

**Greenland ice core evidence of the 79 AD Vesuvius eruption**

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# Greenland ice core evidence of the 79 AD Vesuvius eruption

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Received: 2 October 2012 – Accepted: 26 October 2012 – Published: 7 November 2012

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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## Abstract

Volcanic tephra are independent age horizons and can synchronize strata of various paleoclimate records including ice and sediment cores. Before such paleoclimate records can be synchronized, it is essential to first confidently identify individual independent marker horizons. The Greenland Ice Core Project (GRIP) ice core from Central Greenland is often used as a “golden spike” to synchronize Northern Hemisphere paleoclimate records. The Holocene section of the GRIP ice core is dated by multi-parameter annual layer counting, and contains peaks in acidity,  $\text{SO}_4^{2-}$  and microparticle concentrations at a depth of 428.4 to 429.6 m, which have not previously been definitively ascribed to a volcanic eruption. Here, we identify tephra particles and determine that volcanic shards extracted from a depth of 429.2 m in the GRIP ice core are likely due to the 79 AD Vesuvius eruption. The chemical composition of the tephra particles is consistent with the K-phonolitic composition of the Vesuvius juvenile ejecta and differs from the chemical composition of other major eruptions ( $\geq$  VEI 4) between 50–100 AD.

## 1 Introduction

Major volcanic eruptions are phenomena which have dramatic consequences for climate and human lives. Volcanic tephra can blanket landscapes thousands of kilometers from the eruptive site (Davies et al., 2005) thereby destroying underlying vegetation and property. In many cases vast amounts of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and associated aerosols pollute the stratosphere for several years. This stratospheric veil reduces the solar radiation reaching Earth’s surface and causes a general cooling for months to decades (Briffa et al., 1998). The climatic impact of volcanos depends on the volume of aerosols injected into the stratosphere as well as the geographic site of the eruption. Major low-latitude explosive volcanoes that inject  $\text{H}_2\text{SO}_4$  into the stratosphere are capable of cooling the global climate for several years (Kelly et al., 1996). The most extreme recent examples of such global cooling include the eruption of Tambora,

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Indonesia resulting in the “year without a summer” (Stothers, 1984; Briffa et al., 1998) or Pinatubo, Philippines which masked global warming trends during the 1990s (Soden et al., 2002). Knowledge of past volcanic activity, especially eruptions which have sufficiently polluted the stratosphere to influence the climate over several years, is essential to interpreting past climatic trends.

Ice cores from polar ice sheets offer quantitative and well-dated records of past volcanic activity reaching back several millennia (Davies et al., 2010). The volcanic signals observed in ice cores include increased concentrations of sulfuric acid and/or sulfates. Volcanos release  $\text{SO}_2$  into the atmosphere which oxidizes in the eruption plume to form  $\text{H}_2\text{SO}_4$  (Langway et al., 1988).  $\text{H}_2\text{SO}_4$  is able to reach the stratosphere and this atmospheric height means that even  $\text{H}_2\text{SO}_4$  that forms in low-latitude volcanic clouds can eventually reach the polar regions (Langway et al., 1988). Volcanically-produced acids including  $\text{H}_2\text{SO}_4$  are scavenged by precipitation and are deposited by snow onto the Greenland ice sheet (Clausen and Hammer, 1988; Langway et al., 1988; Clausen et al., 1997; Zielinski and Germani, 1998). During years without major eruptions the snow falling onto the ice sheet only contains background amounts of  $\text{H}_2\text{SO}_4$ . This alternation ultimately creates ice layers with varying acid concentrations. The volcanic  $\text{H}_2\text{SO}_4$  preserved in ice cores can be detected as acidity peaks determined from electrical conductivity measurements (ECM) and/or as increased concentrations in sulfate ions ( $\text{SO}_4^{2-}$ ) (Clausen et al., 1997; Bigler et al., 2007; Davies et al., 2010). Volcanos also eject HCl and HF into their plume which may work to enhance the ECM signals (Langway et al., 1988; Clausen et al., 1997).

The intensity of the volcanic signal recorded in polar ice cores depends to some extent on the eruption site, where neighboring volcanoes have a greater impact than low-latitude eruptions. Greenland ice cores mainly record Northern Hemisphere volcanic activity (e.g. Clausen and Hammer, 1988; Langway et al., 1988; Clausen et al., 1997) although it has been speculated that a few Southern Hemisphere eruptions such as 186 AD Taupo, New Zealand may have reached sufficient stratospheric heights (55 km) that they were deposited on the the Greenland Ice Sheet (Hammer, 1984; Zielinski

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et al., 1994). When a volcanic signal is faint in the ice core stratigraphy additional information is generally required in order to identify the eruption. Acidity peaks are not always indicative of volcanic eruptions (Davies et al., 2010) and additional information may be necessary to develop more robust conclusions to determine if an ice layer indicates a past eruption. Often only the chemical signature or presence of micrometer size tephra particles in the ice helps to “fingerprint” the acidity signal to a specific eruption site.

Volcanoes eject silicate particles with distinct chemical compositions and these airborne glass particles are deposited on ice sheets. Due to their size and insolubility in the atmosphere, these particles are often deposited as dry deposition on glacier surfaces before the other byproducts such as  $\text{H}_2\text{SO}_4$  arrive (Hammer et al., 2003; Vinther et al., 2006; Davies et al., 2010). This difference in depositional timing sometimes leads to tephra horizons in ice cores located stratigraphically below  $\text{H}_2\text{SO}_4$  peaks. Individual glass shards can be extracted from the ice layers and can be matched to the the chemical composition of tephra from known eruptions (Palais, Kirchen and Delmas, 1990) to determine the source of the volcanic material. Developments in analyzing and geographically compiling data on tephra horizons in ice cores that are not easily seen by the naked eye have widely expanded our knowledge regarding the scope and impact of past volcanic eruptions (Davies et al., 2010 and references within). Tephra forms independent marker horizons across distances up to 1000s of kilometers and allows the synchronization of ice and marine core records (Davies et al., 2005, 2010; Blockley et al., 2007).

The number of eruptive explosions with well-documented historical information are limited, and the majority of observational data on volcanic activity exists from 1500 AD until present (e.g. Lamb, 1970). One exception is the Vesuvius eruption in 79 AD that resulted in the destruction of Pompeii and Herculaeum (Sheridan et al., 1981). The concensus of historical data and volcanological literature suggests that the eruption occurred between 24–25 August 79 AD (Stothers and Rampino, 1983). The Vesuvius

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eruption may be the oldest eruption that can be dated to an exact year (Zielinski and Germani, 1998) and is therefore an important horizon for synchronizing chronologies.

The famous observations of Pliny the Younger form the bulk of the historical record of the 79 AD Vesuvius eruption, and the term “plinian” is applied to eruptions characterized by a basal gas thrust and an upper steady sustained convective column (Cioni et al., 2000). The deposits of the 79 AD eruption record a complex eruptive sequence, with a thick blanket of pyroclastic fall and flow products covering the volcano and a wide surrounding area. During the plinian phase a mixture of gas and tephra particles were injected into the atmosphere which returned to the surface primarily by dry deposition (Carey and Sigurdsson, 1987; Cioni et al., 1992, 2000). The plinian phase created two composite eruption units formed by a sequence of white and grey pumice intercalated by ash flow. Deposits are compositionally zoned from early phonolitic white pumice to late phono-tephritic grey pumice. In both the white and grey pumice the main phenocrysts are sanidine and clinopyroxene (Cioni et al., 1995). However, the groundmass of the white and grey pumice varies where the white pumice is characterized by colorless glass while the grey matrix contains a greater percentage of brown glass microliths. The white pumice forms a SSE dispersal fan and deposits record a progressive increase of magma discharge rate (up to  $8 \times 10^7 \text{ kg s}^{-1}$ ) resulting in the continuous rise of a convective column up to 26 km. The grey pumice has a SE dispersal, with a slight counterclockwise rotation with respect to the white pumice axis. Following the shift in magma composition a new, rapid increase of magma discharge rate (up to  $1.5 \times 10^8 \text{ kg s}^{-1}$ ) occurred with the growth of a column up to 32 km (Carey and Sigurdsson, 1987; Sigurdsson et al., 1990). The final phreatomagmatic phase caused pyroclastic flows and surges following the caldera collapse (Carey and Sigurdsson, 1987; Cioni et al., 1992, 2000). These high-temperature avalanches of gas and dust caused the majority of ground damage but due to their surficial nature likely did not cause any major contribution to the stratospheric tephra. The total mass injected to the atmosphere and surroundings by the Vesuvius eruption is estimated as approximately  $4 \text{ km}^3$  dense rock equivalent (Sigurdsson et al., 1985). Hence the mass of material

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ejected by Vesuvius and the height of the convective columns suggest that tephra and volcanic acids could reach the Greenland ice sheet surface.

The Greenland Ice Core Project (GRIP) ice core from the summit region in Central Greenland (72.58° N, 37.63° W, 3232 m a.s.l.) and the North Greenland Ice Core Project (NGRIP; 75.1° N, 42.32° W, 2917 m a.s.l.) ice core are multi-parameter climate archives dated for the past 60 000 from their stratigraphic records (Hammer et al., 1997, Svensson et al., 2008). The Greenland Ice Core Chronology 2005 (GICC05) (Rasmussen et al., 2006; Vinther et al., 2006; Andersen et al., 2006; Svensson et al., 2008) serves as a paragon for determining the chronology of other climate records, and thus it is essential to study independent markers within ice layers with as much precision as possible. Here, we investigate the GRIP ice core between 428 to 430 m depth to determine if evidence of the 79 AD Vesuvius eruption is preserved in the ice strata.

## 2 Experimental section

### 2.1 Field sampling

The 3029 m GRIP ice core was drilled at the summit of the Greenland ice cap from 1989–1992. The 10 cm diameter core was first cut into 55 cm lengths and then sub-sampled with longitudinal cuts for further measurements. A continuous ~2 mm resolution ECM acidity profile was created in situ in the GRIP sub-surface laboratories. The ECM profile reveals acid peaks ascribed to volcanic signals through the Holocene and constituted the basis for selecting ice core sequences for more detailed chemical analysis (Clausen et al., 1997). More than 100 000 samples were cut in situ using a stainless steel band saw for laboratory analyses of stable oxygen isotopes ( $\delta^{18}\text{O}$ ) (Johnsen et al., 1997). The seasonal variation of  $\delta^{18}\text{O}$  provided the basis of precise stratigraphic dating back to 1800 BC. Major volcanic signals were later used to tie the Holocene GRIP record to the NGRIP and DYE-3 Greenland ice core records (Johnsen

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et al., 1997; Vinther et al., 2006), resulting in an estimated dating accuracy of  $\pm 2$  yr for the 2000 yr old ice strata (Hammer et al., 1997).

## 2.2 Sample preparation

### 2.2.1 Decontamination

5 The ECM data demonstrate only one major volcanic signal (429.1 m depth) between 60 to 90 AD (Fig. 1) where ECM peaks  $> 4 \mu\text{eq kg}^{-1}$  are generally considered to signify volcanic eruptions in Greenland ice cores (Clausen et al., 1997). We concentrated our study on the ice strata between 428.4 to 429.6 m depth, which correspond to an initial age range of 77 to 82 AD. We decontaminated 2 ice core sections (3 × 3 cm wide, 55 cm  
10 long) under a laminar flow clean bench in a  $-20^\circ\text{C}$  cold room. We used stainless steel chisels to mechanically remove successive veneers of ice from the outer periphery of the core sections. The inner core obtained after chiseling was divided into 16 equal depth intervals.

### 2.2.2 Microparticle and major ion sample preparation

15 Decontaminated samples for major ions remained frozen in Coulter Accuvettes until just before analysis when they were melted under a Class 100 laminar flow bench at the University of Copenhagen (Steffensen, 1997). Dust concentrations were measured by melting a groove along a decontaminated ice core section and measuring the intensity of  $90^\circ$  scattered laser light (633 nm) in the melt water stream (Hammer, 1985). The  
20 laser light system was calibrated by measuring sequences of samples on both the laser system and continuous flow analysis system. Major ion samples were measured using a DX 500 ion chromatograph at the University of Copenhagen on the same ice sections as the samples used for microparticle analysis.

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### 2.2.3 SEM-EDS sample preparation

The decontaminated samples were filtered using a Milipore (Bedford, MA, USA) stainless steel filtration system mounted on a high density polyethylene (HDPE) support that was cleaned in a 10 % ultrapure nitric acid bath and then a Mili-Q bath for a week in a Class 100 clean room. Polycarbonate Milipore filters (porosity 0.4 mm; diameter 13 mm), previously cleaned using successive 0.1 and 0.01 % ultrapure diluted nitric acid baths, were used for sample filtration. The filters containing the samples were kept frozen at  $-20^{\circ}\text{C}$  until the day of their analysis. Immediately preceding their analysis, individual filters were fixed with double-sided tape onto aluminum stubs and then carbon coated in order to amplify sample conductivity.

## 2.3 Analytical techniques

### 2.3.1 SEM-EDS

Individual particle analyses of the 16 samples were conducted using a Scanning Electron Microscope with an Energy Dispersive System (SEM-EDS, Philips XL30 equipped with an X-ray energy dispersive spectrometer, EDAX DX4) at the Department of Earth Sciences, University of Pisa. Instrumental conditions included 20 kV accelerating energy and 1 nA beam current. Before each session the quality of the analyses was checked using certified minerals and glasses as reference standards (Marianelli and Sbrana, 1998). The 2–5 micron sample size and unpolished specimen surfaces limits the accuracy of SEM-EDS analyses of tephra (Kuehn et al., 2011). The EDAX software normalizes analyses to 100 resulting in the analytical error affecting mainly the more abundant elements (i.e.  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ). The particles did not have any inclusions or secondary particles accreted on the tephra surfaces, and such a homogenous structure improves the accuracy of the SEM-EDS analyses.

When performing EDS analyses on glasses, a raster area of  $100\ \mu\text{m}^2$  is usually used to prevent the loss of sodium (Na). The size of the analyzed particles prevents

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the application such a large raster area, so we applied the empirical correction method proposed by Nielsen and Sigurdsson (1981) in order to control the time-dependent loss in intensity of the Na line during the electron bombardment. The Na decay curve was determined on homogenous and microlith-free glasses from white pumice filtered from the ice strata assumed to be 79 AD. We collected several spectra at 10, 20, 30, 40 . . . . 100 s live times in order to make a regression line and extrapolate the Na content at 0 s, before any Na diffusion occurs (Nieslen and Sigurdsson, 1981). A least squares fit of the sodium decay curve as a function of time during electron bombardment was determined. The regression line gives initial Na concentration under normal operating conditions (100 s live time) and assuming that the Na decay begins at  $t = 0$ . Analyses (100 s live time) were then corrected for the estimated Na loss (up to 25 % for 79 AD Vesuvius phonolites) and then normalized to 100.

### 2.3.2 Major ions and microparticle concentrations

Microparticle concentrations were measured at the University of Copenhagen with a continuous flow analysis system. Here, we examine samples from 428.4 to 429.6 m depth to examine if a spike in the particulate concentrations ratios were present over the relevant ice core section. The major inorganic soluble components ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ , MSA) were determined at the University of Copenhagen with a Dionex 4000i ion chromatograph (Steffensen, 1997) to explore if the acid peak revealed by the in situ ECM measurements at 429.1 m correlated with major ions potentially caused by a volcanic eruption. Each sample was melted prior to measurement and decanted into 5 ml vials for automatic injection into the ion chromatograph.

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### 3 Results and discussion

The GRIP ice core contains an acidity peak at 429.1 m as revealed by ECM data (Fig. 1). This acid peak is a common signal in Greenland ice cores including DYE-3 and NGRIP (Clausen et al., 1997; Vinther et al., 2006) and was originally dated to 80 AD in the DYE-3 ice core based on multi-parameter annual layer counting (Clausen et al., 1997). Later this date was revised to 79 AD in the GICC05 dating effort (Vinther et al., 2006) based on the assumption that the acidity peak derived from the Vesuvian eruption. Species other than  $H_2SO_4$  may influence the ECM and so parallel investigations of sulfate concentrations help determine if acidity peaks indicate an increase in  $H_2SO_4$ , and hence may be a marker of volcanic activity (Taylor et al., 1997). Ion chromatograph measurements clearly demonstrate that the acid peak was caused by sulfuric acid and therefore is the result of a volcanic eruption (Fig. 2).

The isotopic and major ion records (Figs. 2 and 3) demonstrates that the major deposition of sulfuric acid on the ice sheet lasted between 0.5 to 0.7 yr. The slightly elevated sulfate concentrations and acidity from 428.8 to 429.0 m suggest that a fraction of the volcanic acid may also have been deposited during the following year. This elevated sulfur signal for more than one season agrees with suggestions by Davies et al. (2010) that sulfuric acid may be deposited on ice sheets months after the volcanic eruption.

The GRIP sulfuric acid flux between 428.8 to 429.0 m is consistent both with elevated sulfuric acid concentrations in the DYE-3 ice core for strata dated within the same range and with the quantity of sulfuric acid ejected by the 79 AD Vesuvius eruption (Clausen et al., 1997). The estimated amount of sulfuric acid released into the atmosphere from this volcanic event ranges between 38 to 52 Mt (Zielinski, 1995; Clausen et al., 1997). A similar estimate from the same volcanic signal in the DYE-3 ice core (from an annual layer dated to 80 AD) suggests  $\sim 47$  Mt of sulfuric acid was injected into the atmosphere by Vesuvius (Clausen et al., 1997). The variability between sites may be due to wind erosion or the spatial distribution of deposition (Clausen and Hammer, 1988; Zielinski,

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1995). These estimates of the ejected sulfuric acid are up to four times greater than the present average global annual flux of 13 Mt SO<sub>2</sub> emissions from explosive and non-explosive volcanism (Bluth et al., 1993), demonstrating the likelihood that Vesuvius eruption products would have been sufficient to change hemispheric concentrations of sulfuric acid.

Elevated sulfuric acid concentrations should be double-checked with tephra layers to provide conclusive proof of the source of past volcanic activity (Davies et al., 2010). Both differences in atmospheric transport paths and preferential gravitational settling of the tephra particles can result in their deposition on ice sheet surfaces before the stratospherically-transported sulfuric acid arrives in snowfall, resulting in stratigraphic offsets between the two materials (Vinther et al., 2006; Davies et al., 2010). Microparticle concentrations (Fig. 2) peak between 429.25 and 429.15 m, and are stratigraphically below the sulfuric acid peak at 429.1 m. The microparticle profile in a core sequence only serves to indicate if an unusually high concentration of particles are present rather than serving as a guaranteed indicator of where to search for volcanic ash particles in a core sequence, as the majority of microparticles in Greenland ice cores originate from continental dust (Steffensen, 1997). Previous analyses of volcanic glasses in Greenland ice cores indicate that the concentration of volcanic shards in ice may vary by orders of magnitude and can range from visible ash layers to as few as < 10 particles per kg of ice (Davies et al., 2010 and references within).

No volcanic glass particles were found in the 429.15–429.25 m microparticle peak, and all microparticles had elemental chemical compositions typical of continental crust. However, the microparticle concentration peak at 429.3 m contained six tephra particles with a K-phonolitic composition where this composition is indicative of Vesuvius 79 AD volcanic products (Table 1; Balcone-Boissard et al., 2009). For many Vesuvius eruptions, groundmass glasses generally exhibit a larger scatter than bulk rock analyses. This microscale compositional heterogeneity is particularly accentuated by the large microlith content of many of the Vesuvius volcanic products (Santacroce et al., 2008). The analyzed shards in this paper do not contain microliths, however, their

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composition is comparable to glass composition box plots of Veuvius eruptions (San-  
tacroce et al., 2008). The particles filtered from the GRIP ice core sections have similar  
compositions to Vesuvius (Pompeii 79 AD) tephra (Table 1 and Fig. 4). The ice core  
tephra composition is especially similar to the white pumice glass composition (Mess-  
chumacher, 1994). We also extracted and analyzed other materials from the filtered  
samples. The microparticles contained sanidine fragments, a mineral phase very com-  
mon in products of K-phonolitic eruptions, and these fragments add further support for  
the hypothesis of Vesuvius as a source of this microparticle layer.

Between 50 to 100 AD eruptive products from different sources could have poten-  
tially reached the Greenland ice sheet. A list of potential relatively coeval volcanoes  
with similar eruptive strengths are reported in Table 2. The volcanic explosivity index  
(VEI) measures the magnitude and associated tephra volumes of eruptions (Newhall  
and Self, 1982). A VEI of 4 or greater suggests that the volcano was sufficiently explo-  
sive to have injected material into the stratosphere (Newhall and Self, 1982), and so  
Southern Hemisphere volcanoes with a VEI of  $\geq 4$  are included in Table 2. Although  
stratospheric particles originating in the Southern Hemisphere can reach Greenland  
(Zielinski et al., 1994), tephra from neighboring or Northern Hemisphere volcanoes  
are more likely to be deposited on the ice sheet (Langway et al., 1988, Clausen and  
Hammer 1988, Clausen et al., 1997). Many of the coeval eruptions, such as Ambrym,  
Vauatu or Raoul Island in the Kermadec Island chain, are located in areas where it  
is difficult for the volcanic aerosols to have reached the Greenland ice sheet. The K-  
phonolitic characteristics of the Vesuvius products differ from the composition of the  
tephra from known explosive eruptions between 50–100 AD (Table 2). The geochem-  
istry of the tephra extracted from the GRIP ice core at 429.3 depth are consistent with  
such a K-phonolitic composition. In the neighboring Greenland Ice Sheet Project 2  
(GISP2) ice core, only one  $\text{SO}_4^{2-}$  peak between 0–150 AD is attributed to a volcanic  
eruption (Zielinski, 1995). The cumulative dating error of the most recent 2100 yr of the  
GISP2 core is 0.5 %, suggesting that even though a  $\text{SO}_4^{2-}$  peak occurs at 78 AD on  
the GISP2 age scale, the 79 AD Vesuvius eruption is a likely source (Zielinski, 1995).

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Our identification of Vesuvian tephra deposited one year before the main acidity peak in the GRIP ice core, indicates that the acidity peak observed in Greenland should be assigned to the year 80 AD, supporting the original DYE-3 interpretation, whereas the GICC05 timescale (shown in Fig. 2) is offset by one year.

## 4 Conclusions

We demonstrate that the high acidity signal and  $\text{SO}_4^{2-}$  spike found at 429.1 m depth and the microparticle peak at 429.3 m in the GRIP ice core are caused by a major volcanic eruption. We identified volcanic glass fragments at 429.3 m depth, where the elemental compositional analysis strongly suggests that they originated from the 79 AD Vesuvius eruption. This offset between the location of increased acidity and  $\text{SO}_4^{2-}$  is consistent with the literature as tephra can be deposited on surfaces before the stratospherically-transported  $\text{SO}_4^{2-}$  (Vinther et al., 2006; Davies et al., 2010). Elemental compositional analysis of the six volcanic glass strongly suggest that they originated from the 79 AD Vesuvius eruption. The low number of glass fragments in the ice is likely due to the relatively low height of the eruption column (26–32 km), and the SSE trajectory of the plinian phase of the eruption (Carey and Sigurdsson, 1987; Sigurdsson et al., 1990). This low number of volcanic glass fragments is consistent with quantities of volcanic ejecta in ice cores (Palais et al., 1992). The 79 AD Vesuvius eruption may be the oldest volcanic eruption with detailed historic records that can be dated to an exact year (Zielinski and Germani, 1998), and this independent tephra horizon helps extend the match between the historic and paleo records. Our results can help refine chronologies and synchronization between ice core and marine sediment records.

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*Acknowledgement.* This work was supported in Italy by the Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile (ENEA) as part of the Antarctic National Research Program (Environmental Contamination and Glaciology) and in Denmark by Statens Naturvidenskabelig Forskningsråd (SNF) as well as the XII Directorate of CEC, the Carlsberg Foundation and the Commission for Scientific Research in Greenland. We thank L. Pozzato for laboratory assistance and A. Sbrana for the useful discussions.

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**Table 1.** Concentrations (wt%) of major oxides and Cl in the six micrometer-sized volcanic glass particles found at a depth of 429.3 m in the GRIP ice core. Mean and standard deviations from 10 K-phonolitic volcanic glasses from the 79 AD eruption (data from Balcone-Boissard et al., 2009). Totals have been normalized to 100 %.

	Particle 1	Particle 2	Particle 3	Particle 4	Particle 5	Particle 6	Vesuvius	Vesuvius (SD %)
SiO <sub>2</sub>	61.36	60.52	56.42	57.12	57.30	57.75	55.55	0.39
TiO <sub>2</sub>	0.92	0.34	0.63	0.57	0.66	0.58	0.25	0.08
Al <sub>2</sub> O <sub>3</sub>	19.93	21.14	20.41	20.90	20.97	21.16	22.42	0.20
FeO	0.77	0.30	4.63	4.79	3.63	2.48	2.35	0.22
MgO	0.14	0.10	1.29	1.19	0.93	0.79	0.20	0.02
CaO	2.95	3.71	3.11	2.99	3.19	3.03	2.56	0.09
Na <sub>2</sub> O	7.54	9.46	5.64	5.11	5.63	6.53	6.66	0.07
K <sub>2</sub> O	6.21	4.25	7.04	6.70	6.84	7.14	9.89	0.13
P <sub>2</sub> O <sub>5</sub>	0.00	0.16	0.19	0.00	0.11	0.10		
Cl	0.18	0.02	0.64	0.63	0.74	0.44	0.33	0.05

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**Table 2.** Known major volcanic eruptions between 50–100 AD. The Krafla, Iceland eruption is included due to its proximity to the GRIP ice core site. Other than the Krafla and Asos eruptions, the volcanic explosivity index (VEI) data are compiled in the Smithsonian Global Volcanism Program (<http://www.volcano.si.edu/world/largeeruptions.cfm>).

Eruption	Location	Year	VEI	Tephra Volume	Eruptive characteristics:	Magma and/or tephra composition	References
Tolbachik	Kamchatka	50 AD (?)	4+	$9.0 \times 10^8 \text{ m}^3$	Flank (excentric) vent Radial fissure eruption Explosive eruption Lava flow(s)	high-MgO and high-Al <sub>2</sub> O <sub>3</sub> basalts.	Doubik and Hill, 1999, Kersting and Arculus, 1995
Ambrym	Vanuatu	50 AD ±100 yr	6+	$> 7.0 \pm 1.0 \times 10^{10} \text{ m}^3$	Central vent eruption Explosive eruption Pyroclastic flow(s) Lava flow(s) Caldera collapse	Dacite	Baker and Condliffe, 1996; Robin et al., 1993
Krafla	Iceland	50 AD	2			Tholeiitic rhyolite, Icelandite, Dacite	Lacasse C., Garbe-Schonberg C.D., 2001; Jonasson, 1994
Pelee	West Indies	50 AD (?)	3–6?		Central vent eruption Explosive eruption Pyroclastic flow(s)	Course-grained andesitic pumice	Westercamp and Traineau, 1983
Churchill	Alaska	60 AD ±200 yr	6	$> 2.5 \times 10^{10} \text{ m}^3$	Central vent eruption Explosive eruption	Rhyodacite	Lerbekmo and Campbell, 1969
Guagua Pichincha	Ecuador	70 AD ±75 yr	4	$5 \times 10^8 \text{ m}^3$	Central vent eruption Explosive eruption Pyroclastic flow(s)	Dacitic composition (61.5–65.7 wt.% SiO <sub>2</sub> )	Robin et al., 2008
Cotopaxi	Ecuador	70 AD ±150 yr	4	$5.6 \times 10^8 \text{ m}^3$	Central vent eruption Explosive eruption Pyroclastic flow(s)	Basaltic-andesites, andesites, rhyolites	Blass and Bonadonna, 2011, Garrison et al., 2011
Tacana	Mexico	70 AD ±100 yr	4?	$> 1.2 \times 10^8 \text{ m}^3$	Flank (excentric) vent Explosive eruption Pyroclastic flow(s) Lava flow(s) Lava dome extrusion Damage (land, property, etc.) Mudflow(s) (lahars) Evacuation	Andesite with basaltic-andesite inclusions (54% SiO <sub>2</sub> ) capped with andesitic to dacitic (62%–64% SiO <sub>2</sub> ) lava flows	Macias et al., 2000

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**Table 2.** Continued.

Eruption	Location	Year	VEI	Tephra Volume	Eruptive characteristics:	Magma and/or tephra composition	References
Vesuvius	Italy	79 AD	5?	$3.3 \pm 0.5 \times 10^9 \text{ m}^3$	Central vent eruption Explosive eruption Pyroclastic flow(s) Fatalities Damage (land, property, etc.) Mudflow(s) (lahars) Tsunami Caldera collapse Evacuation	K-phonolite	Siggurdson et al., 1990; Blacone-Boissard et al., 2009
Furnas	Azores	80 AD $\pm 100 \text{ yr}$	5	$1.5 \times 10^9 \text{ m}^3$	Central vent eruption Explosive eruption Pyroclastic flow(s) Mudflow(s) (lahars) resulting from magmatic and hydromagmatic eruptions	Basanite and alkali olivine basalt, potassic trachybasalt, basaltic trachyandesite (shoshonite) trachandesite (latite) to trachyte	Guest et al., 1999
Sete Cidades	Azores	90 AD $\pm 100 \text{ yr}$	4	$3.9 \times 10^8 \text{ m}^3$	Central vent eruption Explosive eruption Pyroclastic flow(s)	Trachite,	Wolff and Storey, 1983
Aso	Japan	100 AD	–			Rhyodacite	Machida and Arai, 1983
Raoul Island	Kermadec Islands	100 AD (?)	4	$> 1 \times 10^8 \text{ m}^3$	Flank (excentric) vent Explosive eruption Pyroclastic flow(s)	Pumiceous dacite low $K_2O$ content (0.8 wt%)	Shane and Wright, 2011 and references within
Shiveluch	Kamchatka	100 AD (?)	4	$5 \times 10^8 \text{ m}^3$	Central vent eruption Explosive eruption	Rhyolitic	Kyle et al., 2011

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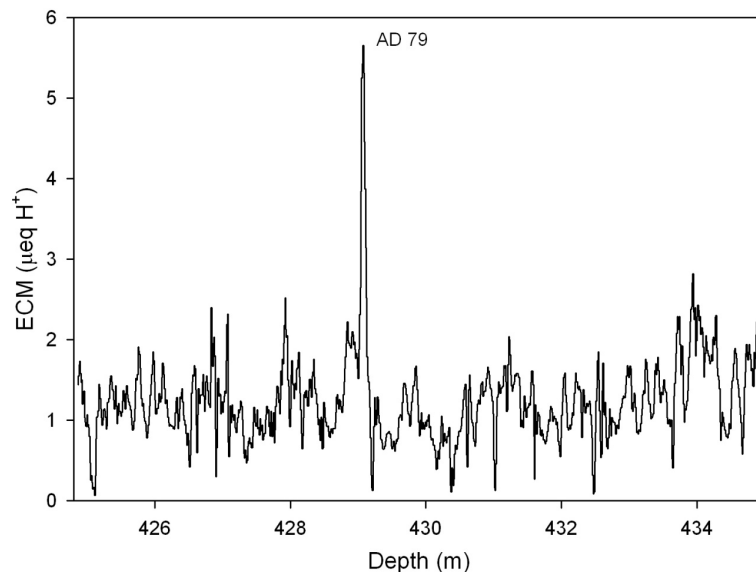
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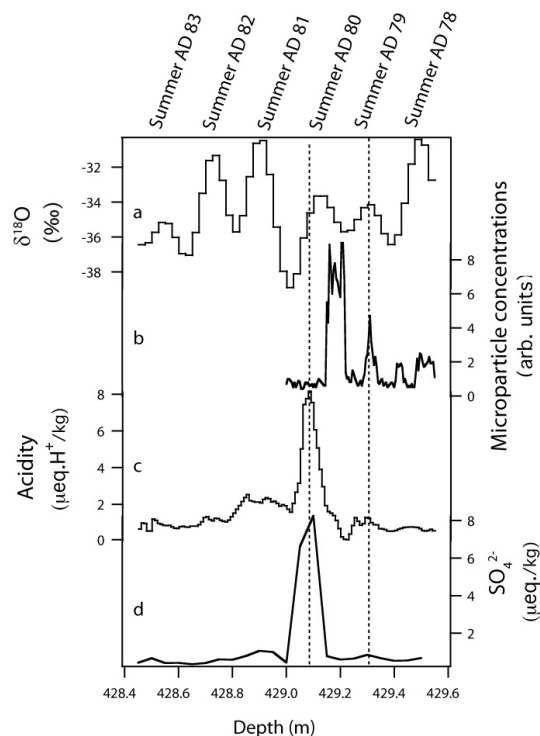


**Fig. 1.** Acid concentrations in the GRIP ice core determined by high-resolution electrical conductivity measurements (ECM) over 425–435 m demonstrating the acid spike attributed to the 79 AD Vesuvius eruption.

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**Fig. 2.** High resolution  $\delta^{18}\text{O}$ , microparticle, acidity, and sulfate concentrations from 428–430 m in the GRIP ice core. The vertical dashed bars note depths that were examined for tephra particles. The ages are from the GICC05 annual layer counting, but offset by one year to conform with the Vesuvian tephra layer detected at 429.3 m. The “arbitrary units” for the dust concentrations were determined by calibrating the signal from the laser device to Coulter counter results to obtain an arbitrary scale where 1.0 mV =  $50 \pm 15 \mu\text{g kg}^{-1}$  dust, 8 mV =  $400 \pm 130 \mu\text{g kg}^{-1}$  dust (ash). The error associated with the dust curve is  $\pm 30\%$ .

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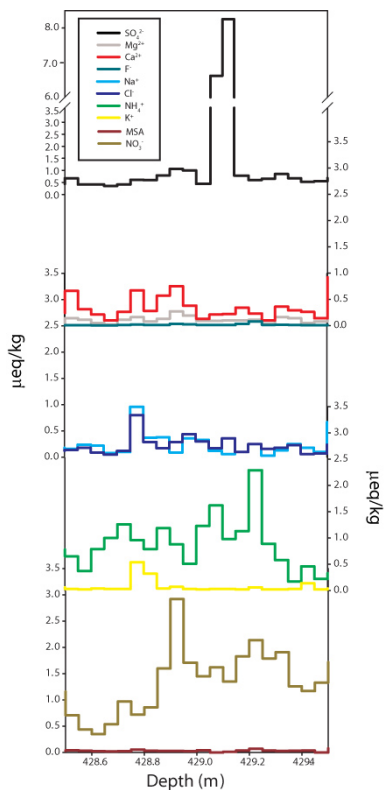
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**Fig. 3.** Major ion concentrations in the GRIP ice core between 428.4 and 429.6 m depth. The  $\text{SO}_4^{2-}$  peak is attributed to volcanic activity. The major ions are grouped by the information that they represent where  $\text{NO}_3^-$  and MSA are indicative of biological activity,  $\text{NH}_4^+$  and  $\text{K}^+$  can be used as biomass burning markers,  $\text{Na}^+$  and  $\text{Cl}^-$  often represent the contribution of sea salts, and  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{F}^-$  are crustal markers.

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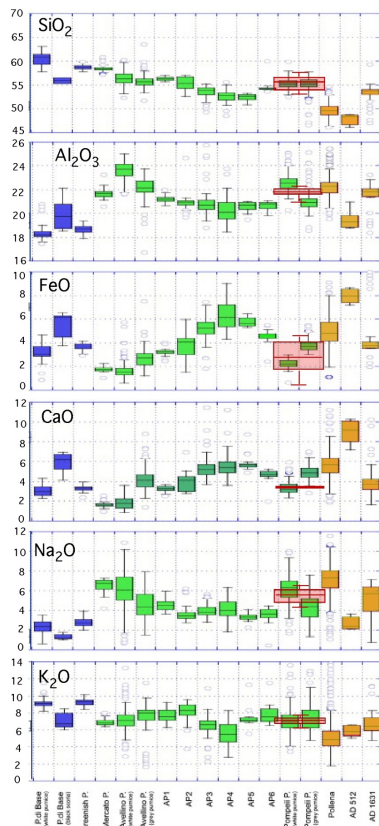
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**Fig. 4.** Box plots representing analyses of this work (red) compared with the range of EDS glass analyses of Vesuvius tephra (Santacroce et al., 2008). AP1 to AP6 signify explosive activity occurring between the larger Avellino and Pompeii eruptions (Santacroce et al., 2008 and references within).

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