Reject, samples are statistically different
Bo-1 (HAMMER *et al.*)	Aniakchak (UT2011, this study)	136.8	Reject, samples are statistically different
A1340-7 (HAMMER *et al.*)	Aniakchak (UT2011, this study)	14.40	Accept, samples are possible correlatives
A1340-7 (HAMMER *et al.*)	Minoan tephra, Gölhisar Gölü, (PEARCE *et al.*)	47.84 (67.02)	Reject, samples are statistically different
Aniakchak (UT2011, this study)	Minoan tephra, Gölhisar Gölü, (PEARCE *et al.*)	259.8 (810.9)	Reject, samples are statistically different

Table 4 Distance function calculations for a range of possible correlative pairs of samples in this study for the 12 trace elements Rb, Sr, Zr, Nb, Y, Cs, Ba, La, Ce, Pr, Nd and Sm using the methods described by (PERKINS *et al.*, 1998; PERKINS *et al.*, 1995). $D^2_{critical}$ at a 99% confidence level is 26.22. Where $D^2_{calculated} > D^2_{critical}$, the null hypothesis (that the two samples are identical) is rejected. In comparisons including the LA-ICP-MS analyses of the Minoan tephra from Gölhisar Gölü (PEARCE *et al.*, 2002), the first $D^2_{calculated}$ uses the standard deviation of all single shard analyses (which reflects the natural variation between individual shards, not the analytical precision); the $D^2_{calculated}$ in parentheses uses an estimate of the analytical error for the LA-ICP-MS analyses (i.e. 10% relative for all elements, except Zr and Ba at 5%, see PEARCE *et al.* 2004)

REE profile. Figure 2 shows a Thompson-type incompatible element spidergram (THOMPSON, 1982) that compares the Minoan (from PEARCE *et al.* 2002) and Aniakchak (UT2011) tephras with the A1340-7 ice-core glass. The Aniakchak tephra and A1340-7 glass are essentially identical, and they both have markedly different Rb, Sr, Ba, Ti, and Sm from the Minoan tephra. It is clear that the trace element analyses concur with the major element analyses and deny the suggested correlation between the ice-core glass and the Minoan tephra from Santorini; instead they clearly show that the ice-core glass (A1340-7) correlates with the late Holocene Aniakchak tephra (UT2011).

Comparing samples using statistical distance

PERKINS *et al.* (1998; 1995) have developed methods to test the possibility of a correlation between silicic tephra beds using a measure of the statistical distance between pairs of samples. PERKINS *et al.* (1998) define the statistical distance between samples as:

$$D^2 = \sum_{k=1}^{n} (x_{k1} - x_{k2})^2 / (\sigma_{k1}^2 + \sigma_{k2}^2)$$

where n is the number of elements used in the comparison, x_{k1} and x_{k2} are the concentrations of the kth element in the first and second samples, and s_{k1} and s_{k2} are the precisions of the determinations of the kth element in each sample (i.e. the standard deviations of analyses). The value of $D^2_{calculated}$ has a Chi-squared distribution amongst compositionally identical sam-

ples (PERKINS *et al.*, 1995). If $D^2_{calculated} > D^2_{critical}$ for a given confidence level (defined at the outset of the comparison), then the null hypothesis (that the two samples are identical) is rejected and the two samples can be considered to be different at that confidence level. The trace element analyses given by HAMMER *et al.* (2003), PEARCE *et al.* (2002) and the new analyses of the Aniakchak tephra (this study) have been compared using this measure of statistical distance. In this comparison, the heavy REE have been excluded from these calculations because of their relatively large analytical uncertainties. In the LA-ICP-MS data from PEARCE *et al.* (2002) the standard deviation of all single shard trace element analyses (which reflects the wide, natural, inter-shard variation) has been used in the calculations, as well as an estimate of the real analytical error (see PEARCE *et al.* 2004). The results are presented in Table 4, and show that, at the 99% confidence level, neither the Bo-1 (HAMMER *et al.*, 2003) nor the Gölhisar Gölü Minoan (PEARCE *et al.*, 2004) samples can be correlated with A1340-7, the ice-core glass. The data for the Aniakchak tephra (UT2011) and A1340-7 can, by this measure, be regarded as possible correlatives.

CONCLUSIONS

Small volcanic glass shards recovered from the 1645±4 BC layer of the Greenlandic GRIP ice-core are chemically distinct from glass from the Minoan

eruption of Santorini. Instead, they can be confidently correlated with the late Holocene Aniakchak tephra. The precise chronology which can be obtained from the ice-cores thus places a firm date of 1645±4 BC on the eruption of Aniakchak, and this is in good agreement with the published age ranges from ^{14}C dating. The eruption of Aniakchak at 1645 BC is also consistent with the suggestion that the acid volcanic signal in the Greenlandic ice-core results from a major eruption south of Greenland, but north of 30°N (HAMMER *et al.*, 2003). Indeed, the prevailing atmospheric circulation has the potential to readily carry glass north and east from Alaska towards and across Greenland, as exemplified by the Aniakchak tephra fall. The presence of glass shards trapped within the ice-core in this case directly links the Aniakchak eruption with the acid peak at 1645 BC, and while this does not rule out a coincidental eruption of San-

torini at the same time, it leaves the debate over the exact age of the Minoan eruption open.

Acknowledgements

Methods

Major element analyses of UT2011 (Aniakchak tephra) were performed using a Cameca SX-50 WDS electron microprobe at the University of Toronto. Trace elements were determined by solution ICP-MS at the University of Wales, Aberystwyth for UT2011. Full descriptions of all methods used are given elsewhere (PEARCE *et al.*, 1997; PEARCE *et al.*, 2004).

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