The cryptotephra record of the Marine Isotope Stage 12 to 10 interval (460–335 ka) at Tenaghi Philippon, Greece: Exploring chronological markers for the Middle Pleistocene of the Mediterranean region

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Highlights:

- 18 cryptotephra layers identified for the 460–335 ka interval at Tenaghi Philippon.
- Major- and trace-element compositions reveal Italian and Aegean Arc sources.
- One cryptotephra can be traced to the Santorini Cape Therma 1 eruption.
- Nine cryptotephras originate from a yet unknown Eastern Mediterranean source.
- Cryptotephra ages derived from orbitally tuned high-resolution pollen data.
Abstract

Precise chronologies that allow direct correlation of paleoclimate archives are a prerequisite for deciphering the spatiotemporal characteristics of short-term climate variability. Such chronologies can be established through the analysis of tephra layers that are preserved in the respective sedimentary archives. Here we explore the yet untapped tephrochronological potential of the Eastern Mediterranean region for the Middle Pleistocene, specifically for the interval spanning Marine Isotope Stages (MIS) 12–10 (460–335 ka). High-resolution cryptotephra analysis was carried out on peat cores spanning the MIS 12–10 interval that have been recovered from the iconic climate archive of Tenaghi Philippon, NE Greece. Eighteen primary cryptotephras were identified, and major- and trace-element analyses of single glass shards from all cryptotephras were performed in order to correlate them with their eruptive sources. The results suggest origins from both Italian and Aegean Arc volcanoes. Specifically, one cryptotephra layer could be firmly correlated with the Cape Therma 1 eruption from Santorini, which makes it the first distal tephra finding for this eruptive event. While eight further cryptotephras could be tentatively correlated with their volcanic or even eruptive sources, the provenance of another nine cryptotephras as yet remains unknown. The relatively large number of cryptotephras that could not be assigned to specific volcanic sources and eruptive events reflects the still considerable knowledge gap regarding the geochronology and geochemistry of proximal tephra deposits from the Middle Pleistocene of the Central and Eastern Mediterranean regions. Due to the lack of well-dated Middle Pleistocene eruptions, we provide age estimates for all cryptotephra layers identified in the MIS 12–10 interval at Tenaghi Philippon based on high-resolution pollen data from the same cores. While eight of the identified cryptotephras were deposited within MIS 12 (~438–427 ka), one cryptotephra was deposited at the onset of MIS 11 (~419 ka), five
cryptotephra during the younger part of MIS 11 (~391–367 ka), and four cryptotephra during MIS 10 (~359–336 ka). The high number of cryptotephra from multiple sources as recorded in the MIS 12–10 interval at Tenaghi Philippon highlights the key role of this archive for linking tephr stratigraphic lattices for the Middle Pleistocene of the Central and Eastern Mediterranean regions.

1 Introduction

The Middle Pleistocene period, spanning Marine Isotope Stages (MIS) 19 to 6 (c. 781–126 ka; Cohen et al., 2013), contains some of the arguably most interesting episodes of Quaternary climate evolution. It includes interglacials that represent the two best orbital analogues for the Holocene (i.e., MIS 11 and 19) and as such allow insight into the natural evolution of the present interglacial without human influence (e.g., Past Interglacials Working Group of Pages, 2016). At the same time, it comprises the two strongest glaciations of the past 800 ka (i.e., MIS 12 and 16; Lisiecki and Raymo, 2005).

Over the past decades, Middle Pleistocene climate dynamics have been studied in a number of proxy records from marine (e.g., Barker et al., 2015; Herbert et al., 2010), terrestrial (e.g., Cheng et al., 2016; Melles et al., 2012) and ice-core (e.g., Jouzel et al., 2007; Loulergue et al., 2008) archives that comprise multiple glacial/interglacial cycles. The synchronization of the datasets from these archives is a prerequisite for a mechanistic understanding of short-term climate variability, notably for the quantification of leads and lags between different components of the climate system. This is, however, hindered by the often considerable uncertainties in the age models that exist for the individual archives (Bronk Ramsey et al., 2015; Lowe et al., 2015).

An interesting avenue for the direct synchronization of geological archives is provided by tracing, dating and fingerprinting of tephra layers (Lowe, 2011; Lowe et al., 2015). Tephra layers represent time-sensitive marker horizons because of their geologically
instantaneous eruption and deposition. They circumvent chronological uncertainties as they are intrinsically connected to the application of absolute dating techniques. The geochemical composition of tephra glass shards represents their connection to a source volcano/individual eruption. Therefore, once a particular tephra layer has been geochemically characterized, it can be used to link, synchronize and potentially date sedimentary archives where it has been found. Ideally, a tephra layer can be dated via correlation to a previously dated eruptive event. Alternatively, it can be dated directly by K-Ar, Ar-Ar, U-series, and fission-track methods, or indirectly via dating of the host sediments (Bronk Ramsey et al., 2015). Identification of non-visible ash layers (i.e., cryptotephras) in distal localities has greatly extended the geographical area over which some eruptions can be traced (e.g., Davies, 2015). This approach has greatly boosted the establishment of tephrostratigraphic frameworks for the Late Pleistocene and Holocene in many parts of the world.

The Eastern Mediterranean is a key region for paleoenvironmental research. Due to its intermediate position between the climate systems of the higher and lower latitudes, it exhibits particularly high climatic and environmental variability (Lionello et al., 2012). At the same time, it has particular relevance for paleoanthropological, protohistorical and archeological research. It can help shed light on the dispersal dynamics of archaic and modern humans from Africa into Eurasia (e.g., Lowe et al., 2012; Müller et al., 2011; Zanchetta et al., 2018), and at the same time it represents the cradle of ancient civilizations (Freeman, 2014).

Although the Eastern Mediterranean region has yielded long sedimentary archives both from the marine (e.g., ODP Sites 964, 967, and 968 – e.g., Grant et al., 2017; Lourens, 2004; Fig. 1) and the terrestrial realm (e.g., Tenaghi Philippon – Pross et al., 2015; Lake Ohrid – Wagner et al., 2017; Lake Van – Litt et al., 2014) that cover the Middle Pleistocene, the precise correlation of these archives has remained challenging. For such
efforts, the massive explosive volcanism in the Eastern Mediterranean region as it has occurred from the Eocene onwards (Peccerillo, 2017) has great potential via the generation of a tephrostratigraphic lattice (Keller et al., 1978). However, the tephrostratigraphic framework for the Eastern Mediterranean region as available today does not extend beyond the past ~200 ka (e.g., Aksu et al., 2008; Wulf et al., 2018), and the vast majority of the Middle Pleistocene has yet remained unexplored (Leicher et al., 2016). In light of these limitations, a ‘deeper-time’ extension of tephrostratigraphic research in the Eastern Mediterranean region is required in order to facilitate precise correlation of already existing and newly emerging paleoclimate records of the Middle Pleistocene.

Within this context, the climate archive of Tenaghi Philippon (NE Greece; Fig. 1) plays a pivotal role. This archive, which lithologically consists predominantly of peat, spans the past 1.35 Ma continuously (Pross et al., 2015, and references therein). It has unique potential for a tephrostratigraphic approach not only because of its stratigraphic length and completeness, but also the favorable geographical setting with regard to the proximity of numerous volcanic sources (including Italy, the Aegean Arc and Anatolia; Fig. 1), and the peat-dominated lithology that warrants good preservation and straightforward detection of (crypto)tephra layers (St. Seymour et al., 2004; Wulf et al., 2018). Here we present a detailed cryptotephra study that has been carried out on new core material from Tenaghi Philippon covering the time interval between c. 460 and 335 ka, broadly corresponding to MIS 12–10 as defined by previously published and new high-resolution pollen data.

2 Tenaghi Philippon as a tephrostratigraphic archive

The Philippi peatland, which harbors the study site, is located in the southeastern part of the intramontane Drama Basin on the SE Balkan Peninsula (Fig. 1). Mostly referred to as
‘Tenaghi Philippon’, the Philippi peatland has emerged as a unique paleoclimate archive for the Quaternary in Europe. The succession consists of a nearly 200 m thick sequence of fen peat and lignite with intercalated lake marls and calcareous clays, making it the thickest known peat-dominated succession worldwide (Christanis et al., 1998). Based on pollen data from early drill cores, the succession spans the past ~1.35 Ma continuously (Pross et al., 2015; Tzedakis et al., 2006; Van der Wiel and Wijmstra, 1987; Wijmstra and Smit, 1976). New, high-quality cores were recovered from the 50–200 m interval of the Tenaghi Philippon archive in 2009 (Pross et al., 2015), providing the material for this study. Importantly, Tenaghi Philippon is located within the dispersal areas of many major explosive eruptions produced by the Italian and Aegean volcanic provinces, which makes it the only known long terrestrial archive from the Balkan Peninsula that documents tephras of both volcanic provenances (Wulf et al., 2018).

The exceptionally favorable conditions for (crypto)tephrostratigraphic studies at Tenaghi Philippon have yielded considerable information on tephrostratigraphic markers for the Upper Pleistocene and Holocene (c. 130–3 ka) of the Eastern Mediterranean region (e.g., Albert et al., 2015; Lowe et al., 2012; Pross et al., 2015; St. Seymour et al., 2004; Wulf et al., 2018). These studies demonstrate that the archive of Tenaghi Philippon is exceptionally well suited to expand the tephrostratigraphic framework for the Middle Pleistocene of the Central and Eastern Mediterranean region.

3 Potential tephra sources in the Eastern Mediterranean region during MIS 12–10

Considering the distance to the Tenaghi Philippon site and the prevailing westerly winds in the Eastern Mediterranean region, the potassium-rich Italian (820–870 km W of Tenaghi Philippon) and calcalkaline Aegean Arc volcanic provinces (370–550 km S of Tenaghi Philippon) can be expected as the main sources for tephra material at Tenaghi Philippon during the Middle Pleistocene (Fig. 1). The most prominent Italian volcanic
provinces that were explosively active during that time are the Roman and Ernici-Roccamonfina Provinces (Peccerillo, 2017) including the volcanoes of Vulsini, Vico, Sabatini, Colli Albani, Ernici, and Roccamonfina (Fig. 1), which produced particularly large explosive eruptions (e.g., Giaccio et al., 2013a; Marra et al., 2014; Nappi et al., 1998; Rouchon et al., 2008). A number of other Italian volcanic provinces exhibited explosive volcanism during MIS 12–10, including the Sicily Province with the volcanic centers of Etna, Pantelleria and Ustica, and potentially the Aeolian Islands with older volcanoes of Lipari, Salina and Filicudi (Peccerillo, 2017) as well as the Campanian Volcanic Zone (De Vivo et al., 2001; Rolandi et al., 2003).

In the Aegean Arc, the most voluminous and frequent explosive activity during the Middle Pleistocene took place at Santorini volcano (Fig. 1). For the MIS 12–10 interval, this activity is documented by at least one major and numerous minor pyroclastic units of the first explosive cycle of the Thera Pyroclastic Formation as well as the cinder cones of the Akrotiri Peninsula and subordinate tuffs of the preceding Peristeria volcano in the Santorini volcanic complex (Druitt et al., 1999). Other volcanic centers that experienced explosive volcanism during MIS 12–10 include Milos and Antimilos (Fytikas et al., 1986b; Marinos, 1959), Methana (Fytikas et al., 1976, 1986a; Gaitanakis and Dietrich, 1995; Matsuda et al., 1999; Pe, 1974) and probably Kos (Bachmann et al., 2010; Dalabakis and Vougioukalakis, 1993; Pasteels et al., 1986) (Fig. 1). The Middle Pleistocene tephrostratigraphy of Aegean Arc volcanoes has remained poorly studied; better age constraints and glass geochemical data to characterize proximal pyroclastic deposits sufficiently are needed even for Santorini, which arguably represents one of the best studied volcanoes in this region (e.g., Druitt et al., 1999; Huijsmans, 1985). Furthermore, because distal tephra occurrences in the Aegean Arc during MIS 12–10 are yet unknown, their dispersal areas have remained elusive.
Apart from the Italian and Aegean volcanoes, there are other volcanic centers in the greater Eastern Mediterranean region (Fig. 1) that were likely active during MIS 12–10 and were able to distribute tephra via seasonally occurring northerly and southeasterly winds reaching Tenaghi Philippon. These include (i) the alkaline Gölcük volcano in Western Anatolia (c. 650 km SE of Tenaghi Philippon; e.g., Nemec et al., 1998; Platevoet et al., 2008, 2014), (ii) the calcalkaline volcanic complexes of Central Anatolia (Acigöl, Erciyes and Hasan Dagi, c. 900–1000 km ESE of Tenaghi Philippon; e.g., Bigazzi et al, 1993; Deniel et al., 1998; Druitt et al., 1995; Schmitt et al., 2011; Şen et al., 2003), and (iii) the Eastern Carpathians in Romania (Ciomadul, c. 600 km N of Tenaghi Philippon; e.g., Harangi et al., 2015; Karátson et al., 2016; Molnár et al., 2018; Seghedi et al., 2004; Szakács et al., 2015). However, because pyroclastics from these regions still lack detailed chronological and glass-geochemical information, it has not yet been possible to trace them distally. Finally, more distant and hence less likely volcanic sources are located in Eastern Anatolia (e.g., Nemrut and Süphan Dagi, c. 1600 km E of Tenaghi Philippon; Schmincke and Sumita, 2014; Sumita and Schmincke, 2013a, b) and France (Sancy volcano, Mont-Dore, c. 1800 km W of Tenaghi Philippon; e.g., Nomade et al., 2012; Pastre and Cantagrel, 2001).

4 Material and methods

4.1 The Tenaghi Philippon peatland core “TP-2009”

Core TP-2009 (coordinates: 40° 57’ 39.5” N, 24° 16’ 03.1” E, 40 m a.s.l.), spanning from 50 to 200 m depth (c. 260 to 1350 ka), was recovered in 2009 and is located 4.4 km and 1.0 km ESE of the previously drilled sites TP-2005 and TF-II, respectively (see Pross et al., 2015, for a review). The investigated core interval from 82 to 63 m depth corresponds to an age of c. 480–350 ka based on the correlation of low-resolution pollen data to marine
isotope stages (Pross et al., 2015) and consists of peat, peaty mud and lake marls (Fig. 2).

4.2 Proximal correlative tephra samples

We sampled seven pumice and scoria fall deposits on Santorini in 2015 (see Supplement 1) and used data from the literature in order to correlate tephras found in core TP-2009 on the basis of their composition with proximal tephras in the region.

4.3 Tephra preparation and analysis

4.3.1 Tephra extraction and processing

To detect cryptotephra layers in the studied core material, extraction and analysis of volcanic glass shards were first performed on 10-cm-long contiguous sub-samples. Intervals in which glass shards were detected were then inspected in 1-cm increments in order to refine the stratigraphic positions of the identified cryptotephras. The volumes of the low- and high-resolution tephra samples were 10 cm³ and 1 cm³, respectively. In both cases, the sample material was taken from the central part of the cores to avoid potential tephra cross-contamination.

Extraction of glass shards from peat was performed using standard techniques (e.g., Gehrels et al., 2008) including removal of organic matter and carbonate material, enrichment of glass shards by density separation, as well as handpicking and mounting of glass shards in Epofix™ resin, and subsequent polishing for microanalytics (see Supplement 1). The documented cryptotephras were labeled following the scheme previously introduced for Tenaghi Philippon (Wulf et al., 2018); in this scheme, the abbreviation of the coring campaign (TP09) is followed by the mid-point of the sample depth interval (in meters) in which a cryptotephra was found (e.g., cryptotephra TP09-65.95).
The proximal samples from Santorini composed of pumice/scoria clasts were crushed, sieved into a 20-100 μm fraction and mounted onto stubs using Epofix™ resin prior to grinding and polishing for geochemical analysis.

### 4.3.2 Geochemical analysis of glass shards

#### 4.3.2.1 Electron probe microanalysis (EPMA)

Major-element compositions of single glass shards were determined using a wavelength-dispersive (WDS) electron microprobe JEOL JXA-8500F at the German Research Centre for Geosciences in Potsdam. The instrument used an accelerating voltage of 15 kV, a 10 nA beam current, and a 3–10 μm beam with count times of 20 s for the elements Mg, P, Cl, Ti, Mn, and Fe, and 10 s for F, Ca, Al, Si, K, and Na (analyzed first). A range of MPI-DING reference glasses including GOR128-G (komatiite), GOR132-G (komatiite), ATHO-G (rhyolite) and StHs6/80 (andesite) (Jochum et al., 2006) as well as natural Lipari obsidian (Hunt and Hill, 1996; Kuehn et al., 2011) were employed as secondary glass standards, and measured once prior to sample analyses in order to maintain interlaboratory consistency of analytical data (Supplements 2, 3). The EPMA data were normalized to 100% total oxides on a volatile-free basis to allow data comparison. Low values (<90% for rhyolitic and <95% for other glasses) of total oxides were rejected, except for one tephra for which better quality data were not available.

#### 4.3.2.2 Secondary Ion Mass Spectrometry (SIMS)

Trace-element compositions of selected glass shards were analyzed at Heidelberg University using a CAMECA IMS 3f ion probe. The operating conditions were a current intensity of 10 nA, a spot diameter of 10 μm, a width of the energy slit of 50 eV, and a voltage offset applied to the sample accelerating voltage (+4.5 kV) of -105 V.
Pre-sputtering time was 120 s, and five acquisition cycles with the following count times per cycle were obtained: Si (2 s), Rb (5 s), Sr (5 s), Y (5 s), Zr (5 s), Nb (5 s), Ba (5 s), La (5 s), Ce (5 s), Th (20 s), and U (20 s). As an internal (primary) standard for the instrument, the NIST-SRM 610 glass standard was used, and the rhyolitic ATHO-G, the andesitic StHs6/80-G, and the basaltic GOR132-G glass standards (Jochum et al., 2006) were used as secondary reference materials.

4.4 Pollen analysis

In the present study, pollen data were used as a reference dataset in order to provide age constraints for the detected cryptotephras. For this purpose, the previously published, low-resolution pollen dataset of Pross et al. (2015) was augmented by an additional 100 new pollen samples for the 82.00–62.50 m depth interval of the TP-2009 core that were taken every 13 to 28 cm (mean: c. 20 cm) corresponding to an average temporal resolution of 0.8–1.8 ka. Palynological processing followed the methods given in Pross et al. (2015); for details see Supplement 1. At least 300 pollen grains were counted per sample whenever possible, excluding Poaceae, Cyperaceae, aquatic plants, and fern spores.

Arboreal pollen (AP) percentages were used to identify glacial-interglacial cycles in the study interval, on the basis that forest expansion at Tenaghi Philippon occurs under interglacial boundary conditions and vice versa (Pross et al., 2015; Tzedakis et al., 2006). Specifically, we have aligned our new palynological data from core TP-2009 to the old palynological record from Tenaghi Philippon (TF-II; Van der Wiel and Wijmstra, 1987; Wijmstra and Smit, 1976) using the orbitally tuned age model of Tzedakis et al. (2006). The two records were aligned using minima, maxima and inflection points of the tree-pollen percentages using the AnalySeries software (Paillard et al., 1996; see Table S1-1 in Supplement 1 for details).
5 Results

5.1 Identification of cryptotephra layers

Glass-shard extraction across the 82–63 m depth interval of core TP-2009 yielded 20 cryptotephra layers for which EPMA analysis was carried out (Table 1; Fig. 2). An additional five samples also contained glass shards; however, due to the extremely low concentrations (1 shard per 10 cm³ of peat) and small sizes (<50 µm) of the shards in these samples, no geochemical analysis was possible (Table 1). Trace-element compositions were analyzed in 13 of the 20 cryptotephras; the remaining seven cryptotephras consisted of glass shards that were too small and/or vesicular to expose sufficiently large polished surfaces for the 10 µm beam of the SIMS apparatus.

Representative EPMA and SIMS data of the identified cryptotephras are given in Table 2, whereas full geochemical data are provided in Supplement 2. Normalized (volatile-free) EPMA glass data as plotted on the total alkali vs. silica (TAS) classification diagram (Le Bas et al., 1986) are shown in Fig. 3a. Tephra-shard counts range from 1 to 27 shards per cryptotephra sample (volume: 1–10 cm³). Because of the scarcity of volcanic glass in all samples, shard concentrations per gram dry weight were not calculated. In the following, we give an account of the cryptotephras encountered, starting with the oldest cryptotephras of MIS 12 and finishing with the youngest cryptotephras of MIS 10.

5.1.1 MIS 12 cryptotephras (82–75 m core depth)

5.1.1.1 Cryptotephras TP09-77.95 to TP09-75.75 (eight layers)

Eight consecutive samples between 78.00 and 75.70 m core depth contained glass shards of similar rhyolitic composition. The number of shards, partly measured by EPMA (Table 2), varied from seven (TP09-77.65) to one (TP09-76.95 and TP09-77.35) in each
sample (Table 1). SIMS analysis was possible for all samples but TP09-76.05 and TP09-76.75, and the number of analyzed shards varied from four to one per sample (Table 2). Their major-element compositions define the cryptotephras as low-silica rhyolites (72.4–75.7 wt% SiO₂; normalized data) with high-K calcalkaline affinity (3.4–6.4 wt% K₂O) (Fig. 3a, b). Na₂O concentrations are much lower (0.36–1.20 wt%) than K₂O values, resulting in high alkali (K₂O/Na₂O) ratios of 3.80–12.83 (Fig. 3c). MgO (1.3–2.9 wt%) and CaO (1.6–7.3 wt%) show high values with a greater degree of scatter. Trace-element data support compositional homogeneity of the tephras (Supplement 2).

5.1.2 MIS 11 cryptotephras (75–66 m core depth)

5.1.2.1 Cryptotephra TP09-74.75

Cryptotephra TP09-74.75 consists of two shards; one of them was analyzed by EPMA and SIMS and yielded a composition reminiscent of that of the older cryptotephras TP09-77.95 to TP09-75.75 as described above (Table 2). The TP09-74.75 cryptotephra is defined as a low-silica rhyolite (73.3 wt% SiO₂), however, unlike the older cryptotephras, it has calcalkaline affinity due to the slightly lower K₂O concentrations (3.0 wt% K₂O) (Fig. 3a, b). At the same time the Na₂O content is higher (2.1 wt%) and the alkali ratio is lower (1.41) than in the older cryptotephras (Fig. 3c). The trace-element concentrations of cryptotephra TP09-74.75 are compatible with those of the older cryptotephras (Supplement 2).

5.1.2.2 Cryptotephra TP09-70.45

Cryptotephra TP09-70.45 is represented by a single shard of trachytic composition (Fig. 3a). One more shard was detected in the high-resolution sample TP09-70.405, but could not be extracted for geochemical analysis. Due to the lack of EPMA data proving that this
shard represents the same cryptotephra as in the low-resolution sample, the stratigraphic position of cryptotephra TP09-70.45 cannot be constrained more precisely.

The composition of cryptotephra TP09-70.45 is defined by 63.4 wt% SiO₂, 7.2 wt% Na₂O, 4.8 wt% K₂O, 0.83 wt% CaO, 0.33 wt% MgO, and 0.82 wt% Cl (Table 2). The alkali ratio of 0.67 classifies it as sodium-rich (Fig. 3c). In comparison with other trachytic tephras in the MIS 12–10 interval of core TP-2009, this tephra exhibits lower contents of K₂O and CaO as well as a lower K₂O/Na₂O ratio.

5.1.2.3 Cryptotephra TP09-68.95
Cryptotephra TP09-68.95 is represented by a single glass shard detected in a 10-cm resolution sample. Based on EPMA data (Table 2), TP09-68.95 can be classified as a calcalkaline low-silica rhyolitic tephra with SiO₂ values of 69.8 wt% (Fig. 3a). It straddles the boundary between medium and high K₂O concentrations (3.1 wt%) (Fig. 3b). The Na₂O content (4.6 wt%) is higher than the K₂O content, yielding an alkali ratio of 0.68 (Fig. 3c).

5.1.2.4 Cryptotephras TP09-67.15, -67.05 and -66.95
The dacitic cryptotephra TP09-67.15 and the rhyolitic cryptotephras TP09-66.95 and TP09-67.05 were isolated from three consecutive low-resolution samples. Cryptotephra TP09-67.15 is represented by 27 glass shards, which makes it the best documented tephra in the examined interval of core TP-2009. Four and three glass shards were analyzed by EPMA and SIMS, respectively. From the rhyolitic cryptotephras, three and two shards were counted, respectively, and one shard of each cryptotephra was analyzed by EPMA and SIMS.

Cryptotephra TP09-67.15 is a calcalkaline dacite (Fig. 3a, b) and has a well-constrained compositional range of major-element concentrations, e.g., SiO₂ (63.6–64.0 wt%), Na₂O
(4.5–4.7 wt%), and K₂O (2.1 wt%) (Table 2). The alkali ratios are 0.45–0.47 (Fig. 3c). Trace-element compositions of three glass shards also show narrow ranges of element concentrations (Supplement 2).

Cryptotephras TP09-66.95 and TP09-67.05 are both calcalkaline to high-K calcalkaline low-silica rhyolites (Fig. 3a, b), with major-element compositions that are similar to that of the previously described cryptotephra TP09-68.95 (Table 2). The respective concentrations of some major elements are 69.6 and 69.9 wt% SiO₂, 4.3 and 4.6 wt% Na₂O, and 3.7 and 3.1 wt% K₂O (Supplement 2). Both tephras have Na₂O values exceeding K₂O values, resulting in alkali ratios of 0.66–0.86 (Fig. 3c). Trace-element data confirm the similarity between cryptotephras TP09-66.95 and TP09-67.05 (Table 2).

5.1.3 MIS 10 cryptotephras (66–63 m core depth)

5.1.3.1 Cryptotephras TP09-65.95, -65.835a and -65.835b

Three glass shards were detected in a 10-cm resolution sample at 65.9–66.0 m depth, one of which was analyzed by EPMA. Despite the low analytical total, we use the EPMA data of the only available glass shard of this sample for further discussion. One more glass shard was found in the adjacent low-resolution sample at 65.8–65.9 m depth. Detection of four more glasses at 65.83–65.84 m depth further refined the stratigraphic position of the cryptotephra. EPMA and SIMS compositions of two glasses from the 1-cm resolution sample are distinctly different, and thereby two cryptotephras were distinguished at the same depth (TP09-65.835a and TP09-65.835b).

The major-element composition of cryptotephra TP09-65.95 indicates a calcalkaline dacite (Table 2; Fig. 3a, b) with concentrations of 66.7 wt% SiO₂, 2.7 wt% K₂O and 4.4 wt% Na₂O, yielding a K₂O/Na₂O ratio of 0.61 (Fig. 3c). Cryptotephra TP09-65.835a shows trachytic affinity with 62.1 wt% SiO₂ and a K₂O/Na₂O ratio of 1.2 indicative of shoshonites (Fig. 3a, c). It contains 7.0 wt% K₂O, 6.0 wt% Na₂O,
2.3 wt% CaO, 0.34 wt% MgO, and 0.82 wt% Cl. SIMS analysis of cryptotephra TP09-65.835a yielded trace-element data (Table 2).

Cryptotephra TP09-65.835b is a calcalkaline rhyolite with high contents of SiO₂ (76.8 wt%) and K₂O (5.0 wt%) (Fig. 3a, b) whereby K₂O is more abundant than Na₂O (K₂O/Na₂O = 1.94) (Fig. 3c). Trace-element data further define its composition (Table 2).

5.1.3.2 Cryptotephras TP09-63.05, -63.015a and -63.015b

Twelve glass shards were detected in the 63.0–63.1 m depth range of core TP-2009. Nine of them were analyzed by EPMA and revealed three different compositions. Cryptotephra TP09-63.05 comprises three glass shards of trachytic composition. Four more trachytic glass shards were found during high-resolution tephra search. They are, however, geochemically different from the ones found in the low-resolution sample and therefore form a separate cryptotephra (i.e., TP09-63.015a). The third cryptotephra of rhyolitic affinity was first detected in the low-resolution sample and then constrained to the same depth as the trachytic cryptotephra TP09-63.015a. It is represented by two glass shards and was labeled TP09-63.015b. Two more tephra shards from another high-resolution sample TP09-63.005 appear to be from a sodium-rich trachyte, but were not considered further because they yielded Na values that were considerably higher (8.27–8.62 wt%) than those typical for sodium-rich trachytes. SIMS data were obtained only from two glasses of cryptotephra TP09-63.05.

The trachytic cryptotephra TP09-63.05 has a tight compositional range (60.6–61.7 wt% SiO₂, 7.6–7.8 wt% K₂O, 3.8–4.5 wt% Na₂O, 2.7–2.9 wt% CaO, 0.77–0.88 wt% MgO, and 0.32–0.37 wt% Cl) and is characterized by an alkali ratio of 1.7–2.0 indicating potassium-rich rocks (Table 2; Fig. 3a, c). SIMS trace-element concentrations of two glass shards also show homogenous compositions (Supplement 2).
Cryptotephra TP09-63.015a straddles the trachyte-phonolite boundary and has comparable SiO₂ contents (61.5–62.0 wt%), but lower alkali ratios (0.9–1.0) relative to cryptotephra TP09-63.05, which assigns it to shoshonites (Fig. 3a, c). Lower concentrations of K₂O, FeO, CaO and MgO (5.9–7.1, 2.9–3.1, 1.2–1.8, and 0.34–0.37 wt%, respectively) and higher Na₂O and Cl values (6.9–7.2 and 0.79–0.84 wt%, respectively) of cryptotephra TP09-63.015a further discriminate it from cryptotephra TP09-63.05.

The rhyolitic cryptotephra TP09-63.015b has 71.4–72.5 wt% SiO₂ and straddles the boundary between medium and high K₂O values (3.2–3.3 wt%) (Fig. 3a, b). One of the analyzed shards shows a very low Na₂O content, apparently resulting from Na loss during EPMA analysis. The other glass shard is characterized by higher Na₂O than K₂O concentrations and has an alkali ratio of 0.70 (Fig. 3c).

6 Discussion

6.1 Sources of identified cryptotephras

The cryptotephras identified in the MIS 12–10 interval of the TP-2009 core were grouped into five main geochemical populations (POP#) with the first one (POP1) subdivided in three sub-populations (POP1A to POP1C) based on their major-element glass compositions (Table 1; Fig. 3) and compared with previously published glass-compositional data of proximal and distal tephra deposits from the Mediterranean region. The compositional groups were discriminated using classification diagrams (Fig. 3) as well as other major- and trace-element plots presented in Figs. 4 to 8 (see also figures in Supplement 4). These populations have the potential to represent different provenances of the identified cryptotephras. In the following, we therefore provide a detailed discussion on the proposed volcanic sources and tephra correlations for the trachytic population.
POP1 (see Section 6.1.1), the dacitic population POP2 and the rhyolitic population POP3 (Section 6.1.2.1), and the rhyolitic populations POP4 and POP5 (Section 6.1.2.2).

6.1.1 Sources of trachytic cryptotephras

During the Quaternary, Italian volcanism produced numerous compositionally diverse pyroclastics ranging from mafic to felsic and from sub-alkaline to ultra-alkaline (e.g., Peccerillo, 2017). Its distinctive characteristics within the Mediterranean magmatic realm are the high abundance of sodic and particularly potassic alkaline volcanics (Peccerillo, 2017), a feature that we also observe in the four trachytic TP-2009 cryptotephra layers of POP1 (TP09-63.05, -63.015a, -65.835a, and -70.45). Given that trachytic pyroclastics were massively produced by the Roccamonfina, Sabatini, Vico and Vulsini volcanoes in Italy during the studied time interval (Marra et al., 2014; Palladino et al., 2014; Rouchon et al., 2008), these Italian volcanoes are the most likely sources for these tephras.

Trachytes are also common eruptive products of the Campanian Province (e.g., Ischia, Campi Flegrei), which was characterized by violent explosive activity during the Late Pleistocene. The oldest volcanic rocks exposed on Ischia and within the Campi Flegrei are dated at c. 150 and 60 ka, respectively (e.g., Poli et al., 1987; Pappalardo et al., 1999), whereas outside the Campanian Plain, in the western foothills of the Apennine Mountains, ignimbrites produced by Campanian activity yielded ages from 290 to 116 ka (De Vivo et al., 2001; Rolandi et al., 2003). Therefore, based on the evidence from proximal sites Campanian tephra deposits are too young to be present in our record. In contrast, however, several much older tephras from marine and lacustrine sediment records in central-southern Italy and on the Balkan Peninsula that yielded geochemical signatures of Campanian provenance suggest that Campanian volcanoes might potentially be older than previously thought. These tephras include the V5/Parmenide tephra (c. 723 ka) found in the Montalbano Jonico sequence as well as in the Crotone
and Sulmona basins (Giaccio et al., 2013b; Petrosino et al., 2015), the V7 tephra (c. 687 ka) from Montalbano Jonico (Petrosino et al., 2015), the A12/A11 and SC2 tephras (514.2±5.6 ka) from the Acerno and Mercure basins (Giaccio et al., 2014; Petrosino et al., 2014), which are equivalent to tephra OH-DP-2017 in Lake Ohrid (SW Balkan Peninsula; Leicher et al., 2016), and the TAV2 tephra from the Mercure basin (c. 494–438 ka; Giaccio et al., 2014). Another potential Campanian tephra, the exceptionally thick Morphi ash fall deposit in western Epirus (SW Balkan Peninsula), dates to 374±7 ka (Pyle et al., 1998). Based on major-element characteristics and Sr isotope ratios of the SC2 and TAV2 tephras, Giaccio et al. (2014) have proposed an alternative correlation of these tephras with trachytes from Ponza Island off the Italian Campania-Latium coast. Because, however, of the older ages of its volcanic products (final volcanic activity ~1 Ma; Cadoux et al., 2005) we can firmly exclude Ponza as a source for our cryptotephras during MIS 12–10. We therefore consider Campanian volcanoes as potential sources for the trachytic cryptotephras in the MIS 12–10 section of the TP-2009 core.

6.1.1.1 Cryptotephras TP09-63.015a (trachytic component) and TP09-63.05

The chemical composition of cryptotephra TP09-63.015a lies at the boundary between the Campi Flegrei and the Ischia compositional fields, while cryptotephra TP09-63.05 falls within the overlap of the Roccamonfina and Campi Flegrei compositional fields (Figs. 4, S4-2). All glass-based major-element compositions of cryptotephra TP09-63.05 match those of the upper flow unit of the Campanian Ignimbrite (CI, 39.85±0.14 ka; Giaccio et al., 2017a), while two shards of cryptotephra TP09-63.015a match the CI basal fall and lower and intermediate flow units with respect to their major-element chemistry (Figs. 4b, 5, S4-3). The SIMS trace-element data obtained from two glass shards of cryptotephra TP09-63.05 confirm that it fits both LA-ICPMS (Tomlinson et al., 2012a) and SIMS (Wulf et al., 2018) compositions of the CI upper flow unit (Figs. 5, S4-3). The CI occurs as a 23-
cm-thick tephra layer further upcore at 12.87 m depth in the Tenaghi Philippon sequence (Müller et al., 2011), and coring-related re-deposition from that tephra in the top core segments of the 40-130 ka part of the sequence has been reported (Wulf et al., 2018). We therefore interpret both the TP09-63.05 and -63.015a shards to be re-worked from the CI.

6.1.1.2 Cryptotephra TP09-65.835a (trachytic component)

The trachytic glass component TP09-65.835a of the bimodal cryptotephra layer at 65.835 m core depth can be assigned to Campanian volcanic activity, which is shown by the CaO/FeO vs. Cl plot (Giaccio et al., 2017b) where it matches the Campi Flegrei compositional field (Fig. 4b). It falls partly within the geochemical envelope of the basal fall and lower and intermediate flow units of CI on major- and trace-element plots (Figs. 5, S4-3). However, it can be discriminated from the CI on the basis of the lower Cl to CaO/FeO ratio (Fig. 4b). Consequently, we consider cryptotephra TP09-65.835a a primary fallout deposit of Campanian origin.

TP09-65.835a plots close to, but does not overlap with the trachytic Middle Pleistocene tephra layers that have been attributed to the Campanian Province by several authors (e.g., Giaccio et al., 2014; Petrosino et al., 2015; Leicher et al., 2016) based on their major-element chemistry (Figs. 5, S4-3). Only one of these tephras is defined in terms of trace-element composition (V5; Petrosino et al., 2015); it shows a considerably lower Nb content than TP09-65.835a (Fig. 5). Two eruptions that occurred during MIS 12–10 are those causing the Morphi (374±7 ka, Pyle et al., 1998) and TAV2 tephras (c. 494–438 ka, Giaccio et al., 2014). Published EPMA data of the Morphi and TAV2 tephras show major-element concentrations that are strongly similar to that of TP09-65.835a, but reveal differences in their MgO, CaO and Na2O contents (Figs. 5, S4-3). The TAV2 tephra can be clearly discriminated from TP09-65.835a in the Cl vs. CaO/FeO diagram (Fig. 4b).
Hence, at this stage we cannot correlate the TP09-65.835a cryptotephra with a dated eruptive event, but we suggest an origin from an unknown MIS 10 eruption in the Campanian Province.

6.1.1.3 Cryptotephra TP09-70.45

The sodium-rich trachytic glass composition of cryptotephra TP09-70.45 differs from that of the three younger trachytic cryptotephras found by a substantially lower alkali ratio (0.67), slightly lower K2O (4.8 wt% compared to 5.9–7.8 wt%) and CaO values (0.83 wt% compared to 1.2–2.9 wt%), and higher SiO2 concentrations (63.4 wt% compared to 60.6–62.1 wt%) (Figs. 4a, 5, S4-3). Together with the relatively high Cl content (0.82 wt%) and the very low CaO/FeO ratio (0.27) matching the Ischia compositional field (Fig. 4b), this composition suggests a Campanian provenance. A correlation of cryptotephra TP09-70.45 with the Morphi tephra (374±7 ka, Pyle et al., 1998) or the TAV2 tephra (c. 494–438 ka, Giaccio et al., 2014) is not supported by the major-element compositions (Figs. 5, S4-3). Therefore, we propose that cryptotephra TP09-70.45 represents an unknown eruption from the Campanian Province during MIS 11.

6.1.2 Sources of dacitic and rhyolitic cryptotephras

A total of 16 cryptotephra layers from the studied interval of the TP-2009 core show either calcalkaline dacitic or rhyolitic glass compositions of either Aegean Arc or yet undefined Eastern Mediterranean provenance (Figs. 3a, d, 6, S4-1, S4-4). Out of these, the two dacitic layers (TP09-65.95 and TP09-67.15) and four rhyolitic layers of glass population POP3 (cryptotephras TP09-63.015b, TP09-66.95, TP09-67.05 and TP09-68.95) show compositions that are typical for Santorini tephras (see Section 6.1.2.1). Cryptotephra TP09-65.835b (glass population POP4) and nine older layers of glass population POP5 have high-silica rhyolitic glass compositions that either overlap with the tephra
compositions of Aegean Arc volcanoes, or partly overlap with those of Aegean Arc/Eastern Carpathian volcanoes; they cannot yet be assigned to individual volcanic sources (see Section 6.1.2.2).

6.1.2.1 Tephras of Santorini provenance

The six TP09 cryptotephras of Santorini provenance exhibit two different glass compositions. Cryptotephras TP09-65.95 and TP09-67.15 are calcalkaline dacites and can be grouped into glass population POP2. In contrast, cryptotephras TP09-63.015b, TP09-66.95, TP09-67.05 and TP09-68.95 are calcalkaline to high-K calcalkaline low-silica rhyolites and represent glass population POP3 (Figs. 3, 6, S4-4).

Santorini is the most explosive caldera-forming volcano within the Southern Aegean Arc and has been active since at least 650 ka (Druitt et al., 1999). Its younger activity is divided into two main explosive cycles, and a total of twelve major and numerous minor pyroclastic eruptions (labeled as M1 to M12; Druitt et al., 1999). Most of the major explosive eruptions are characterized by some degree of magma heterogeneity and/or zoning, and two types of compositional zoning present in magma reservoirs based on bulk-rock (XRF) compositional data can be distinguished (Druitt et al., 1999): (i) a predominantly silicic (rhyodacitic) magmas (66.3–71.4 wt% SiO$_2$) with a subordinate basaltic-andesitic component (47–62 wt% SiO$_2$) showing large compositional gaps, and (ii) a predominantly intermediate (andesitic-dacitic) composition (56-64 wt% SiO$_2$) with a minor, more evolved dacitic component (61.8–67.0 wt% SiO$_2$) showing large as well as small compositional gaps and zoning.

6.1.2.1.1 Cryptotephra TP09-63.015b (rhyolitic component)

The rhyolitic cryptotephra TP09-63.015b of glass population POP3 with SiO$_2$ contents of c. 72 wt% is comparable with the bulk composition of the first group of predominantly
rhyodacitic eruptions of Santorini (Fig. S4-5). It best matches the newly obtained EPMA glass composition of the pumice fall deposit of the Cape Therma 2 (CT-2) eruption (sample SAN15-28, Supplements 1, 3; Figs. 7, S4-6). The CT-2 pumice fall has not yet been dated directly, but its age (c. 224 ka) can be constrained by the directly overlying rhyodacitic lava flows of Cape Alonaki that yielded a K-Ar age of 224±5 ka (Druitt et al., 1999). Given the compositional similarity and the absence of a paleosol between the CT-2 pumice fall and the Cape Alonaki lavas, they were probably produced by a single eruption (Druitt et al., 1999). Because cryptotephra TP09-63.015b is older than the CT-2 eruption by more than 100 ka (see Section 6.2), it may potentially represent reworked material from an undetected primary CT-2 tephra layer in the yet unstudied interval upcore in the Tenaghi Philippon record. This interpretation is strongly supported by the reworked CI material in the same sample (see Section 6.1.1).

6.1.2.1.2 Cryptoteprs TP09-65.95 and TP09-67.15

The dacitic glass population POP2 (63.6–66.7 wt% SiO₂) best matches the bulk composition of more evolved components of the second group of predominantly intermediate eruptions of Santorini (Fig. S4-5). Potential explosive Santorini eruptions with dacitic compositions that occurred during the studied time interval are the Cape Therma 1 (CT-1) and younger Cape Therma 3 (CT-3) eruptions (Druitt et al., 1999). Comparisons of newly obtained EPMA glass data of basal pumice fall and ignimbrite deposits from the CT-3 (sample SAN15-26) and CT-1 eruptions (samples SAN15-33, SAN15-34, and SAN15-36, Supplements 1, 3) show strong similarities and a close match with both the TP09-65.95 and the less evolved TP09-67.15 cryptotehrs (Figs. 7, S4-6). The age of the CT-3 eruption is bracketed between those of the preceding CT-2 (c. 224 ka; Druitt et al., 1999) and the post-dating Lower Pumice 1 (c. 184 ka; Gertisser et al., 2009) eruptions of Santorini, and thus appears to be considerably younger than the
studied time interval. The published age of the CT-1 eruption of ≤360 ka is based on
dating of andesites at Cape Alai that underlie CT-1; they yielded values ranging from
145±64 to 425±39 ka based on K/Ar, and 456±138 ka based on 40Ar/39Ar dating (Druitt et
al., 1999). This age is compatible with those of both cryptotephras TP09-65.95 and TP09-
67.15 (see Section 6.2), and we therefore correlate them with the CT-1 eruption. The
trace-element glass data of cryptotephra TP09-67.15 compared to the only available bulk
trace-element compositions of the CT-3 and CT-1 eruptions further support this
interpretation; on most bivariate plots it falls either within the CT-1 geochemical envelope
or within the overlap of the CT-1 and CT-3 envelopes (Figs. 7, S4-6). Although TP09-
67.15 contains a much larger number of glass shards (n=27) compared to TP09-65.95
(n=3), we consider the latter to represent the primary layer because its age is more
compatible with that of the proximal CT-1 deposits, and TP09-67.15 to be likely reworked
material that has been displaced by post-depositional processes. An alternative
interpretation of cryptotephra TP09-67.15 is that it might represent a yet unknown
interplinian eruption within the minor pyroclastic sequence M1 below the CT-1 deposits
on Santorini (Druitt et al., 1999).

6.1.2.1.3 Cryptotephras TP09-66.95, TP09-67.05 and TP09-68.95
The three remaining rhyolitic TP09 cryptotephras of glass population POP3 with SiO₂
contents of c. 70 wt% also derive from predominantly rhyodacitic magmas of Santorini
eruptions (Fig. S4-5) and are stratigraphically older than the CT-1 eruption. However, little
information is yet available on the pyroclastic activity that predated the first explosive
cycle at Santorini (Druitt et al., 1999). Peristeria volcanic deposits, which predate (530–
430 ka, Druitt et al., 1999) the Thera pyroclastics on Santorini, are predominantly basaltic
to andesitic, rarely dacitic, lavas with subordinate tuffs. A correlation of MIS 11
cryptotephras from the TP-2009 core with Peristeria deposits is precluded not only by the
age discrepancy, but also the lack of published glass EPMA data on Peristeria pyroclastic units.

At Cape Plaka (Santorini), two white and well-sorted pumice fall deposits underlie the CT-1 pyroclastic unit, namely layer SAN15-35 (directly underlying CT-1) and SAN15-37 (underlying SAN15-35; Supplement 1); they most likely relate to the yet undated minor pyroclastic unit M1 of Druitt et al. (1999). Newly obtained major-element glass data of these two deposits (Supplement 3) reveal a rhyolitic composition that is similar to that of cryptotephra TP09-66.95, -67.05 and -68.95. In general, SAN15-35 and SAN15-37 are both less evolved than CT-2, with SAN15-37 partly overlapping the CT-2 composition. Cryptotephra TP09-66.95, -67.05 and -68.95 plot compositionally between SAN15-35 (67.7–69.4 wt% SiO₂) and SAN15-37 (70.3–72.3 wt% SiO₂), and some element concentrations (e.g., TiO₂, MgO, CaO) overlap with the SAN15-35 compositions (Figs. 7, S4-6).

The trace-element glass compositions of cryptotephra TP09-66.95 and -67.05 show a close match with the bulk trace-element data of the CT-2 eruption (Figs. 7, S4-6). Due to the lack of trace-element data for SAN15-35 and SAN15-37 we can only establish a tentative correlation of the identified cryptotephra layers with unit SAN15-35. All three cryptotephra layers most likely derive from one single volcanic event, of which TP09-66.95 is interpreted as the primary layer (three glass shards). TP09-67.05 and TP09-68.95 are most likely reworked material derived from the primary layer that have been displaced downward by post-depositional processes within the Tenaghi Philippon peat sequence.

6.1.2.2 Tephra of undefined provenance

A total of ten TP09 cryptotephra layers have high-silica rhyolitic compositions of undefined provenance. Cryptotephra TP09-65.835b of glass population POP4 can only
tentatively be assigned to Aegean Arc activity (Figs. 3d, 6, S4-1, S4-4). The nine cryptotephras of glass population POP5 show compositions that do not match any known potential volcanic sources (Figs. 3d, 6, S4-1, S4-4).

6.1.2.2.1 Cryptotephra TP09-65.835b (rhyolitic component)

The major-element data of cryptotephra TP09-65.835b of glass population POP4 overlaps with the geochemical compositions of Quaternary tephras from Aegean Arc volcanoes (excluding Santorini) as well as with that of younger rhyolitic tephras from the Aeolian Arc (<55 ka), the Eastern Carpathians (<53 ka), and Central Anatolia (<27 ka) (Figs. 6, S4-4).

Potential volcanic sources within the Aeolian Arc include Lipari and Salina Islands, which started their eruptive history c. 267 and c. 244 ka ago, respectively (Peccerillo, 2017). However, the earliest eruptive epochs of these islands are exclusively characterized by effusive and explosive eruptions with basaltic and basalt-andesitic compositions, while rhyolitic magmatism only commenced during the latest eruptive epochs (<55 ka; Albert et al., 2017; Forni et al., 2013; Lucchi et al., 2013). Furthermore, the trace-element glass compositions of younger rhyolitic tephra deposits from Lipari and Salina are distinct from that of cryptotephra TP09-65.835b (Figs. 6a, S4-4). Despite its compositional similarity with Late Pleistocene tephras with regard to major elements and partly also trace elements (Figs. 6b, S4-4), we cannot correlate cryptotephra TP09-65.835b with Eastern Carpathian and Central Anatolian volcanic eruptions because of the scarcity of tephrostratigraphic information available for these centers. A more likely source of cryptotephra TP09-65.835b is the Aegean Arc, which also provides the best match for the cryptotephra on the basis of both major- and trace-element concentrations (Figs. 6a, S4-4). Apart from Santorini, other volcanoes of the Aegean Arc are also known to have erupted during MIS 12–10 (Figs. 8, S4-7). These are (i) the volcanic archipelago of Milos,
with the Trachilas complex of the Island of Milos and the entire Island of Antimilos emplaced at c. 370–320 ka (Fytikas et al., 1986b); (ii) the peninsula of Methana with volcanics of the Chelona Series dated at c. 380–290 ka (Fytikas et al., 1976; Gaitanakis and Dietrich, 1995; Matsuda et al., 1999), and (iii) Kos Island with the pyroclastics of the Kefalos Series, dated at c. 550 ka, but considered to be potentially younger (Bachmann et al., 2010; Pasteels et al., 1986). However, reliable correlations of these pyroclastics with cryptotephra TP09-65.835b are hindered by the scarcity of glass compositional data of proximal products, since bulk chemical data may provide false information. This can be best demonstrated by the comparison of bulk chemical data of the Chelona pyroclastics of Methana (Fytikas et al., 1986a; Mitropoulos et al., 1987) with interstitial glass data of older cognate xenoliths (Pe, 1974): the former shows compositional ranges from basaltic andesites to dacites, while the latter displays a rhyolitic affinity (73.9–78.4 wt% SiO2). With regard to its composition (e.g., SiO2, MgO, FeO and CaO), the interstitial glass is partially similar to the single-glass composition of cryptotephra TP09-65.835b (Figs. 8, S4-7).

One bulk-pumice analysis of the Kefalos Tuff from Kos (Dalabakis and Vougioukalakis, 1993) yielded a high-SiO2 rhyolitic composition (77.6 wt% SiO2), which approximates the glass composition of cryptotephra TP09-65.835b (Figs. 8, S4-7). EPMA glass data available from the younger Kos Plateau Tuff (c. 161 ka) indicate a high-silica rhyolitic association with SiO2 contents of 76.5–78.3 wt% (Aksu et al., 2008; Zouzias and St. Seymour, 2013), while bulk pumice analyses yield less SiO2-rich values of 73.2–77.0 wt% (Pe-Piper and Moulton, 2008; Zouzias and St. Seymour, 2008) (Fig. 8). Cryptotephra TP09-65.835b plots within the Kos glass geochemical envelope on all bivariate plots, except for the Na2O vs. SiO2 diagram where it shows lower Na2O contents (Figs. 8, S4-7). The rhyolites of the Kos Plateau Tuff and the Kefalos Series are similar in composition and mineralogy, and both were probably generated by fractional crystallization from
magmas similar to the Kefalos dacites (Bachmann and Schnyder, 2006). This would support a tentative correlation of cryptotephra TP09-65.835b with the Kefalos Series from Kos. Although pyroclastic deposits were documented on Antimilos (Fytikas et al., 1986b), only bulk analyses of lava flows and domes are available from this center (Fytikas et al., 1986b; Marinos, 1959), precluding a possible correlation with cryptotephra TP09-65.835b. In contrast, more compositional data are available from the Island of Milos including few EDS-EPMA analyses of perlite from the Trachilas tuff ring. These data indicate highly evolved magmas with SiO2 values between 76.7 wt% and 80.8 wt% (Filippou, 2014; Fytikas et al., 1986b; Koukouzas and Dunham, 1998). Cryptotephra TP09-65.835b falls into the geochemical field of Milos and particularly of Trachilas in all bivariate plots (Figs. 8, S4-7). Only its Na2O content is lower than that of Milos, which may be related to sodium loss during EPMA. In addition to the similarity in chemical composition, K/Ar dates of 370±90 ka and 320±50 ka for the rhyolites of Trachilas and Antimilos, respectively (Fytikas et al., 1986b), broadly correspond to the stratigraphic position of cryptotephra TP09-65.835b within MIS 10 (358 ka). They suggest that one of these volcanic centers could also be the source of the cryptotephra. In summary, the limited availability of glass chemical data of Aegean Arc volcanoes allows only a tentative correlation of cryptotephra TP09-65.835b with volcanic centers from either Kos or Milos.

6.1.2.2.2 Cryptotephras TP09-74.75 to TP09-77.95 (nine layers)
The nine cryptotephra layers of glass population POP5 have a rhyolitic composition that is distinctly different from all volcanic sources discussed so far. They are characterized by SiO2 (72.4–75.7 wt%), K2O (3.0–6.4 wt%), FeO (0.30–1.56 wt%), TiO2 (0.05–0.26 wt%), and Al2O3 (12.9–15.4 wt%) concentrations that best match Aegean Arc and Carpathian tephra compositions; however, they show considerably higher CaO and MgO
concentrations as well as lower Na₂O concentrations (Figs. 6, S4-4). Trace-element glass and even bulk data for tephras from this time range are lacking from the Eastern Carpathians and are very rare from the Aegean Arc. Middle Pleistocene tephra deposits from the Aegean Arc are yet characterized by bulk trace-element analyses only, and single-glass analyses are only available for few Late Pleistocene tephras from that region. Nevertheless, the available data demonstrate that population POP5 does not overlap with Aegean Arc (Santorini, Nysiros) and Central Anatolian (Acigöl, Erciyes Dagi) compositional fields in most trace-element plots (Figs. 3d, 6, S4-1, S4-4). The plots, however, indicate that this population derives from a volcano in a subduction-related tectonic setting, although it is not clear whether it relates to an active- or a post-subduction setting (Figs. 3d, S4-1). Hence, the sources of the cryptotephras within the POP5 glass population remain yet unknown.

6.2 Ages of the MIS 12–10 cryptotephras at Tenaghi Philippon

Although the detected cryptotephras from the 460–335 ka interval at Tenaghi Philippon have distinct geochemical signatures, their correlations with well-dated volcanic eruptions remain difficult. This is because the eruptive history of the Mediterranean region during the Middle Pleistocene is as yet largely unexplored (Leicher et al., 2016; Petrosino et al., 2015). Moreover, Middle Pleistocene volcanic eruptions in the Eastern Mediterranean region lack accurate chronologies because of limited dating of proximal deposits (Bachmann et al., 2010; Sumita and Schmincke, 2013b). This is illustrated by the fact that for the only cryptotephra from the MIS 12–10 interval at Tenaghi Philippon that could be confidently assigned to a known eruption (i.e., TP09-65.95) no accurate dates exist that are derived from its proximal correlative. Instead, the available age estimate for its proximal correlative, i.e., the CT-1 eruption, is ≤360 ka (Druitt et al., 1999), which only confirms that the TP09-65.95 cryptotephra was deposited during the Middle Pleistocene.
To circumvent these limitations, we here provide tentative ages of the identified cryptotephras based on the alignment of the TF-II and TP-2009 pollen datasets from Tenaghi Philippon (Fig. 9). The cryptotephras TP09-77.95 to TP09-75.75 are situated within an interval characterized by tree-pollen percentages <20%, which implies that they were deposited during the MIS 12 glacial between 438 and 427 ka (Table 1; Fig. 9). Cryptotephras TP09-74.75 to TP09-66.95 are located within an interval characterized by high (>80%) tree-pollen percentages, implying that they were deposited during the MIS 11 interglacial (Fig. 9). More specifically, cryptotephra TP09-74.75 occurs close to the onset of the interglacial and has a pollen-derived age of c. 419 ka. Cryptotephras TP09-70.45, -68.95, -67.15, -67.05, and -66.95 have been deposited during the younger interval of MIS 11 between 391 and 367 ka (Table 1; Fig. 9). The cryptotephras TP09-65.95 and -835a,b are associated with relatively low tree-pollen percentages (~50%) at the transition to the MIS 10 glacial (c. 359–358 ka; Table 1; Fig. 9). Finally, the cryptotephras TP09-63.05 and -63.015a,b are located within an interval of increasing tree-pollen percentages that marks the transition to the MIS 9 interglacial; they then can be assigned a pollen-based age of c. 336 ka (Table 1; Fig. 9).

The age assignments for the cryptotephra layers as derived from tree-pollen percentages provide a stratigraphic framework that is essential for correlation with other paleoclimatic records. Although the age model of the TF-II pollen dataset (Tzedakis et al., 2006; Van der Wiel and Wijmstra, 1987; Wijmstra and Smit, 1976) has received general acclaim and is regularly used in comparisons with terrestrial (e.g., Gasse et al., 2015; Litt et al., 2014; Sadori et al., 2016; Wagner et al., 2017) and marine (e.g., Bahr et al., 2018; Martrat et al., 2007) paleoclimate records from the Middle Pleistocene, it may be somewhat compromised by tuning uncertainties, which would by extension affect the palynologically derived ages of the cryptotephras. This holds particularly true for the younger parts of MIS 11. Specifically, the first strong forest contraction at Tenaghi Philippon during MIS
11 occurred at c. 380 ka as documented by the decline in tree-pollen abundances by c. 40–50 % (Fig. 9). This post-dates the first strong cooling event in the North Atlantic by c. 10 ka (e.g., Barker et al., 2015; Bassinot et al., 1994; Voelker et al., 2010) (Fig. 9). Considering the extremely sensitive response of the Tenaghi Philippon pollen record to northern hemisphere climate dynamics (e.g., Müller et al., 2011; Pross et al., 2009), the difference in the timing of the two events cannot be attributed to natural processes, but instead is to be sought in age-model uncertainties. This interpretation is supported by a new, chronologically well-constrained high-resolution MIS 11 palynological record from Lake Ohrid (SW Balkan Peninsula; Kousis et al., 2018). On this basis, the ages of the cryptotephra layers TP09-70.45 to TP09-66.95 can be c. 10 ka older than those deduced from the alignment of the TF-II and TP-2009 pollen records. The tentative ages of the remainder of the cryptotephra layers appear better constrained considering the good agreement between the Tenaghi Philippon pollen record with marine proxy records (e.g., ODP Site 983, Fig. 1; Barker et al., 2015) for the MIS 12 and 10 glacials as well as the MIS 12/11 and MIS 10/9 transitions (compare Fig. 9).

6.3 Implications for MIS 12–10 tephrostratigraphy of the Mediterranean region

High-fidelity synchronization of climate archives across the Mediterranean region hinges critically on the availability of a tephrostratigraphic framework (Blockley et al., 2014; Lowe et al., 2015). Notably, such an effort requires connecting the regional tephrostratigraphies of the Central and Eastern Mediterranean regions, i.e., those of Italy, the Aegean Arc and Anatolia (Zanchetta et al., 2011). In this respect, the Eastern Mediterranean region plays a key role as it is situated downwind of the Italian volcanoes, which enables tephras of Italian origin to be widely distributed eastwards as far as the Levantine Sea (Federman and Carey, 1980; Keller et al., 1978; Vinci, 1985) and the Black Sea (Cullen et al., 2014). Tephra from the Aegean Arc, in turn, are restricted to the Eastern Mediterranean region.
and have not yet been detected in the Central Mediterranean (e.g., Matthews et al., 2015; Wulf et al., 2004), as this would require transport against the mostly prevailing wind directions. Tephras from Anatolian sources have yet rarely been reported beyond Asia Minor, although recent studies suggest that there is dispersal of Anatolian tephras as far as the Levantine Sea (Hamann et al., 2010), the Dead Sea and the NW Arabian Peninsula (Neugebauer et al., 2017).

While studies towards the establishment of a (crypto)tephrostratigraphic scheme for the Holocene and Late Pleistocene of the Eastern Mediterranean region are well underway (e.g., Aksu et al., 2008; Karkanas et al., 2015; Keller et al., 1978; Margari et al., 2007; Zanchetta et al., 2011; Wulf et al., 2018), comparable efforts for the Middle Pleistocene are as yet at an early stage. Important progress towards extending the Eastern Mediterranean tephrochronology beyond the past ~200 ka has recently been made based on the succession from Lake Ohrid, where at least 36 (crypto)tephras have been identified in the MIS 15–1 interval (Kousis et al., 2018; Leicher et al., 2016). However, to date this record has only yielded tephras of Italian origin. As such, our study on MIS 12–10 from Tenaghi Philippon brings together for the first time regional tephrostratigraphies from the Central and Eastern Mediterranean regions for the Middle Pleistocene.

In the Central Mediterranean region, tephra records spanning the MIS 12–10 interval are to date largely known from the Italian Peninsula (Fig. 10). Four tephra layers appear to be particularly widely dispersed: Pozzolane Rosse (~457 ka), Tuffo Rosso a Scorie Nere (TRSN, ~452 ka), Rio Rava (~439 ka), and Vico β (~410 ka), produced by the Colli Albani, Sabatini, Roccamonnfina and Vico volcanoes, respectively (e.g., Galli et al., 2010; Giaccio et al., 2014; Regattieri et al., 2016; Russo Ermolli et al., 2010). Moreover, Pozzolane Rosse and Vico β (previously erroneously labeled as Vico α, Fabrizio Marra, pers. comm. 2018; compare Kousis et al., 2018) were recently discovered on the western Balkan Peninsula (Kousis et al., 2018; Leicher et al., 2016). None of these tephras are present
at Tenaghi Philippon. Instead, the here discovered cryptotephras TP09-70.45 (c. 391 ka) and TP09-65.835a (c. 358 ka) represent large, previously unknown eruptions of Campanian volcanoes. They may provide valuable stratigraphic markers for the MIS 11–10 interval that allow the connection of climate records from the Central and Eastern Mediterranean regions. Moreover, several tephra layers from presumably Italian sources have been detected at ODP Site 964 as well as in the cores KC01 and KC01B from the Ionian Sea during the MIS 12–10 interval (Fig. 10; Lourens, 2004). Ongoing work aiming at geochemical characterization of these tephras (Vakhrameeva et al., in prep.) will further contribute to the establishment of land-sea correlations during MIS 12–10 in the Mediterranean region.

An important result of our study is the first discovery of the Cape Therma 1 tephra deposit outside Santorini, which is represented by cryptotephra TP09-65.95 at Tenaghi Philippon. The age of this unit was not well constrained before, and our finding thus provides it with the best age estimate so far, i.e., c. 359 ka (Fig. 9). The identification of the CT-1 tephra at Tenaghi Philippon indicates that it might be widespread in the Aegean Sea region, with the potential of being important marker horizon for MIS 10. Cryptotephra TP09-63.015b (c. 336 ka) has a similar geochemical signature to the Cape Therma 2 eruption of Santorini, but it is older by more than 100 ka (Druitt et al., 1999) and most likely re-deposited.

Moreover, although still being tentative, the correlation of cryptotephra TP09-66.95 (c. 367 ka) with a minor Santorini pyroclastic deposit that directly underlies the CT-1 tephra indicates that even eruptions that resulted in only relatively minor pyroclastic units on Santorini may have led to tephras that became widely dispersed across the Aegean region, which may allow to use them as marker beds. To further explore this possibility, more research on older pyroclastic deposits from Santorini is needed that would include collection of major- and trace-element glass data as well as dating of tephra deposits. A
refined age model for the Tenaghi Philippon archive via higher-resolution pollen data would allow to further constrain the age estimates for all identified cryptotephras. Because many cryptotephras in this study are characterized by low glass-shard abundances, replication of our findings in other tephra records will be instrumental in proving their significance.

7 Conclusions
The detailed cryptotephra analysis of core TP-2009 allowed identification and geochemical characterization of eighteen primary cryptotephra layers in the MIS 12–10 (460–335 ka) interval of the Tenaghi Philippon archive. Major- and trace-element glass compositions were used to establish correlations between the cryptotephras detected in core TP-2009 and their volcanic and eruptive sources in the Aegean Arc and Italy. Cryptotephra ages were estimated based on palynostratigraphic information from the same archive. This yielded the first distal tephrostratigraphic framework for the Eastern Mediterranean region during MIS 12–10 and notably the first record that integrates information from both the Italian and Aegean Arc volcanic provinces during that time. With regard to eruptive sources from the Aegean Arc, six cryptotephra layers of Santorini origin were identified in the Tenaghi Philippon record. One of them represents the oldest major explosive eruption of Santorini, i.e., Cape Therma 1. Based on palynostratigraphic information from that site, its age can be estimated to c. 359 ka. One re-deposited cryptotephra with an age estimate of c. 336 ka compositionally matches the second oldest major explosive eruption of Santorini, i.e., Cape Therma 2, suggesting a deposition of the primary tephra further upcore. Another cryptotephra constrained at c. 367 ka can be tentatively correlated with the pumice fall directly underlying the Cape Therma 1 deposit on Santorini. A cryptotephra with an age of c. 358 ka most likely derives from an Aegean Arc volcano other than Santorini, probably either Kos or Milos. A more precise correlation
would require currently lacking geochronological and glass compositional data for tephra deposits from these volcanoes. Interestingly, the oldest nine cryptotephras in our record (438–419 ka) do not match any volcanic sources in the Mediterranean region. This clearly demonstrates a yet considerable gap in our knowledge about volcanic history of the Eastern Mediterranean region. Cryptotephras with an unequivocally Italian origin have been identified at c. 391 ka and c. 358 ka; they can be attributed to major, yet unknown eruptions of Campanian volcanoes.

In light of our findings, future work towards refining the Middle Pleistocene tephrostratigraphy for the Eastern Mediterranean region should focus on (i) detailed studies involving major- and trace-element glass analyses as well as age determinations of proximal pyroclastic sequences in the volcanic regions of the Aegean Arc, Anatolia, and the Carpathians, and (ii) further (crypto)tephra analysis of marine and terrestrial records in order to identify key tephra isochrones in the Eastern Mediterranean region.

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Figure captions

Figure 1: Map of the Central and Eastern Mediterranean regions showing the location of Tenaghi Philippon and other Middle Pleistocene tephra archives considered in this study: 1 – Piánico paleolake; 2 – Ficoncella site; 3 – Campo Felice basin; 4 – Paganica-San Demetrio-Castelnuovo basin; 5 – Sulmona basin; 6 – Sessano basin; 7 – Boiano basin; 8 – Mercure basin; 9 – ODP Site 964; 10 – Lake Ohrid; 11 – Lake Van. The main volcanic centers active (or possibly active) during MIS 12–10 are also marked: A, Aeolian Islands; Ac, Acigöl; C, Ciomadul; CA, Colli Albani; CF, Campi Flegrei; Ch, Christiana Islands; E,
Etna; ED, Erciyes Dagi; G, Gölcük; HD, Hasan Dagi; Is, Ischia; K, Kos; M, Milos and Antimilos; Me, Methana; N, Nemrut; P, Pantelleria; Pz, Ponza Island; R, Roccamonfina; S, Sabatini; Sn, Sancy; St, Santorini; Sü, Süphan; U, Ustica; V, Vico; Vs, Vulsini; Vt, Monte Vulture. The inset map shows the location of ODP Site 983 (12) in the North Atlantic.

**Figure 2:** Lithostratigraphy, arboreal pollen record (AP) and distribution of cryptotephras with glass-shard counts in the 82–63 m depth interval of the Tenaghi Philippon TP-2009 core. Cryptotephras are color-coded according to their provenance as inferred in this study.

**Figure 3:** Individual cryptotephra layers in core TP-2009 plotted in (A) total alkali vs. silica diagram (Le Bas et al., 1986); (B) K$_2$O vs. SiO$_2$ diagram (Peccerillo and Taylor, 1976); (C) K$_2$O/Na$_2$O vs. SiO$_2$ diagram with a close-up part of the diagram showing classification of Italian volcanic rocks on the basis of the K$_2$O/Na$_2$O ratio (modified after Peccerillo, 2017); (D) tectonic setting discrimination diagrams Rb vs. Y+Nb and Nb/Rb vs. Th/Rb (Tomlinson et al., 2015) for anorogenic, active-subduction and post-subduction settings. Tephra are grouped into geochemical populations and indicated by colors. Rock types: A – andesite; B – basalt; BA – basaltic andesite; BTA – basaltic trachyandesite; D – dacite; F – foidite; L – latite; P – phonolite; PB – picrobasalt; PT – phonotephrite; R – rhyolite; S – shoshonite; SB – shoshonitic basalt; TB – tephrite or basanite; TP – tephriphonolite; Tr – trachyte; TrA – trachyandesite; TrB – trachybasalt; TrD – trachydacite.

**Figure 4:** (A) Major-element plots and (B) Cl vs. CaO/FeO plot (Giaccio et al., 2017b) showing comparison of trachytic TP09 cryptotephra with potential Italian source
volcanoes. Geochemical envelopes corresponding to the basal fall, lower and intermediate flow units, and the upper flow unit of CI are plotted as well. A N$_2$O/K$_2$O ratio of 0.6 is used to discriminate the two components of CI following Tomlinson et al. (2012a). The TAV2 tephra of Campanian provenance (Giaccio et al., 2014) is shown as a potential correlative for cryptotephras from Tenaghi Philippon. Data sources: Campi Flegrei – Leicher et al. (2016), Margari et al. (2007), Müller et al. (2011) Smith et al. (2011), Tomlinson et al. (2012a); Campanian Ignimbrite – Leicher et al. (2016), Margari et al. (2007), Müller et al. (2011), Tomlinson et al. (2012a); Etna – Albert et al. (2013), Wulf et al. (2004, 2012); Ischia – Tomlinson et al. (2014, 2015); Pantelleria – Leicher et al. (2016), Margari et al. (2007), Tamburrino et al. (2012), Tomlinson et al. (2015); Roccamonfina – Giaccio et al. (2014), Giannetti and Luhr (1983), Leicher et al. (2016), Regattieri et al. (2016); Sabatini – Aureli et al. (2012), Giaccio et al. (2014), Leicher et al. (2016), Marra et al. (2014), Palladino et al. (2014), Petrosino et al. (2014); Ustica (bulk analyses) – Cinque et al. (1988); Vico – Leicher et al. (2016), Marra et al. (2014), Palladino et al. (2014), Perini et al. (2000), Regattieri et al. (2016); Vulsini – Leicher et al. (2016), Nanni et al. (1994, 1998), Palladino et al. (2014).

**Figure 5:** Major- and trace-element plots refining the correlation of trachytic cryptotephras from Tenaghi Philippon with Italian source volcanoes and individual eruptions during the MIS 12–10 interval. * Old Campanian Tephras – tephras with Campanian geochemical fingerprints that are older than proximal Campanian volcanics (~290 ka), including the Morphi and TAV2 tephras; see text for details on particular tephra layers. SIMS (purple dotted/dashed lines) and LA-ICPMS (dark blue dotted/dashed lines) data of CI on trace-element plots are shown separately. Data sources: Ischia – Tomlinson et al. (2014, 2015)$^{1,2}$; Campanian Ignimbrite – Leicher et al. (2016)$^1$, Margari et al. (2007)$^1$, Tomlinson et al. (2012a)$^{1,2}$, Wulf et al. (2018)$^{1,2,3}$; pre- and post-Campanian Ignimbrite series of
Campi Flegrei – Smith et al. (2011)\textsuperscript{1,2}, Tomlinson et al. (2012a)\textsuperscript{1,2}; Old Campanian Tephras – Giaccio et al. (2013b, 2014)\textsuperscript{1}, Leicher et al. (2016)\textsuperscript{1}, Petrosino et al. (2014\textsuperscript{1,2}, 2015\textsuperscript{1,2}), Pyle et al. (1998)\textsuperscript{1}. Analytical techniques used in the data sources: 1 – EPMA; 2 – LA-ICP-MS; 3 – SIMS.

**Figure 6:** Major- and trace-element plots showing comparison of dacitic and rhyolitic cryptotephras from Tenaghi Philippon with potential volcanic sources: (A) Aegean Arc, including only Quaternary rocks of Methana, Milos, Kolumbo, Kos, Nisyros, Yali, and (plotted separately) Santorini; Aeolian Islands, including Salina and Lipari; (B) Western (Gölcük), Central (Acigöl; Erciyes Dagi) and Eastern (Nemrut, Süphan) Anatolia, Carpathians (Ciomadul), and Pianico (T21d) tephra. Data sources: Aegean Arc – Aksu et al. (2008)\textsuperscript{1}, Dalabakis and Vougioukalakis (1993)\textsuperscript{3}, Federman and Carey (1980)\textsuperscript{1}, Cantner et al. (2014)\textsuperscript{1}, Filippou (2014)\textsuperscript{3}, Fuller (2015)\textsuperscript{1}, Fytikas et al. (1986a,b)\textsuperscript{3}, Koukouzas (1997)\textsuperscript{3}, Koukouzas and Dunham (1998)\textsuperscript{3}, Margari et al. (2007)\textsuperscript{1}, Mitropoulos et al. (1987)\textsuperscript{3}, Pe (1974)\textsuperscript{3}, Pe-Piper and Moulton (2008)\textsuperscript{3}, Tomlinson et al. (2012b)\textsuperscript{1,2}, Vinci (1985)\textsuperscript{1}, Zouzias and St. Seymour (2008, 2013)\textsuperscript{1,3}; Santorini – Druitt et al. (1999)\textsuperscript{3}, Huijsmans (1985)\textsuperscript{3}, Margari et al. (2007)\textsuperscript{1}, Satow et al. (2015)\textsuperscript{1}, Tomlinson et al. (2015)\textsuperscript{1,2}, this study\textsuperscript{1}; Salina and Lipari – Albert et al. (2012, 2017)\textsuperscript{1,2}; Western and Central Anatolia – Tomlinson et al. (2015)\textsuperscript{1,2}; Eastern Anatolia – Macdonald et al. (2015)\textsuperscript{1}, Schmincke and Sumita (2014)\textsuperscript{1}, Sumita and Schmincke (2013a,b)\textsuperscript{1,3}; Carpathians – Karátson et al. (2016)\textsuperscript{1}, Molnár et al. (2018)\textsuperscript{3}; Pianico (T21d) – Brauer et al. (2007)\textsuperscript{1}. Analytical techniques used in the data sources: 1 – EPMA; 2 – LA-ICP-MS; 3 – bulk analyses.

**Figure 7:** Major- and trace-element plots showing comparison of dacitic (POP2) and rhyolitic (POP3) cryptotephras from Tenaghi Philippon with potential Santorini tephra
equivalents: Cape Therma 1, 2 and 3; 1st and 2nd pumice falls below Cape Therma 1. Bulk trace-element data are from Druitt et al. (1999).

**Figure 8:** Major-element plots showing comparison of rhyolitic cryptotephras from Tenaghi Philippon (POP4 and POP5) with Middle Pleistocene volcanic sources of the Aegean Arc. Data sources as in Fig. 6.

**Figure 9:** Ages of cryptotephras from Tenaghi Philippon as estimated by aligning the pollen record from core TP-2009 to other climate records. (A) Percentages of the planktonic foraminifer *Neogloboquadrina pachyderma* (NPS %) from ODP Site 983 (Barker et al., 2015) tuned to the LR04 stack (Lisiecki and Raymo, 2005); (B) Tree-pollen percentages (AP %) from core TP-2009 (this study); (C) Tree-pollen percentages (AP %) from the old Tenaghi Philippon core TF-II (Van der Wiel and Wijmstra, 1987; Wijmstra and Smit, 1976) plotted on the orbitally tuned age model of Tzedakis et al. (2006). The yellow band marks an offset between the age models of the TF-II and ODP Site 983 records. The MIS boundaries shown in the figure are from the low-latitude oxygen isotope stack of Bassinot et al. (1994).

**Figure 10:** Tephrostratigraphic framework for the Central and Eastern Mediterranean for the MIS 12–10 (460–335 ka) interval in Tenaghi Philippon. The MIS boundaries shown in the figure are from the low-latitude oxygen isotope stack of Bassinot et al. (1994). The following tephra records are shown (from W to E): Ficoncella site (Aureli et al., 2012, 2015); Campo Felice basin (Giraudi and Giaccio, 2015); Paganica-San Demetrio-Castelnuovo basin (Galli et al., 2010; Giaccio et al., 2012); Sulmona basin (Giaccio et al., 2013b; Regattieri et al., 2016); Valle Guimentina basin (Villa et al., 2016); Sessano basin (Russo Ermolli et al., 2010); Boiano basin (Amato et al., 2014); Mercure basin (Giaccio
et al., 2014); ODP Site 964 (Lourens, 2004); Lake Ohrid (Kousis et al., 2018; Leicher et al., 2016); Tenaghi Philippon (this study); Lake Van (Engelhardt et al., 2017). The dashed lines mark tephra layers that have been found in at least two distal sequences. Tephras from ODP Site 964 and Lake Van have been included for completeness despite the absence of geochemical data.

Table titles

Table 1: Summary of cryptotephra samples in the MIS 12–10 interval of core TP-2009 including glass shard counts, geochemical affinity, likely sources and estimated ages.

Table 2: Representative EPMA (non-normalized) and SIMS glass data of cryptotephras in the MIS 12–10 interval of core TP-2009.

Supplementary files

Supplement 1: Supplementary information on peat tephra archives, material and methods, and sampling sites for proximal tephra samples on Santorini, as well as micrographs of glass shard from Tenaghi Philippon.

Supplement 2: Full EPMA and SIMS glass analytical data of cryptotephras from Tenaghi Philippon.

Supplement 3: EPMA glass data of proximal tephra samples from Santorini.

Supplement 4: Additional major- and trace-element plots supporting the interpretation.
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</table>
Old Campanian Tephra

- Morphi (374 ka)
- TAV2 (494-438 ka)

CI basal fall, lower and intermediate flow (39.85 ka)

CI upper flow (39.85 ka)

Pre-CI

Ischia

Post-CI

Figure 5
Figure 6
1. Peatlands as tephrostratigraphic archives

PEATLAND SETTINGS ARE IDEALLY SUITED TO PRESERVE INORGANIC SOLIDS SUPPLIED BY ATMOSPHERIC DEPOSITION SUCH AS TEPHRA FALLOUT BECAUSE OF THEIR LOW-ENERGY DEPOSITIONAL ENVIRONMENT WITH NEGligible erosional processes and bioturbation (Davies, 2015; Watson et al., 2015). Moreover, extraction and detection of cryptotephra is more straightforward in peat than in sediments dominated by inorganic components as they typically prevail in lacustrine and marine settings (e.g., Gehrels et al., 2008). In addition, post-depositional tephra movement in peatlands related to gravitational sinking, rainfall percolation as well as fluctuations of the water table is generally minor and has little effect on the actual stratigraphic position of a tephra layer (Payne and Gehrels, 2010). However, in the case of thick visible tephra layers, both up- and downcore tephra movement in peat can occur over longer distances (Wulf et al., 2018).

2. Material and methods

PROXIMAL CORRELATIVE TEPHRA SAMPLES FROM SANTORINI
Deposits of the Cape Therma 3 (c. 224–184 ka; Druitt et al., 1999; Gertisser et al., 2009; sample SAN15-26) and Cape Therma 1 (≤360 ka; Druitt et al., 1999; samples SAN15-33, -34, -36) eruptions were sampled from the caldera wall at Cape Plaka, whereas deposits of the Cape Therma 2 eruption (c. 224 ka; Druitt et al., 1999; sample SAN15-28) were sampled from a road cut near Athinios harbor (Table S1-2; Fig. S1-1). In addition, two samples from white pumice fall deposits that stratigraphically underlie the Cape Therma 1 deposits and derive from two different, yet unknown older Santorini eruptions (SAN15-35 and SAN15-37) were also collected in the area.

TEPHRA EXTRACTION AND PROCESSING
To remove organic matter, samples were oven-dried for 12–24 hours at 105 °C and subsequently combusted in a muffle furnace for 4 hours at 550 °C. The weight differences between wet, dry and ashed samples were measured to calculate water and organic matter contents. The ash residues were immersed in ~15% H₂O₂ overnight to remove remaining traces of organic matter. Carbonate material was dissolved by immersion in ~7.5–10% HCl. Samples were sieved through 20 and 100 μm nylon meshes to isolate the 20–100 μm grain-size fraction. Density separation of the 20–100 μm fraction was performed with sodium polytungstate following the protocol of Turney (1998). The material was separated into two density fractions (<2.55 g/cm³ and >2.55 g/cm³) using the heavy liquid sodium polytungstate, and the lighter fraction was transferred into rectangular plastic lids to be examined for tephra components under a light microscope at 100x magnification. Identified glass shards were handpicked with a single-hair brush into an aluminum stub, mounted in Epofix™ resin, and subsequently sectioned and polished to allow geochemical analysis.

POLLEN ANALYSIS
Palynological processing comprised sediment freeze-drying, weighing, spiking with Lycopodium marker spores, treatment with HCl (10%), NaOH (10%) and HF (when necessary; 40%), heavy-liquid separation with Na₂WO₄ x 2H₂O (when necessary), acetolysis, sieving through a 7 μm mesh, and slide preparation using glycerin jelly. Slides were analysed under an Imager.A2 Zeiss light microscope at 400x and 1000x magnification.
Table S1-1: Tie points for the tuning of the arboreal pollen record from core TP-2009 to that from the old Tenaghi Philippon core (TF-II; Van der Wiel and Wijmstra, 1987; Wijmstra and Smit, 1976) using the orbitally tuned age model of Tzedakis et al. (2006).

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Age (ka)</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.14</td>
<td>336.87</td>
</tr>
<tr>
<td>64.64</td>
<td>349.08</td>
</tr>
<tr>
<td>66.60</td>
<td>364.04</td>
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<tr>
<td>67.98</td>
<td>376.61</td>
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<tr>
<td>68.57</td>
<td>379.41</td>
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<tr>
<td>75.53</td>
<td>423.42</td>
</tr>
<tr>
<td>75.96</td>
<td>430.02</td>
</tr>
<tr>
<td>76.66</td>
<td>433.07</td>
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<tr>
<td>78.71</td>
<td>440.42</td>
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<tr>
<td>79.84</td>
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<tr>
<td>81.65</td>
<td>455.79</td>
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<tr>
<td>81.91</td>
<td>458.15</td>
</tr>
</tbody>
</table>

3. Sampling sites for proximal tephra samples on Santorini

Table S1-2: Details of pumice-fall sampling sites on Santorini.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Unit</th>
<th>Latitude</th>
<th>Longitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAN15-26</td>
<td>Cape Therma 3, basal pumice fall (Cape Plaka)</td>
<td>36°22'35.8&quot; N</td>
<td>25°25'26.5&quot; E</td>
</tr>
<tr>
<td>SAN15-28</td>
<td>Cape Therma 2, white pumice fall (street to Athinios harbour)</td>
<td>36°23'22.8&quot; N</td>
<td>25°26'05.0&quot; E</td>
</tr>
<tr>
<td>SAN15-33</td>
<td>Cape Therma 1, black non-lithified ignimbrite (Cape Plaka)</td>
<td>36°22'35.9&quot; N</td>
<td>25°25'30.2&quot; E</td>
</tr>
<tr>
<td>SAN15-34</td>
<td>Cape Therma 1, basal pumice fall, pinkish scoriae and strongly altered white pumices, base rich in lithics (Cape Plaka)</td>
<td>36°22'35.9&quot; N</td>
<td>25°25'30.2&quot; E</td>
</tr>
<tr>
<td>SAN15-35</td>
<td>white pumice fall (40-60 cm), ca. 6 m below Cape Therma 1 (Cape Plaka)</td>
<td>36°22'36.3&quot; N</td>
<td>25°25'30.0&quot; E</td>
</tr>
<tr>
<td>SAN15-36</td>
<td>Cape Therma 1, basal pink pumice fallout (Cape Plaka)</td>
<td>36°22'36.8&quot; N</td>
<td>25°25'27.5&quot; E</td>
</tr>
<tr>
<td>SAN15-37</td>
<td>white pumice fallout (20-30 cm), ca. 21 m below Cape Therma 1 (Cape Plaka)</td>
<td>36°22'37.6&quot; N</td>
<td>25°25'24.8&quot; E</td>
</tr>
</tbody>
</table>
Figure S1-1: Photoaereal map of sampling locations of pyroclastic fall deposits on Santorini.
Figure S1-2: Stratigraphic position of pumice and scoriae fall deposits sampled on Santorini. For details see Table S1-2.

Santorini tephrostratigraphy  
(modified after Druitt et al., 1999)

- Minoan
- Cape Riva
- Upper Scoriae 2
- Upper Scoriae 1
- Vourvoulos
- Middle Pumice
- Cape Thera
- Lower Pumice 2
- Lower Pumice 1
- Cape Therma 3
- Cape Therma 2
- Cape Therma 1

Sample No. (SAN)

26
28
33
34
36
35
37
4. Glass shard micrographs

TP09-63.015a

TP09-63.015b

TP09-63.05

TP09-65.95

TP09-66.95
References


Figure S4-1: Complementary trace-element plots to Fig. 3 in the text.
Figure S4-1: (continued)
Figure S4-2: Complementary major-element plots to Fig. 4 in the text.
**Figure S4-3**: Complementary major- and trace-element plots to Fig. 5 in the text.
Figure S4-4: Complementary major- and trace-element plots to Fig. 6 in the text.
Figure S4-4: (continued).
Figure S4-4: (continued).
Figure S4-5: (A) $K_2O$ vs. $SiO_2$ diagram (Peccerillo and Taylor, 1976) and (B) $FeO/MgO$ vs. $SiO_2$ diagram (Miyashiro, 1974) showing dacitic (POP2) and rhyolitic (POP3) cryptotephras from Tenaghi Philippon in comparison with Santorini major pyroclastic units. Data sources: see Fig. 6 in the text.
Figure S4-6: Complementary major- and trace-element plots to Fig. 7 in the text.
Figure S4-6: (continued).
Figure S4-7: Complementary major-element plots to Fig. 8 in the text.