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Volcanic ash retrieved from the GRIP ice core is not from Thera

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[1] Tephra found in an ice core from Greenland (GRIP) has been claimed to be from the Minoan eruption of Thera (Santorini), Greece. If true, this would date the eruption, thereby resolving a decades-long debate in chronology. Herein, it is shown that the methods used to match the Greenlandic tephra with Thera are flawed and that the geochemical data imply the tephra is not from Thera.

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1. Introduction

[2] The date of the eruption of the volcano Thera (Santorini), Greece, during the Minoan archaeological period in the second millennium BC, has been much debated. There have been tens of research papers [e.g., *Warren*, 1984; *Hammer et al.*, 1987; *Baillie and Munro*, 1988; *Zielinski and Germani*, 1998a, 1998b; *Wiener*, 2003] and at least two books [*Hardy and Renfrew*, 1990; *Manning*, 1999] devoted to the eruption date. The date has generated such debate because of its potential for resolving Ancient Near Eastern chronology. *Hammer et al.* [2003]—hereinafter "the H report"—have presented tephra (i.e., volcanic ash) found in the GRIP (Greenland Ice core Program) ice core, from Greenland. The H report claims that this tephra is from Thera. If the claim were true, then the eruption would be dated (because the layer of ice in which the tephra was found dates the corresponding eruption). The present work considers the claim.

2. Tephra Matchings

2.1. Prologue

[3] The H report presents geochemical data on tephra from Greenland and also on tephra known to be from Thera. The report asserts that the differences between the two sets of data are "insignificant," but presents little analysis to support this. The assertion is apparently based on an error: treating the standard deviations of the tephra data as though they denoted measurement errors, rather than interparticle variations. This error has also been made in at least two other tephrochronological studies [*Manning*, 1999, section 5.3; *Schmid et al.*, 2000]. (Two data sets can overlap at even one standard deviation and still be recognizably distinct, because

their means are substantially different. What is relevant is the "standard error". An example is given in section 2.2. For a short, informal, elaboration on this topic, see D. J. Keenan, Standard Error in Statistical Analysis, 2003, available at http://www.informath.org/StdErr.pdf.)

[4] The most common method used in statistical analysis to judge the significance of the difference between two sets of data is the *t*-test (i.e., Student's *t* test; descriptions of this can be found in most introductory statistics texts). The *t*-test is not extremely sensitive, but conversely, if it indicates that the two data sets are different, then the conclusion (that they are in actuality different) is very strong. I use it herein.

2.2. Major Constituents

[5] The H report presents the mean, median, and standard deviation for each of ten major chemical constituents of particles from Thera (38 particles) and Greenland (174 particles). For the most abundant constituent, SiO_2, the mean ± stddev (weight%) are 73.2 ± 1.6 (Thera) and 69.6 ± 1.8 (Greenland). The *t*-test gives $p < 10^{-20}$; i.e., if the two tephras were indeed the same, then the chance of having measured values so different is less than 1 in 10^{20}. The same test can be applied to the second-most abundant constituent, Al_2O_3 (Thera, 13.7 ± 0.83; Greenland, 14.5 ± 0.97): this gives $p < 0.000005$.

[6] The statistical significances are great because the numbers of particles are large, which reduces uncertainty. For example, consider SiO_2: the standard error for Thera is $1.6/\sqrt{38} = 0.26$ and for Greenland it is $1.8/\sqrt{174} = 0.14$. This implies that the means are 73.2 ± 0.26 and 69.6 ± 0.14; these do not even overlap at eight standard deviations.

[7] The *t*-test assumes that the underlying populations have normal (i.e., Gaussian) distributions; this is perhaps not true exactly, but it would be easily good enough here, because the *t*-test tends to be robust to departures from normality, and the qualitative conclusions are extremely strong. Additionally, the *t*-tests are not independent, e.g., because a percentage increase in one constituent forces decreases in others; the strength of the individual conclusions, though, implies that this does not matter.

[8] One possible complication to the above is sample contamination. By far the most common contaminant of Theran tephra is plagioclase [*Vitaliano et al.*, 1990; *Pearce et al.*, 2002]. The chemical composition series of plagioclase ranges between $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$. Some arithmetic then readily shows that plagioclase contamination cannot be the cause of the measured differences. (For example, if the high Greenlandic Al_2O_3 was due to plagioclase contamination, then this would also have led to high Greenlandic SiO_2—which is the opposite of the measurements.)

[9] It might be interesting to *t*-test more of the reported major constituents. If a constituent's mean/stddev is near zero, however, then the assumed normal distribution has a significant probability of having a value less than zero, whereas the chemical concentration can never be less than zero. Thus a mean/stddev near zero implies that the normal distribution would be inaccurate. The normal distribution should be accurate enough for the *t*-test if mean/stddev >2.5 in both Theran and Greenlandic data sets. There are four (other) major constituents that have mean/stddev >2.5 in both (see Table 1). To those constituents, then, the *t*-test can be reasonably applied: Na_2O ($p = 0.003$), CaO ($p = 0.004$), K_2O ($p = 0.38$), and FeO ($p < 0.0000001$).

[10] The main conclusion is plain. The two tephras have different compositions. (It might be noted that there is well-developed literature on how to statistically compare compositional data sets, e.g., *Aitchison* [1986] and *Barceló-Vidal et al.* [2001]. Such methods are unneeded here, because the differences are clear from a *t*-test.)

[11] Some additional points deserve mention. The constituents presented by the H report sum to about 99.1% (in both Theran and Greenlandic tephras). The remaining 0.9% is not considered by the H report, but it is likely mostly water. Indeed, Theran tephra particles recovered from a lake in Turkey

Table 1. Major Constituents of Theran and Greenlandic Glasses[a]

	Vitaliano et al. Bo1 Mean	Vitaliano et al. Bo3 Mean	Eastwood et al. Theran Mean	Eastwood et al. Theran Std. Error	Hammer et al. Bo1 Mean	Hammer et al. Bo1 Std. Error	Hammer et al. GRIP Mean	Hammer et al. GRIP Std. Error
SiO_2	74.0	74.0	73.9	0.06	74.2	0.26	70.8	0.14
TiO_2	0.2	0.2	0.3	0.01	0.6	0.08	0.9	0.05
Al_2O_3	13.8	14.1	14.1	0.02	13.9	0.14	14.7	0.07
FeO	2.2	2.0	2.0	0.01	2.2	0.14	3.4	0.08
MgO	0.3	0.3	0.3	0.01	0.3	0.06	0.6	0.04
CaO	1.4	1.3	1.4	0.01	1.8	0.09	2.1	0.05
Na_2O	4.7	4.8	4.8	0.07	3.2	0.19	3.8	0.07
K_2O	3.4	3.3	3.2	0.01	3.8	0.15	3.7	0.04

[a] Abundances (weight percentages) of the eight most-abundant constituents. Abundances are standardized to sum to 100.0 (thus some data appears slightly different from that presented in the cited reports). Bo1 indicates the first climactic phase of the eruption (data from *Vitaliano et al.* [1990, Table 2] is as emended by I. A. Nicholls, private communication, June 2003). Bo3 indicates the third climactic phase. (The second phase input relatively little solids into the atmosphere.) The standard error is the standard deviation for the mean. Vitaliano et al. measured bulk samples retrieved from Thera. *Eastwood et al.* [1999] measured 68 particles retrieved from a site in Turkey, about 400 km away (those particles are a priori more likely to be from the third phase than the first, because the third phase was much the more massive [*Pyle*, 1990; *Sigurdsson et al.*, 1990]). *Hammer et al.* [2003] measured 38 particles from Bo1. Greenlandic data is based on measurements of 174 particles. (Table 1 of the H report reproduces major-constituent data from Vitaliano et al., for comparison with the authors' own data; the reproduced data, however, is not for the Minoan eruption. Table 2 of the H report reproduces trace element data sets from three other teams of researchers; two of those are also incorrectly copied.)

were determined to have a water content of 2.3 ± 1.5% [*Pearce et al.*, 2002]; possibly some of this was due to post-depositional hydration, but the investigators argued against such, noting that other researchers' calculations indicated a magmatic water content of 2.5–3.0%. Substantial variance of water content implies that presenting the data on an anhydrous basis (i.e., as percentages of the non-water component) would considerably decrease the variances of the (other) major constituents. Hence if the H report had presented data on an anhydrous basis, as other investigators have long been doing [e.g., *Smith and Westgate*, 1969; *Vitaliano et al.*, 1990], then the differences between the Theran and Greenlandic tephras would presumably have been even more salient.

[12] The nonwater component of the Theran tephra presented by the H report seems erroneously large, indicating that the H report abundances are inaccurate. Indeed, inaccuracies are apparent from Table 1. The reported abundances of constituents whose differences with Greenlandic tephra are the greatest (SiO_2, Al_2O_3, and FeO), though, are accurate, and inaccuracies in other abundances are insufficient to alter the main conclusion. (Greenlandic abundances are unlikely to be much less accurate than Theran abundances, otherwise the Greenlandic variances would presumably be greater than the Theran variances—see section 3.2.)

2.3. Trace Constituents

2.3.1. Introduction

[13] The H report obtained trace element data on individual particles via SIMS (Secondary Ion Mass Spectrometry; for a detailed survey of this and other techniques, see *Gill* [1997]); the measurement-error relative standard deviation should be about 10% and at most 20% (P. Hoppe, private communication, September 2002). The H report also used pure glass from Theran tephra in making comparisons with Greenlandic tephra, which is much more accurate than using (bulk) pumice.

[14] Before considering the H report further, it is worth briefly reviewing other trace element analyses that have been reported on Theran tephra. The one other report of trace elements of individual particles of Theran tephra is by *Pearce et al.* [2002]. Pearce et al. analyzed 56 particles of Theran tephra, all glass, retrieved from a lake in Turkey. They used laser-ablation ICP-MS (Inductively Coupled-Plasma Mass Spectrometry), which should be generally similar to SIMS in accuracy, in this context. Pearce et al. also compared their data with the results of other studies that had used XRF (X-Ray Fluorescence), INAA (Instrumental Neutron Activation Analysis), and solution ICP-MS on bulk Theran glass (as reported by *Eastwood et al.* [1998], *Peltz et al.* [1999], and *Schmid et al.*

[2000]), as well as on bulk Theran pumice. Pearce et al. concluded that those studies had failed to exclude contamination (e.g., by inclusions)—which requires checking individual particles. After considering the contamination, Pearce et al. judged that the different data sets seemed to be in generally reasonable agreement. Pearce et al. also observed that, for their own data, the high correlations between different elements is strong evidence for there being very little random noise; furthermore, the relevant data sets presented by Pearce et al. well fit with the normal distribution (see section 2.3.4): the combination of low noise and good distributional fit is indicative of very good data.

2.3.2. Data

[15] Details of how particles were checked for contaminants are not given in the H report. The check, though, was made by looking for large spikes in abundances of elements (G. Kurat, private communication, November 2002). Such a check will find particles that have large amounts of contamination, but will obviously miss particles that have small amounts. Recognition of this could potentially have excluded some of the particles that were used to construct the trace element data sets. (For a method to identify particles with small amounts of contamination, see *Pearce et al.* [2002].)

[16] For trace elements, the H report analyzed only 3 particles from Thera. This is too few for precise comparisons, given the large standard deviations. Nonetheless, serious problems with the H report values for Theran tephra are apparent. In particular, the (average) value in the H report for Ba is greater than all 56 values found by *Pearce et al.* [2002], and it is also substantially greater than the bulk values found by all other researchers [*Pearce et al.*, 2002, Table 3]. The same is true for Nb. As well, the H report value for Rb is much less than the value found by Pearce et al. ($p = 0.007$) and much less than the bulk values found by all other researchers.

2.3.3. Comparisons

[17] The H report employed the same method to compare trace element abundances as for major constituents (using 8 glass particles from Greenland). The report claims that the discrepancies between Thera and Greenland for Ti and Cr are "minor"; yet the greater abundances for Greenland are significant at $p = 0.004$ (Ti) and $p < 0.0001$ (Cr) (although the discrepancy with Cr might indeed be due to the filter, as claimed). The H report also suggests that abundances of all other trace elements except Sr and Ba agree; there are, however, other significant discrepancies, even with the small sample sizes: most notably for Rb ($p = 0.005$, Thera greater).

[18] The explanation given by the H report for why the Greenlandic tephra has much more Sr ($p < 0.0001$) and Ba ($p = 0.007$) than Theran tephra is contamination by seawater in Greenlandic ice. The ice core site, however, is 500 km inland, and seawater is diluted in the freshwater ice there at about 1 μg/g [*De Angelis et al.*, 1997]. Hence the explanation is unrealistic. Indeed, simple mass–mass calculations show that each particle of tephra would have had to exchange Sr and Ba with a volume of water many millions of times that of itself, which is not credible, and besides that, such an exchange mechanism would have destroyed the particles. Additionally, why would water affect only Sr and Ba? In fact, seawater contamination would surely affect Na_2O and would thus be expected to increase the variance of Na_2O; yet the variance is not greater for Greenlandic tephra than for Theran tephra.

[19] Abundances of rare earth elements in the Theran and Greenlandic tephras are not significantly different. Such abundances, though, are similar in many large rhyolitic eruptions. For example, the abundances of reported rare earth elements for tephra from the colossal eruption of Toba, Indonesia (75,000 years ago) [*Pearce et al.*, 1999], are not significantly different than those for Theran tephra. See further Figure 1.

[20] A standard tephrochronological test is to compare elemental ratios. This test can highlight differences that are not apparent when elements are compared directly. As an example, consider La and Nd. For each, the abundances in Theran and Greenlandic tephra, as given by the H report, are not significantly different. The ratio of the two

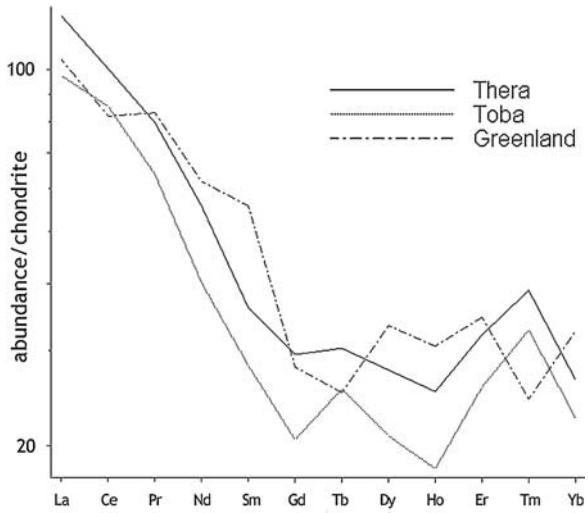

Figure 1. Trace element abundances for tephras from Thera, Toba, and Greenland. Toba, Indonesia, erupted 75,000 years ago. The figure illustrates how different large rhyolitic eruptions can have similar rare earth elemental abundances. (The "Dawson" tephra, erupted in Alaska about 25,000 years ago, is another tephra very similar to the above [*Pearce et al.*, 2003].) Abundances for Toba are from *Pearce et al.* [1999] (measured via solution ICP-MS and scaled relative to their reported Theran abundances). All trace elements that were reported for both Toba and Greenland are shown. Chondrite data for abundance normalization is from *Anders and Grevesse* [1989]. (The H report presented its abundance figure spanning four orders of magnitude, which tends to make even big differences appear little.)

Greenlandic means, however, is 0.88: this is substantially less than the ratio of the Theran means given by the H report, 1.17, and also less than the ratios found by other researchers for bulk glass, which are >1 [*Pearce et al.*, 2002, Table 3], as well as less than the minimum on the 56 particles analyzed by *Pearce et al.* [2002] 1.08. (The linear correlation of La and Nd among the particles analyzed by Pearce et al. is 0.90 ± 0.03.)

2.3.4. Statistical Notes

[21] For every trace element considered herein, mean/stddev $\geq$3.4 for both Theran and Greenlandic data presented in the H report. Additionally, data sets for Yb, Rb, Sr, Nb, Ba, Sm, Ce, Nd, and La in Theran tephra are presented by *Pearce et al.* [2002]. That data fits with the normal distribution (skewnesses 0.0, 0.1, 0.0, −0.1, 0.3, 0.1, −0.2, 0.2, and −0.1, respectively, and kurtoses that are insignificantly different from normal except for Yb—1.0 below normal). Each data set has a substantial linear correlation with every other data set, though; so the statistical tests are not wholly independent.

2.3.5. Conclusions

[22] There are substantial methodological problems with the trace element analyses in the H report. Even allowing for these problems, though, it seems very likely that the Theran and Greenlandic tephras have different trace element compositions.

3. Remarks

3.1. Glass Heterogeneity

[23] Various processes can cause magmatic glass to be heterogeneous, and these could obviously affect tephra comparisons. The primary such process is fractional crystallization (mineral formation) [*Hall*, 1996, chap. 7; *Best and Christiansen*, 2001, chap. 12]. Fractional crystallization occurs in local portions of a magma; so as elements are concentrated into crystals, their abundances throughout the residual melt can vary. Elements with a tendency to go into crystals are called "hygromagmatophobic" (or "compatible") [*Rollinson*, 1993, chap. 4; *Marshall and Fairbridge*, 1999]. In comparing trace elements, it is thus best to focus on nonhygromagmatophobic elements [*Best and Christiansen*, 2001, chap. 12] (and ideally, their ratios, which should naturally be close to constant within a given magma).

[24] An element that is strongly hygromagmatophobic with respect to plagioclase could reasonably have had its abundance vary substantially within the Theran magma. Among the elements presented by the H report though, only one, Sr, is listed by *Rollinson* [1993, Table 4.3] as being strongly hygromagmatophobic with respect to plagioclase. And there is good evidence that plagioclase did not cause the Sr disparity: the Theran Sr mean presented by the H report is within the range of values found by other researchers [*Pearce et al.*, 2002, Table 3], whereas the Greenlandic Sr mean is substantially greater than the Theran values found by other researchers as well as much greater than the maximum value found by Pearce et al.

[25] Although plagioclase was much the most common mineral in the Theran magma, additional minerals were present in small amounts, most notably apatite [*Vitaliano et al.*, 1990; *Pearce et al.*, 2002]. Many elements presented by the H report are strongly hygromagmatophobic with respect to apatite [*Rollinson*, 1993, Table 4.3]. As an example, consider La. Its abundance in Greenlandic tephra (24.5 ± 3.8 ppm) is no greater than its abundance in Theran tephra (29.5 ± 4.5 ppm). The standard deviations are both very low (15% relative, which is lower than that of any element studied by *Pearce et al.* [2002], including La); yet distal tephra, such as from Greenland, is extremely unlikely to be from a single local portion of a magma, and so effects of apatite formation would have led to a large standard deviation for Greenlandic tephra La. Hence apatite could not have affected the Greenlandic La. The same argument applies for Ce. Hence apatite was very unlikely to have affected the Greenlandic tephra; and if it had significantly affected the Theran tephra, the Theran tephra would have had lower abundances than the Greenlandic tephra—which is not the case.

[26] Another process that can lead to glass heterogeneity is the reverse of crystal formation: crystal dissolution. Typically, rock from the top of the magma chamber is melted and slowly assimilated by the magma [*Hall*, 1996, chap. 7]. Thera's eruption had a precursory (or opening) phase [*Heiken and McCoy*, 1990; *Cioni et al.*, 2000], which was presumably sourced from the top of the chamber. Glass from the "A" half of this phase is similar to, but nonetheless significantly different than, glasses from the main climactic phases (unpublished data, cited by S.R. Taylor [*Heiken and McCoy*, 1990, p. 88] and kindly supplied to the author by I.A. Nicholls). This precursor glass, though, is at least as rich in silica as glasses from the main phases, whereas the Greenlandic glass is much less rich in silica. Hence the difference between Greenlandic and Theran glasses cannot be explained by this process.

[27] Tephra believed to be from Thera has been found in northeastern Crete [*Soles et al.*, 1995; *Manning*, 1999, section 4.1], roughly 150 km SSE of Thera. Its sampled glass, however, appears slightly different from the three main Theran glasses [*Soles et al.*, 1995]. A credible source of the Cretan tephra is the "A" half of Thera's precursory phase, because the regional prevailing winds are westerly and the initial dispersion of the "A" half of the phase is S [*Cioni et al.*, 2000] (whereas the initial dispersion of the "B" half is SE [*Cioni et al.*, 2000], and the dispersion of the main phases is broadly E [*Sigurdsson et al.*, 1990; *McCoy and Heiken*, 2000]). Alkalis, especially Na, in the Cretan glass were probably higher than in the published analyses, and when they are adjusted to better match the Al content (via the alumina saturation index), the major constituents of this glass are very similar to those of the precursor "A" glass. (Alkali, especially Na, undermeasurement is an oft-occurring problem [*Hunt and Hill*, 1993]. Indeed, it might be better to ignore Na in tephrochronology: this would improve the precisions for other major constituents.) As well, the analyzed Cretan tephra is visually similar to tephra from the "A" half of the precursory phase only (I.A. Nicholls, private communication, May 2003).

[28] Finally, I note that Thera's eruption had three main climactic phases, and major constituents of glasses from each of these phases are very similar [*Vitaliano et al.*, 1990, Table 2; *Druitt et al.*, 1999, Table 4.5]. To conclude, glass heterogeneity is not a possible cause for the difference between the Theran and Greenlandic tephras.

3.2. Reply of Hammer et al.

[29] A draft of this paper was sent to C.U. Hammer and co-authors, who replied that they were unconvinced. The authors claimed that the Greenlandic tephra originated in a special phase of Thera's eruption and, as well, changed composition due to its residence in the stratosphere—primarily because of acidification and secondarily because of aeolian differentiation; furthermore, they noted that there are substantial uncertainties in the trace element values, due to the small numbers of particles measured (C.U. Hammer, private communication, 2003, cited with permission).

[30] Regarding the Greenlandic tephra originating in a special phase of Thera's eruption, there is no record

of such special tephra anywhere else. Additionally, the eruption's phases were co-genetic (i.e., from the same source magma) [*Druitt et al.*, 1999], and potential differences in glass compositions cannot explain the differences between the Greenlandic and Theran tephras, as discussed in Section 3.1.

[31] Regarding acidification, this would be unlikely to much affect most nonalkalis. As for alkalis, four were measured for the H report: one (Rb) is indeed less abundant in the Greenlandic tephra than in the Theran tephra, but two (K and Cs) are not significantly different in their abundances, and the fourth (Na) is more abundant in Greenland. Moreover, acidification might be expected to increase the variances: among the six major constituents that have distributions that are at least roughly normal (judged by mean/stddev >1.5), none has a significantly greater variance in the Greenlandic tephra, and one (K_2O) has a significantly greater variance in the Theran tephra; also, none of the trace constituents have significantly different variances.

[32] Regarding aeolian differentiation, this would not seem to affect trace constituent abundances per se, and there is no obvious mechanism by which it would substantially affect major constituent abundances, especially for glass.

[33] Last, the trace element sample sizes (3 and 8) were considered in section 2.3. To summarize, the authors' claim is without evidence.

[34] Indeed, using the same reasoning, the Greenlandic tephra could be argued to match any (non-Arctic) eruption.

4. Conclusions

[35] The conclusion to be drawn from the tephra data presented in the H report is clear: the Greenlandic tephra is not from the Minoan eruption of Thera. Additionally, I have shown how better methodologies should have been employed.

Acknowledgments

[36] Kind thanks are offered to N. J. G. Pearce, for encouragement and essential help, and to G. Heiken, R. M. Porter, D. M. Pyle, S. R. Taylor, and W. M. White for comments on drafts.

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