Revisiting the Y-3 tephrostratigraphic marker: a new diagnostic glass geochemistry, age estimate, and details on its climatostratigraphical context

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Abstract

The 'Y-3' tephra is a crucial stratigraphic marker within the central Mediterranean region that falls close to the Marine Isotope Stage 3/2 transition and a cooling event proposed as a correlative of the North Atlantic Heinrich Stadial 3 (HS3). Consequently, this tephra offers great potential to assess potential leads and lags in environmental responses to this abrupt climatic transition. New grain-specific glass analysis (EMPA and LA-ICP-MS) of the type locality Y-3 tephra recorded in the Ionian Sea confirms its origin from Campi Flegrei (CF) but reveals that it is compositionally different from the previously suggested proximal equivalent the VRa eruptive unit (Verdolino Valley, CF). Consequently, the $^{40}\text{Ar}/^{39}\text{Ar}$ age of the VRa should not be exported distally to the Y-3 tephra. Instead, we propose a new robust age for the Y-3 tephra following its identification in the Tenaghi Philippon sedimentary record, NE Greece. A Bayesian-based ^{14}C age model from Tenaghi Philippon provides a distal age of 28,680-29,420 cal yrs BP for the Y-3 tephra. The identification of this tephra in NE Greece markedly extends its known eastern dispersal. Whilst its stratigraphic position falls within the latter part of a period of low tree pollen percentages related to dry stadial conditions. This new age and environmental context suggest that this marker postdates the onset of HS3 in the eastern Mediterranean region by ~2300 years.

Keywords

Y-3 tephra, Ionian Sea, Mediterranean tephrochronology, Tenaghi Philippon, Stadial conditions, Bayesian age modelling.

1. Introduction

Northern hemisphere palaeoenvironmental archives indicate that the last glacial was punctuated by abrupt and high-amplitude climatic variability (Dansgaard et al., 1993; NGRIP Members, 2004; Rasmussen et al., 2006), this variability is also observed in Mediterranean climate archives (Allen et al., 1999; Sanchez Goni et al., 2000; Tzedakis et al., 2002, 2004; Kotthoff et al., 2011; Müller et al., 2011). However, detailed assessment of the spatial and temporal patterning of this extreme climate variability, even at a centennial resolution, is limited by the precision and accuracy of the available chronological information. Radiocarbon dating (^{14}C) remains the most frequently adopted geochronological tool for the last 50 ka BP, but its precision is often insufficient to assess the exact timing of climatic change between different archives and is furthermore complicated by inherent uncertainties associated with variations in marine reservoir offsets (Siani et al., 2001).

Volcanic ash (< 2mm) or tephra associated with explosive volcanism can be used to synchronise palaeoenvironmental archives (i.e. tephrostratigraphy) owing to its widespread and synchronous distribution (Lowe, 2011). Furthermore, where the age of a tephra can be determined it provides a chronological marker (i.e., tephrochronology) (Lowe, 2011). The high frequency of explosive volcanic activity in the Mediterranean region during the Late Quaternary makes tephrochronology a particularly powerful tool. Indeed, visible tephra horizons have been successfully identified as chronological markers within marine (e.g., Keller et al., 1978; Vinci, 1985; Paterne et al., 1986, 1988, 2008; Calanchi et al., 1996; Vezzoli, 1991; Hardiman 1999; Aksu et al., 2008; Albert et al., 2012) and terrestrial (e.g., Ramrath et al., 1999; Wulf et al., 2004, 2008; Margari et al., 2007; Sulpizio et al., 2010; Wagner et al., 2008; Vogel et al., 2010) archives from across the Mediterranean region. More recently, studies of cryptotephra (non-visible ash layers) have both expanded the geographic distribution of known eruptions and increased the number of distal chronological markers available within palaeoenvironmental archives (Siani et al., 2004; Lowe et al., 2007; Bourne et al., 2010; Damaschke et al., 2013).

One of these layers crucial to the central Mediterranean tephrostratigraphy is the 'Y-3' tephra, a tephra first identified and labelled based on its occurrence in the Last Glacial (climate zone Y) marine sediments of the Ionian Sea (Keller et al., 1978) (Fig. 1a). This K-trachytic tephra was reported stratigraphically above the thicker K-trachytic Y-5 layer and was thought to be associated with major explosive activity from the Campanian region (Keller et al., 1978). The presence of the Y-3 tephra was later confirmed in new Ionian Sea sediment cores from the Meteor cruise M25/4 (Keller et al., 1996; Kraml, 1997) (Fig. 1a). The Ionian Sea records can therefore be considered the 'type locality' for the Y-3 distal marker tephra. The thickness of this Ktrachytic ash layer in the Ionian Sea records (Table 1), over 450 km from Campanian Volcanic Zone (CVZ) (Table 1; Fig. 1a), clearly demonstrates the large magnitude of this Campanian eruption. Stratigraphically this tephra layer is very important due to its close association with the marine isotope stage 3/2 transition or Heinrich Stadial 3 (HS3) (Negri et al., 1999). Subsequently this layer has been readily identified in numerous other Mediterranean archives and thus offers a crucial central Mediterranean regional marker layer (Fig. 1a) (Table 1; Munno and Petrosino, 2004, 2007; Wulf et al., 2004; Wagner et al., 2008; Zanchetta et al., 2008; Bourne et al., 2010; Caron et al., 2010; Vogel et al., 2010; Damaschke et al., 2013). The timing of this eruption and its widespread dispersal means that it offers significant potential to precisely synchronise archives, enabling the assessment of spatial leads and/or lags associated with an important environmental transition.

However, complexity still surrounds the use of the Y-3 tephra as a precise stratigraphic and chronostratigraphic marker. The absence of detailed glass chemistry from the type locality Y-3 tephra means that existing distal correlations

have not been subject to the necessary levels of geochemical validation. For this reason it is difficult to know which of the distal ages should be adopted for this marker tephra (Table 1). Determining the precise proximal counterpart of this tephra also presents a further uncertainty. Whilst it is generally regarded that the Y-3 tephra originates from an eruption within the Campi Flegrei (CF) caldera, southern Italy (Fig. 1) (Zanchetta et al., 2008), determining the proximal equivalent remains challenging due to more recent activity and limited exposure in this heavily developed region. Tephrostratigraphic investigations on deposits outside the caldera suggested that the SMP1-e (Santa Maria di Pozzano 1-e) ignimbrite deposits that are exposed along Sorrentine Peninsula (Fig. 1b) were the medial equivalent of the Y-3 tephra (Sulpizio et al., 2003; Di Vito et al., 2008). These deposits show similar stratigraphic, lithological, compositional, and chronological constraints to the distal marker (Table 1). Charcoal material from the palaeosol directly beneath the SMP1-e ignimbrite unit is dated to 29,390-30,720 cal yrs BP, which is older than the interpolated sapropel age of the Y-3 distal marine marker in the Ionian Sea (25.3 ± 3 ka; Kraml, 1997) (Table 1). These SMP1-e tephra deposits, in turn, are correlated to the 4.5 m thick intra-caldera surge and fall deposits of the VRa eruptive unit outcropping in the Verdolino Valley (VR) (Di Vito et al., 2008). The VRa unit represents a single eruption within the Tufi Biancastri stratigraphy (Orsi et al., 1996) e a series of CF eruptions that occurred between the two caldera forming eruptions, the Campanian Ignimbrite (CI)/Y-5 (39.28 ± 0.11 40Ar/39Ar ka, De Vivo et al., 2001) and Neapolitan Yellow Tuff (NYT)/C-2 (14,320- 13,900 cal yrs BP; Blockley et al., 2008a). Pappalardo et al. (1999) dated the VRa to 30.3 ± 0.2 (1s) ka (40Ar/39Ar) which is consistent with the calibrated SMP1-e age (Table 1). Consequently, Zanchetta et al. (2008) suggested that the best age estimate for the Y-3 tephra was ca 30-31 cal ka BP.

Here we present grain-specific major, minor and trace element data for Y-3 glass shards from its type locality in the Ionian Sea (Keller et al., 1978; Kraml, 1997). This data is used to; (1) test proximal links to Campi Flegrei using glass data from the Tufi Biancastri units presented by Tomlinson et al. (2012); (2) assess links to medial-distal extra-caldera tephra deposits recorded on the Sorrentine Peninsula and within the Campanian Plain (i.e., SMP1-e tephra; Di Vito et al., 2008); and (3) use the diagnostic glass geochemistry of the type locality Y-3 to verify existing and new distal-distal correlations that underpin the synchronisation of archives throughout the Mediterranean region. This will refine the known dispersal of the Y-3 tephra and improve the chronological and environmental constraints placed upon this important tephrostratigraphic marker.

2. Materials

2.1 Distal tephra samples

Y-3 in the Ionian Sea core M25/4-12 (Fig. 1a) is a 1 cm thick visible tephra layer that occurs at 117.5-118.5 cm below the sea floor. Core M25/4-12 was retrieved with a piston corer from the Calabrian Rise $37^{\circ}57'98''\text{N}$; $18^{\circ}11'04''\text{E}$ in the Central Ionian Sea at a 2473 m water

depth *Meteor* cruise M25/4 in 1993 (Keller et al., 1996). The position of the tephra within the oxygen isotope stratigraphy occurs close to the MIS 2/3 transition (Negri et al., 1999).

Two cryptotephra layers are investigated within this contribution, the first, TP 9.70 is identified within the core TP-2005 from the terrestrial site of Tenaghi Philippon (TP), NE Greece (Fig. 1a; see Pross et al., 2007, 2009, and Müller et al., 2011 for details on the site and core). The cryptotephra was detected and extracted following the procedures outlined in Blockley et al. (2005). Multiple interrupted peaks in cryptotephra concentrations were detected over a 60 cm interval, by far the largest concentration of shards were found at the base of this interval (9.70 m) where concentrations were as high as 2060 shards/per gram. For this reason a depth of 9.70 is defined as the depth of tephra deposition, geochemical analysis throughout the 60 cm confirm consistent glass chemistries (Supplementary information) and consequently upwards reworking of tephra within the peat sequence is proposed (Hardiman, 2012).

The second is a cryptotephra layer, PRAD 1332, previously recognised by Bourne et al. (2010) at a depth of 1332 cm in the sediments of core PRAD 1-2 (Fig. 1a). PRAD 1-2 was recovered from the western and upper flank of the Mid-Adriatic deep (42°40.34.7826'N; 14°46.13.5565'E) at a water depth of 185.5 m (Bourne et al., 2010). Shards were typically described as platy and had a peak of 53 shards/per gram (Bourne et al., 2010). The tephra layer resides stratigraphically just above the MIS 2/3 transition in the oxygen isotope stratigraphy of the core (Piva et al., 2008).

2.2 Medial (extra-caldera) tephra samples

The SMP1-e tephra (Di Vito et al., 2008) was sampled from two extra-caldera localities (Fig. 1b); The first is the SMP1-e type locality at Santa Maria di Pozzano (SMP), 30 km south-east of Campi Flegrei caldera on the Sorrentine Peninsula (Fig. 1b). This unit comprises of an ash massive, with sparse light grey aphyric pumice lapilli (ZS 98262) and is interpreted as the deposits of a pyroclastic density current (Di Vito et al., 2008). The second locality was

near Cervino, 32 km north-east of the Campi Flegrei caldera (Fig. 1b). Two well sorted pumice beds were sampled (lower ZS 2506; upper ZS 2507) and these pumices were light grey and aphyric. Di Vito et al., (2008) interpret these deposits to be the fall component of the SMP1-e eruption.

3. Methods

Y-3 tephra from the visible Ionian Sea ash layer (M25/4-12) were washed, dried and handpicked under a light microscope. Both cryptotephra layers were identified and extracted following the procedures outlined in Blockley et al. (2005). Distal tephra shards and medial pumices were mounted in Struers Epofix epoxy resin. Mounts were sectioned and polished. Scanning electron and transmitted light microscopy was conducted to label individual clasts to ensure the coupling of major and trace element analysis to a single grain.

3.1 Analytical methods

3.1.1 Electron microprobe analysis (EMPA)

Major and minor element chemistry was determined for individual juvenile clasts (volcanic glass) using a wavelength-dispersive JEOL 8600 electron microprobe (EMPA) in the Research Laboratory for Archaeology and the History of Art, University of Oxford. A beam accelerating voltage of 15kV was used with a 6nA current with a beam diameter of 10 µm. The instrument was calibrated with a suite of appropriate mineral standards and verified using secondary glass standards. Peak count times were 30 s for most elements and 10 s for Na. Secondary glass standards from the Max Plank institute (MPI-DING suite; Jochum et al., 2006) were also analysed with the unknown tephra samples. The MPI-DING reference glasses used include evolved felsic [ATHO-G (rhyolite)], through intermediate [StHs6/80-G (andesite)] to mafic [GOR128-G (Komatiite)] compositions.

Glass data was normalised to 100% for comparative purposes. Analytical totals < 93% were discarded, those with > 93% was used as these highly evolved glasses have a high water

content. Errors are typically $< \pm 0.7\%$ RSD for Si; $\sim \pm 3\%$ for most other major elements, except for the low abundance elements: Ti ($\sim \pm 7\%$), Mn ($\sim \pm 30\%$). Error bars on plots represent reproducibility, 2 standard deviations of replicate analysis of the MPI-DING StHs6/80-G glass.

3.1.2 Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

Analyses of both distal and proximal tephra deposits were performed using an Agilent 7500es ICP-MS coupled to a Resonetics 193nm ArF excimer laser-ablation in the Department of Earth Sciences, Royal Holloway, University of London. Analytical procedures for tephra are reported in Tomlinson et al. (2010). Spot sizes of 20, 25 and 34 μm were used depending on the vesicularity and/or size of glass surfaces. Distal tephra often required smaller laser spot sizes. The repetition rate was 5 Hz and the count time 40 s on the sample and 40s on the gas blank to allow the subtraction of the background signal. Blocks of eight sample/shards of glass and one MPI-DING reference glass were bracketed by NIST612 glass calibration standard (GeoREM 11/2006). In addition MPI-DING reference glasses (Jochum et al., 2006) were used to monitor analytical accuracy.

The internal standard used was ^{29}Si (determined by EPMA analysis). Three geochemically distinct reference glasses were used to cover the possible geochemical spectrum often observed within the tephra deposits and for consistency these were the same secondary standards used for EPMA analysis. LA-ICP-MS data reduction was performed in accordance with Tomlinson et al. (2010), using Microsoft excel. Accuracies of analyses of ATHO-G and StHs6/80-G MPI-DING glass are typically $\leq 5\%$. Relative standard errors (% RSE) for tephra samples are typically $<3\%$ for V, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pr, Nd, Th, U; and $< 6\%$ for Ti, Sm, Eu, Gd, Dy, Er, Yb, Lu, Ta. % RSE increases with smaller spot analyses. Full errors (standard deviations and standard errors for individual sample analyses) are given in the supplementary information. For consistency with EPMA error reporting, error bars on plots

show 2 standard deviations of replicate analyses of MPI-DING StHs6/80-G and ATHO-G glasses.

3.1.3 Secondary Ion Mass Spectrometry (SIMS)

SIMS was carried out on selected Tenaghi Philippon samples where shard size prohibited the use of the LA-ICP-MS technique, SIMS analysis followed the method described in Schiano et al. (2001, 2004). SIMS was performed at the Istituto di Geoscienze e Georisorse (IGG), Unità di Pavia, Italy. Samples were polished and Pt-coated prior to analyses. Analyses were conducted using a Cameca IMS 4f ion microprobe using a 0.5-0.7 nA current intensity with a spot diameter of 5-8 μm . In order to increase the sensitivity on very small samples (< 10 micron diameter), experimental methods were optimised by increasing the acquisition times of secondary ion signals. There was a waiting time of 450 s necessary to obtain steady-state sputtering conditions, and four acquisition cycles with the following counting times per cycle: Li (5s), Be (5s), Si (2s), K (2s), Sc (5s), Ti (4s), V (5s), Cr (5s), Rb (5s), Sr (5s), Y (5s), Zr (5s), Nb (5s), Cs (8s), Ba (8s), La (10s), Ce (10s), Nd (10s), Sm (15s), Dy (20s), Er and Yb (15s each), Th and U (20s each). For Eu and Gd a deconvolution procedure was used to remove BaO, CeO and NdO interferences from Eu and Gd isotopes, respectively. For the deconvolution procedure the counting times were: 10 s (mass 151), 5 s (mass 154), 20 (mass 160 and 162 each). $^{30}\text{Si}^+$ was selected as the isotope of the reference element (Si) for these matrixes. The trace-element concentrations were calculated using the SiO_2 (wt%) values obtained from EMP analyses performed in the same shards selected for the SIMS investigation. The precision of a single analysis from Poisson counting statistics for the various isotopes detected is on the order of few percent rel. and generally better than 10% rel. (as 1σ) at ppm-tens ppm wt concentration. Two international reference materials were used as primary standards including NIST-SRM 610 and BCR-2G, alongside these two well characterised internal standards (BB and WY1) were analysed during the sample runs. Reference data for the standards used is presented in the supplementary information. Considering all the errors involved in the present SIMS investigation, related both to the

reference concentrations assumed for the calibration standards and to the analytical precision of the SIMS data themselves, we can estimate accuracy to be comparable to precision in the range (1-3 σ).

3.2 Bayesian Age-Depth modelling of TP-2005

The age-depth model for Tenaghi Philippon was constructed using Bayesian deposition modelling (e.g. Blockley et al., 2008b) and was undertaken in Oxcal version 4.1 (Bronk Ramsey, 2001, 2009) using the internationally agreed IntCal09 calibration curve (Remier et al., 2009). The age model was developed using the '*P_Sequence*' function in OxCal with '*Boundary*' functions placed where changes in lithology were observed in the TP-2005 stratigraphy (Müller et al., 2011). The final age model was formed of 20 radiocarbon dates (Müller et al., 2011), and imported proximal ages for the Cape Riva tephra (Santorini) using newly modelled radiocarbon based proximal age estimate of 21,410-22,200 yrs BP (Lee et al., 2013) and a $^{40}\text{Ar}/^{39}\text{Ar}$ age for the Campanian Ignimbrite ($39,280 \pm 110$ yrs BP, De Vivo et al., 2001). Both form visible tephra layers within the TP-2005 sequence labelled (TP 7.61 and TP 12.87 respectively; Müller et al., 2011). In order to find an optimal '*K value*' (a poisson constraining parameter) the model was initially run using a low *K value* of 0.001 (as recommended by Bronk Ramsey, 2008 and Blockley et al., 2008) and slowly increased until the '*Agreement Index*' (A_{Overall} and A_{Model}) was no lower than 60% (Bronk Ramsey, 2008). No dates had to be removed from the model and the '*Date*' function was used to form realistic age estimates of undated horizons.

4. Results

Representative glass analyses are given in Table 2. Full glass data sets for individual tephra deposits are presented in the Supplementary material. Table 3 presents diagnostic element concentrations and ratios for the fingerprinting of tephras.

4.1 Distal tephra

4.1.1 Y-3 (M25/4-12) *Ionian Sea*

Y-3 glasses are clear and typically between 100-200 μm in size (major axis). Shards comprised of two main morphologies; (1) highly vesicular, tubular shards and; (2) less vesiculated, blocky/angular shards (Fig. 2 a-f). Phenocryst of sanidine, apatite and biotite were observed within this tephra layer. The SiO_2 concentrations in the Y-3 glasses range from 60.0 to 62.8 wt. % and they are classified as phono-trachytic to trachytic in composition (Fig. 3a). These glasses show variable FeOt (2.7-3.8 wt. %) and CaO (2-2.8 wt. %) and high K_2O (8.2-10.4 wt. %) relative to Na_2O (2.9-4.9 wt.%) (Fig. 3). Major and trace element glass compositions within the Y-3 tephra are heterogeneous, dominated by glass compositions forming two distinct end-members (Fig. 4), with a few glass analyses plotting between the two (Fig. 4, 5).

The higher SiO_2 (> 62 wt. %) trachytes show high levels of trace element enrichment ($\text{Zr/Sr} = 2.69 \pm 0.15$; 2 s.d). Glasses show high concentrations of V (31 ± 1 ppm) given their evolved composition and depletions in Sr and Ba (Sr = 131-146 ppm; Ba = 23-32 ppm) relative to the enrichment in large ion lithophile elements (LILE) and high field strength elements (HFSE). The trachytic glasses show Light Rare Earth Element (LREE) enrichment relative to Heavy Rare Earth Elements (HREE) ($\text{La/Yb} = 22.7 \pm 2.7$; 2s.d) and pronounced Eu depletions ($\text{Eu/Eu}^*_\text{N} = 0.5\text{-}0.9$).

The lower SiO_2 (< 62 wt. %), phono-trachyte, shards show lower levels of incompatible trace element enrichment ($\text{Zr/Sr} = 0.34 \pm 0.11$) and greater enrichment of LREE relative to the HREE ($\text{La/Yb} = 24.5 \pm 3.6$; 2 s.d.) compared to the trachytic end-member. These phono-trachytic glasses show more elevated concentrations of V, Sr, Ba and Eu ($\text{V} = 63 \pm 10$; Sr = 530-638ppm; Ba = 667-845ppm; $\text{Eu/Eu}^*_\text{N} = 1.06 \pm 0.18$; 2s.d.) than the higher silica glasses within the tephra (Fig. 5). Ba, Sr and Eu are compatible within feldspar (sanidine) and consequently concentrations in the glasses decrease with increasing fractionation as

demonstrated by increasing Th (Fig. 5). Incompatible trace element ratios differ between the two compositional end-members (Table 3).

4.1.2 TP 9.70 (Tenaghi Philippon, NE Greece)

Shards within this cryptotephra layer comprised of two main morphologies; (1) highly vesicular, tubular shards and; (2) less vesiculated, more blocky and angular shards. TP 9.70 is a compositionally heterogeneous tephra with 60.1 to 63.1 wt. % SiO_2 , variable FeOt (2.6 - 3.8 wt. %), CaO (2.0-2.9 wt. %), and with high K_2O ($\text{K}_2\text{O} = 8.1\text{-}10.0$ wt. %) relative to Na_2O (3.0-4.9 wt. %) (Fig. 3; 4). Incompatible trace element concentrations in the glasses are also heterogeneous with 12.1-34.3 ppm Th, 168-420 ppm Zr and 21.8-55.8 ppm Nb (Fig. 4, 5). Strontium (648-99 ppm), Ba (880-14 ppm) and V (77-29 ppm) behave compatibly, decreasing as Th increases during fractionation (Fig. 5a-b). Incompatible trace element ratios show subtle variability, whilst the LREE are enriched relative to the HREE (Table 3).

4.1.3 PRAD 1332 (central Adriatic)

The major element data for this cryptotephra is presented in Bourne et al. (2010) and is shown in Figure 3a and 4. This trachytic tephra is bimodal with two distinct populations best illustrated by SiO_2 and CaO concentrations (Fig. 4a-b). Trace element variation between these two major element components is limited (Fig. 4d-e), showing consistent incompatible trace element ratios and LREE enrichment relative to the HREE (Table 3). The major element bi-modality is best reflected at a trace element level by clear differences in Ba, Sr and V concentrations (Fig. 5a-c), with the lower SiO_2 glasses showing higher concentrations (Component 1) and the higher SiO_2 glasses showing lower concentrations (Component 2; Table 2; 3) of these particular trace elements.

4.2 Medial extra-caldera SMP1-e tephra

4.2.1 SMP1-e tephra (Santa Maria di Pozzano, Sorrentine Peninsula)

The highly vesicular pumices (Fig. 2j-l) within this ignimbrite deposit (sample ZS 98262) are very homogeneous with 62.1 ± 0.5 wt.% SiO_2 and 2.1 ± 0.2 wt.% CaO (Fig. 3; 4). Glasses show K_2O (8.5 ± 0.2 wt. %) enriched relative to Na_2O (4.7 ± 0.3 wt. %) and are classified as trachytes (Fig. 3a). Glasses show a homogenous trace element compositions (i.e., 29 ± 5 ppm Th, 54 ± 3 ppm Nb; Fig. 4; 5) and LREE enrichment relative to the HREE (Table 3). Incompatible trace element ratios to Th show some subtle variability (Table 3).

4.2.2 CE1 tephra (Cervino, NE Naples)

The lower fall (sample ZS 2506) glasses were typically more vesicular than the upper pumice fall (sample ZS 2507) (Fig. 2m-o). The lower fall glasses are homogeneous with 58.1 ± 0.4 wt.% SiO_2 and 3.8 ± 0.2 wt.% CaO (Fig 3, 4). Glasses show high K_2O (8.4 ± 0.2 wt. %) relative to Na_2O (3.8 ± 0.2 wt. %) and fall in the phonolite field close to the trachyte boundary (Fig. 3a). The upper fall (ZS 2507) glasses are also homogeneous, but range to slightly less evolved compositions with 57.7 ± 0.5 wt.% SiO_2 and 4.1 ± 0.1 wt.% CaO (Fig 3, 4). Glasses in the upper fall show K_2O (8.2 ± 0.3 wt. %) enriched relative to Na_2O (3.5 ± 0.2 wt. %) and straddle the phono-trachyte classification boundary (Fig. 3a). Both fall deposits show overlapping and largely homogenous trace element concentrations (Fig., 4, 5; Table 2). Both fall units also show consistent LREE enrichment relative to the HREE and consistent incompatible trace element ratios (Table 3). The two deposits can be most easily distinguished using Ba, Sr and V concentrations, the lower fall deposits with the higher SiO_2 glasses show more depleted concentrations in these elements (Fig. 5).

5. Discussion

Major element data presented here re-affirms the previous interpretation that the phono-trachyte to trachyte glass composition of the Y-3 tephra recorded in the Ionian Sea are derived from Campi Flegrei (Keller et al., 1978; Kraml, 1997). Shards show $\text{K}_2\text{O} \gg \text{Na}_2\text{O}$ which is consistent with glasses produced at Campi Flegrei and Somma-Vesuvius, rather than Ischia where higher Na_2O values dominate the glass compositions (Fig. 6a). Somma-

Vesuvius glasses show more elevated CaO at a given MgO content (Santacroce et al., 2008; Tomlinson unpublished data¹) and consequently are easily rejected (Fig. 6b).

Nb/Th ratio values in the more evolved trachyte glass end-member confirm that the Y-3 tephra is associated with the Pre- NYT/NYT series of erupted deposits sourcing from Campi Flegrei (Fig. 6c) (Tomlinson et al., 2012). Indeed, V concentrations in the Y-3 tephra are higher than those observed in the older Pre-CI/CI glass series (Table 3). Levels of incompatible trace element enrichment in the phono-trachyte glass component of the Y-3 are lower than any currently characterised pre-NYT/NYT series glasses (Fig. 6c).

Major and trace element glass data verify that the Y-3 tephra originates from Campi Flegrei and has a Pre-NYT/NYT chemical affinity. The stratigraphic position (above the Y-5/Campanian Ignimbrite) and chronological constraints (25.3 ± 3 ka; Table 1) of the Ionian Sea Y-3 tephra confirm that the precise proximal counterpart of this distal tephra must have been erupted between the caldera forming CI and NYT eruptions. Proximally the eruptive units identified between these two caldera forming eruptions are termed the Tufi Biancastri (Orsi et al., 1996), stratigraphic sequences are recorded at Verdolino and Ponti Rossi and are dominated by the deposits of numerous, and predominantly hydromagmatic, eruptions (Fig. 1b; Orsi et al., 1996). The proposed proximal equivalent of the Y-3 tephra, the VRa eruptive unit is identified at the base of the post-CI stratigraphy recorded in the Verdolino Valley (Di Vito et al., 2008; Zanchetta et al., 2008).

5.1 Proximal VRa - Distal Ionian Sea Y-3 (M25/4-12) tephra correlation

The Ionian Sea Y-3 tephra is chemically bi-modal and dominated by both a phono-trachytic and trachytic end-member compositions (Fig. 3a). The VRa eruptive unit is also compositionally bi-modal, with phono-trachyte and trachyte components (Fig. 3a, 4; Tomlinson et al., 2012). At both a major and trace element level it is apparent that the most fractionated trachytic end-member of the Ionian Sea Y-3 glasses are indistinguishable from

¹ Vesuvius glass data used to evaluate potential geochemical links and to generate this compositional field is available on the RESET database (<https://c14.arch.ox.ac.uk/login/login.php?Location=/resetdb/db.php>)

trachytic end-member of the VRa eruption (Fig. 3-5). However, equally the Y-3 trachytic glasses also overlap the stratigraphically younger VRb and PRa eruptions (Fig. 3-5). This illustrates a problem of repeated glass chemistries through time within the Tufi Biancastri tephras (Tomlinson et al., 2012), a feature also recognised with some of the Holocene tephras erupted at Campi Flegrei (i.e., Smith et al., 2011). Consequently, whilst the trachytic glass component of the Y-3 tephra verifies a Tufi Biancastri link, it is not diagnostic in terms of resolving the precise proximal equivalent of the Y-3 tephra.

The phono-trachytic component of the bi-modal VRa tephra and the Ionian Sea Y-3 differ significantly in their major element compositions (Fig. 3; 4a-c). Y-3 phono-trachytes show higher SiO_2 , K_2O , lower TiO_2 , FeO^t , CaO , MgO and Na_2O than the phono-trachytic component of the VRa. Trace element bi-plots confirm that such a correlation between the Ionian Sea Y-3 tephra and the proximal VRa is not possible (Fig. 5). Trace element variability between the two end-members of the VRa is more restricted than that of the Ionian Sea Y-3 (Fig. 4; 5), indeed inconsistent with the major element variability (Fig. 4a-c). Crucially, the lower silica phono-trachytic glasses observed in the VRa unit, show greater levels of incompatible trace element enrichment than the higher silica phono-trachytic component of the Y-3 tephra (Fig. 5c). Difficulties with this proximal-distal correlation are best illustrated by V, Ba and Sr concentrations plotted against Th (Fig. 5a-b), where the least evolved phono-trachytic glasses of the VRa show far more elevated V, Sr and Ba concentrations than the phono-trachytic component of the Y-3 tephra. Indeed the Ionian Sea Y-3 glasses lie upon a different evolutionary trend emphasised by intermediate compositions between these two end-members (Fig. 5a-b).

Trace element concentrations observed in the phono-trachytic glasses of the Ionian Sea Y-3 are not consistent with any glasses currently characterised from the proximal Pre-NYT/NYT series (Fig. 5c) (Tomlinson et al., 2012) or whole rock data (Pabst et al., 2008). Furthermore, the phono-trachytic glasses of the Y-3 tephra show incompatible trace element ratios more elevated than the proximal Pre-NYT glasses (Table 3). This component of the Ionian Sea Y-

3 show trace element concentrations and ratios arguably more akin to those seen in the older Campanian Ignimbrite upper flow deposits (Table 3) (Tomlinson et al., 2012). Consequently, the phono-trachytic glasses are the diagnostic component of the Ionian Sea Y-3 tephra. The Ionian Sea Y-3 tephra (M25/4-12) is not the distal product of the VRa eruption, and the proximal VRa age (30.3 ± 0.2 ka, Pappalardo et al., 1999) should not be exported distally. The absence of a precise proximal equivalent of the Ionian Sea Y-3 illustrates a need for further grain-specific geochemical characterisation of more proximal Tufi Biancastri eruptive units. However, the prospect of identifying the proximal equivalent of the Y-3 tephra at CF is restricted by the complexity of the proximal volcanic stratigraphy, where limited exposure is available, particularly when subsequent caldera collapse has destroyed and/or buried the older pyroclastic units (Di Vito et al., 2008).

5.2 Medial (SMP1-e tephra) - Distal Ionian Sea Y-3 (M25/4-12) tephra correlation

SMP1-e pumices recorded in the ignimbritic deposits, SE of Campi Flegrei caldera (Fig. 1b), only show a homogenous high-K trachytic glass component (Fig. 3a) consistent with the most evolved trachytic component of the Ionian Sea Y-3 glasses (Fig. 3; 4). Trace element concentrations reinforce the link between the two trachytic glass populations (Fig. 4d-e; 5a-c). However, as illustrated above (section 5.1) establishing a precise correlation between the medial SMP1-e ignimbritic deposits and the Ionian Sea Y-3 tephra currently remains inconclusive using glass chemistry alone given the absence of the diagnostic phono-trachytic glass component.

The phono-trachytic CE1 fall deposits, NE of Campi Flegrei caldera, have glass compositions that are geochemically distinguishable from both end-members of the Ionian Sea Y-3 tephra (Fig. 3-5). Furthermore, the CE1 glasses phono-trachytic tephras can also be distinguished from the proximal VRa eruptive unit at a trace element level (Fig. 5). Despite the stratigraphic and lithological similarities recognised by Di Vito et al. (2008), the SMP1-e ignimbrite and CE1 fall deposits show glasses compositions with differing

incompatible trace element ratios (i.e., Zr/Th; Fig. 5; Table 3), furthermore the absence of intermediate compositions between these compositionally distinct tephras (indicating mixing) might suggest they belong to separate eruptions (Fig. 5). This emphasises both the frequency of explosive activity occurring at Campi Flegrei and the difficulty of correlating tephra units with only limited exposure available.

Currently neither the intra- or extra-caldera deposits investigated here fully satisfy the compositional variability of the distal Ionian Sea Y-3 tephra. The K-trachyte end-member is characteristic of most post-CI/pre-NYT Campi Flegrei eruptions and thus alone this component is not diagnostic. Fortunately, the trace element compositional range of the Y-3 tephra and in particular the phono-trachytic component is unique and diagnostic of this distal tephra. Consequently, it is important to use the complete diagnostic geochemical signature of the Ionian Sea Y-3 tephra when attempting to precisely correlate other distal tephras to this marker layer.

5.3 Distal – Distal Ionian Sea Y-3 (M25/4-12) tephra correlations

Figure 1a shows the location of the archives which record a high-K phono-trachyte tephra stratigraphically close to the MIS 2/3 transition, which has been in turn attributed to the ‘Y-3’ tephra (Munno and Petrosino, 2004, 2007; Wulf et al., 2004; Zanchetta et al., 2008; Wagner et al., 2008; Bourne et al., 2010; Vogel et al., 2010).

Given that major and trace element geochemical variability, and in particular the presence of both a phono-trachytic to trachytic component is diagnostic of the Ionian Sea Y-3 tephra, published average major element compositions (Paterne et al., 1988; Munno and Petrosino, 2004, 2007) are not adequate to fully assess the validity of correlations to the Ionian Sea Y-3 tephra. Whilst we do not refute existing ‘Y-3’ correlations, we recommend that the detailed characterisation of the type locality Y-3 here provides a necessary opportunity to verify distal-distal correlations. Below we evaluate tephra new and published correlations to the Y-3 tephra where grain-specific glass data is available.

5.3.1 TP 9.70 tephra (Tenaghi Philippon, NE Greece)

At Tenaghi Philippon, Greece, cryptotephra layer TP 9.70 can be correlated to the Ionian Sea Y-3 owing to the same major element and trace element compositional variability (Fig. 3-5). Again this is best illustrated by V, Ba and Sr concentrations relative to Th, where the TP 9.70 glasses lie on the evolutionary trend diagnostic of the Ionian Sea Y-3 tephra (Fig. 5a-b). Indeed, TP 9.70 glass compositions extend between both end-members of the type locality Y-3 tephra (Fig. 5). Interestingly, intermediate glass compositions are better represented at Tenaghi Philippon than in the Ionian Sea Y-3 tephra, and their presence demonstrates more clearly the mixing between the two compositional end-members. Whilst the complete evolutionary range of TP 9.70 glass compositions does preclude statistical treatment in this instance (Fig. 3-5), it does further reinforce problems with a proximal VRa correlation (Fig. 5). Correlation of TP 9.70 to the Ionian Sea Y-3 tephra extends the eastern dispersal of this eruption to over 800 km from CF (Fig. 7).

5.3.2 TM-15 tephra (Lago Grande di Monticchio, Italy)

Owing to the regional tephrostratigraphic and palaeoenvironmental importance of the Lago Grande di Monticchio (LGdM) lacustrine archive, it is important to validate the link between TM-15 and the Ionian Sea Y-3 in this archive (Wulf et al., 2004, 2012). The 28 cm thick tephra TM-15 only shows a trachytic component (Tomlinson et al., 2012; Fig. 3), which is equally consistent with the trachytic glass compositions of the Ionian Sea Y-3, medial SMP1-e and the proximal VRa/VRb tephtras (Fig. 3). However, due to TM-15 trace element analyses (Tomlinson et al., 2012), despite the absence of the diagnostic phono-trachytic end-member a robust correlation to the Ionian Sea Y-3 is not precluded. TM-15 glasses showing the least incompatible trace element enrichment correspond to the Y-3 glasses that lie compositionally between the two end-members (Fig. 5a-c). TM-15 glasses show Ba, Sr and V concentration that lie on the evolutionary trend of the Ionian Sea Y-3 rather than extending towards the higher concentrations of the less evolved VRa glasses (Fig. 5a-c).

Consequently, there is considerable geochemical overlap between LGdM TM-15 and the TP 9.70 cryptotephra at TP, Greece. Indeed trace element geochemical data suggests that sites located on an easterly dispersal (Fig. 7) show a greater bias towards glass shards showing intermediate and evolved compositions produced during this eruption (Fig. 3-5).

5.3.3 PRAD 1332 and MD 920-17 tephtras (Adriatic Sea)

The stratigraphic position of the cryptotephra PRAD 1332 cm recorded in core PRAD 1-2 close to the MIS 2/3 transition coupled with its high-K phono-trachyte glass chemistry (Fig. 3a) led Bourne et al. (2010) to correlate this distal tephra to TM-15 and by association the Y-3 tephra. With the VRa unit then the proposed proximal equivalent of TM-15/Y-3 the $^{40}\text{Ar}/^{39}\text{Ar}$ VRa age was imported to PRAD1-2 at a depth of 1332 cm (Bourne et al., 2010). The north-easterly dispersed tephra, PRAD 1332 cm, shows major and trace element compositions that are inconsistent with the Ionian Sea Y-3 tephra presented herein (Fig. 3-5). Instead the geochemically bimodal PRAD 1332 tephra shows a less evolved component (component 1; ca. 58-59 wt. % SiO_2), that has a close major and trace element affinity to the least evolved VRa proximal deposits (Fig. 3-5). The more evolved, component 2 (ca. 60-61 wt. % SiO_2), currently presents a proximally and distally unrecognised composition (Fig. 3-5). Consequently, combined major and trace element geochemical glass data do not preclude a correlation between PRAD 1332 and the VRa eruption, but confirm that PRAD 1332 is not a distal correlative of the Ionian Sea Y-3 tephra (Fig. 3-5). The implications for this erroneous correlation are twofold; (1) the stratigraphic position of PRAD 1332 close to the MIS 2/3 transition demonstrates a high frequency of explosive activity occurring at CF coinciding with this important environmental transition; and (2) this limits the known northern-easterly dispersal of the Y-3 tephra with the central Mediterranean (Fig. 7). Further south in the southern Adriatic a phono-trachytic to trachytic tephra recorded in MD 920-17 (Zanchetta et al., 2008; Fig. 7) shows major element variability broadly consistent with the Ionian Sea Y-3 tephra (Fig. 4) and despite some subtle geochemical offsets (most noticeably lower Na_2O),

probably reflecting different analytical operating parameters (Fig. 3a), this tephra is considered a correlative of the Ionian Sea Y-3 tephra.

5.3.4 Y-3 tephra from the Balkans

In the following, previously proposed 'Y-3' tephra correlatives from Lake Ohrid (Tephra OT0702-4; Vogel et al. 2010) and Lake Prespa (Tephra PT0915-5; Damaschke et al., 2013) are compared to the type locality Y-3 glasses presented herein. Both the Lake Ohrid and Prespa tephras show major element compositional variation to the Ionian Sea Y-3 tephra (Fig. 4), ranging from phono-trachyte to trachyte in composition (Fig. 3a). Furthermore, the Lake Ohrid tephra Oh-986, also considered a correlative of the 'Y-3' tephra from separately sampled Lake Ohrid core was subject to bulk trace element glass analysis (Zanchetta et al., 2008). Incompatible trace element compositions fall between the two end-members of the Ionian Sea Y-3 tephra (Fig. 4c), consistent with an average composition acquired using bulk analytical techniques. However, the Ba concentrations in the 986-Oh tephra do not fall on the diagnostic evolutionary trend observed within the Ionian Sea Y-3 glasses (Fig. 4a), however, this elevated Ba is likely to reflect the incorporation of Ba-rich microcryst phases present in the glass shards, a problem associated with the bulk analysis of glass shards. Overall, the major and minor element variability in the Lake Ohrid and Prespa tephras listed above appear to verify their previous correlations to the Ionian Sea Y-3 tephra (Zanchetta et al., 2008; Wagner et al., 2008; Vogel et al., 2010; Damaschke et al., 2013). Further grain-specific trace element characterisation of these distal tephras would help to verify these distal-distal tephra correlations.

5.4 Age and climatostratigraphic context of the Y-3 tephra

A Bayesian modelled age of 29,350-30,160 cal yrs BP has been obtained for the confirmed Y-3 tephra at Tenaghi Philippon (Fig 8; = TP 9.70). This is based upon multiple radiocarbon ages from both above and below the tephra. Dated material includes mollusc shells, wood and bulk peat sediment, with the latter material providing numerous ages above and below

TP 9.70 (Müller et al., 2011). The 'Date' function within OxCal was used to generate a robust age for the precise depth of the peak in shard concentrations (9.70 m), considered as representative of the timing of deposition and the eruption (Fig. 8). Confidence in the robustness of the Tenaghi Philippon radiocarbon-based Bayesian age-model can be indirectly assessed via the accuracy of the modelled ages for the previously correlated visible tephra layers within the TP-2005 sequence, this was done by removing the visible tephra ages from the model and comparing the modelled age for the tephra depth with the known published age of the tephra. TP 7.60 is correlated to the Cape Riva and TP 12.87 to the Campanian Ignimbrite (Müller et al., 2011). The age-depth model, with only the radiocarbon information included, produced modelled ages of 20,510-22,270 and 38,360-40,510 cal yrs BP respectively for these eruptions. This is in very good agreement with available proximal ages for the Cape Riva (22,200-21,411 cal yrs BP, Lee et al., 2013) and the CI eruption ($^{40}\text{Ar}/^{39}\text{Ar}$ 39,280 $\pm$ 110 yrs BP, De Vivo et al., 2001). Consequently, this demonstrates the integrity of the Tenaghi Philippon radiocarbon ages both above and below the Y-3 tephra.

Whilst geochemical evidence confirms that the Y-3 tephra originates from the Campi Flegrei caldera, it is not the distal equivalent of the VRa eruptive unit (Section 5.1). Chronologically however, the Tenaghi Philippon Y-3 tephra age does overlap, at a 95.4 % confidence limit, with the proximal $^{40}\text{Ar}/^{39}\text{Ar}$ age of the VRa eruption (30.3 $\pm$ 0.2 ka, Pappalardo et al., 1999). Consequently, through integrating geochemical and chronological information it is apparent that the distal Ionian Sea Y-3 tephra represents one of two closely spaced (temporally), yet compositionally distinguishable, eruptions to occur at the Campi Flegrei volcano. A means of validating the absolute ordering of these eruptions will rely upon the identification of these two tephra layers within the same stratigraphic sequence. Given the complexity associated with intra-caldera deposits caused by resurgent activity at Campi Flegrei, it is probable that the stratigraphic superposition of these separate eruptive events will be established in the distal realm.

The medial-distal ignimbritic SPM1-e tephra deposits has an age of 30,310-31,110 cal yrs BP ($25,820 \pm 270$ ^{14}C yrs BP, Di Vito et al., 2008) derived from charcoal in the directly underlying palaeosol. This age pre-dates the Tenaghi Philippon age of the Y-3 tephra and is in better agreement with the absolute age of the VRa eruption. However, this SMP1-e tephra age can only be considered a maximum and therefore as with its glass chemistry (Section 5.2), the age of SMP1-e tephra does not preclude a correlation with the Y-3 tephra as previously suggested (Zanchetta et al., 2008).

There is a significant difference between the varve age of TM-15 at LGdM and the Y-3 ^{14}C modelled age at Tenaghi Philippon, suggesting that the TM-15/Y-3 varve age (25,900-28,620 varve yrs BP) is an underestimate (Fig. 9). This re-affirms the observed offset to younger calendar ages relative to calibrated radiometric ages of the same tephras in this section of the LGdM record (Wulf et al., 2012), further confirming the view that the LGdM chronology is likely to underestimate the true ages of events in this time interval (Brauer et al., 2000). Adopting the TP Y-3 age over existing age determinations for Y-3 (Table 1) does however, reduce the offset from the TM-15 calendar age reported in Wulf et al. (2012). A radiocarbon age of 29,550-30,480 cal yrs BP (Vogel et al., 2010) from lacustrine organic matter directly above the OT0702-4 (= Y-3) tephra in Lake Ohrid, is consistent with the age presented from TP which alongside geochemical data further reinforces this tephra layers existing correlation to the Ionian Sea Y-3 tephra.

Assessing the validity of distal marine ages for proposed Y-3 correlatives recorded in the southern Tyrrhenian Sea (Table 1) is difficult for the following reasons; (1) without grain-specific glass data it is difficult to determine whether these dates reflect that of the Y-3 tephra or another Campi Flegrei eruption (i.e., the VRa/VRb); (2) ^{14}C marine ages are complicated by marine reservoir uncertainties; and (3) ^{14}C ages were determined from foraminifera's underlying the tephra layers and thus probably represent a maximum ages (3-4cm).

Given that the modelled age for the TP 9.70 tephra represents the timing of deposition at Tenaghi Philippon this presents the most precise age currently available for the eruption of the distal Y-3 tephra. Subsequently, using the diagnostic geochemistry of the Y-3 tephra outlined herein, this age can be imported between distal archives as a reliable chronostratigraphic marker. Indeed we can confidently import the TP age (29,350-30,160 cal yrs BP) back to the Ionian Sea core M25/4-12 at the depth of the Y-3 (119.5 cm below sea floor) to provide a more precise chronological constraint in this record.

The identification of the Y-3 tephra in the high resolution palaeoenvironmental archive of Tenaghi Philippon also offers important insights into the environmental conditions at the time of the Y-3 eruption. The Y-3 tephra at Tenaghi Philippon sits within the latter part of a period marked by a major reduction in tree pollen percentages (Fig. 9; 10) related to stadial conditions (Müller et al., 2011). Within this overall period of reduced tree pollen percentages stratigraphically just below the Y-3 tephra there is small increase in total tree pollen percentages which may reflect a brief climatic amelioration (Fig. 9). Comparisons between the Tenaghi Philippon and LGdM (Allen et al., 1999) palynological records using the Y-3 tephra (Fig. 9) reveal that the tephra occurs above the pollen zones both correlated to the same Greenland Interstadial 5 (GI-5) in the respective archives (Fletcher et al., 2011; Müller et al. 2011). Combined evidence from these two sites suggest that the Y-3 tephra post-dates the onset of HS3 (*sensu* Sanchez Goni and Harrison, 2010). The Tenaghi Philippon pollen record, on an independent time scale, suggests that the Y-3 eruption occurred during or after HE3 (Fig. 10), although given the inherent difficulties comparing marine and terrestrial radiocarbon datasets detection of the Y-3 within a high-resolution marine proxy record might be required to resolve this question. The independent dating evidence put forward for the Y-3 tephra herein strongly suggests that this eruption occurred sometime after the onset of Greenland Stadial 5 in the INTIMATE event stratigraphy (Blockley et al., 2012) and before the MIS 3/2 transition as defined by Svensson et al. (2006, 2008) (Fig. 10).

6. Conclusions

The Ionian Sea Y-3 tephra (M25/4-12) has a phono-trachytic to trachytic chemistry, glass compositions confirm a source from the Campi Flegrei caldera. Combined major and trace element glass chemistry shows that the Y-3 tephra is not the distal equivalent of the proximal Tufi Biancastri VRa eruptive unit (30.3 ± 0.2 ka BP). None of the medial-distal tephras investigated from extra-caldera localities fully satisfy the compositional range of the Ionian Sea Y-3 tephra. Ultimately the precise proximal equivalent of this eruption remains unknown. The diagnostic glass chemistry for the Ionian Sea Y-3 tephra is identified and enables us to establish precise distal-distal tephra correlations. Geochemical links between the Y-3 tephra in the Ionian Sea and the record from Tenaghi Philippon, NE Greece, extend the eastern dispersal of this tephra. Furthermore, a Bayesian-based ^{14}C age modelling for the Tenaghi Philippon site enables us to provide a robust age of 29,350-30,160 cal yrs BP for this distal marker tephra. Previous work has shown that at Tenaghi Philippon the Y-3 marker tephra occurs in the later stages of a period linked to stadial conditions (Müller et al., 2011). Dating of the Y-3 would suggest that it was erupted after the onset of Greenland Stadial 5 and post-dates the beginning of Heinrich Stadial 3. Regardless of proximal uncertainty, through detailed geochemical characterisation and independent dating this tephra offers both a crucial tephrostratigraphic and chronostratigraphic marker associated with an important climatic event.

Acknowledgments

PGA was funded by the Reid Scholarship, Royal Holloway University of London and with support from the Central Research council, University of London. PGA, MH and ELT were also supported by the NERC RESET consortium (project number NE/E015905/1). JP acknowledges support through the German Research Foundation (DFG) and the Biodiversity and Climate Centre Frankfurt (BiK-F). This paper forms the RHOXTOR contribution 032. We would like to thank Neil Holloway (Royal Holloway, University of London) for preparing samples in epoxy resin stubs ready for geochemical analysis.

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Figure Captions

Figure 1: (a) A map of the central and eastern Mediterranean showing the location of the M25/4-12 core from which the Y-3 tephra was investigated. The localities of other archives where proposed 'Y-3' tephra correlatives have been reported (See Table 1). Also shown are the main volcanic centres active during the Last Glacial (CF, Campi Flegrei; SV, Somma-Vesuvius; IS, Ischia, Ae, Aeolian Islands; Et, Mount Etna; Pa, Pantelleria). (b) The Neapolitan volcanic region showing the Campi Flegrei, Somma-Vesuvius and Ischia (Adapted from Tomlinson et al., 2012). The localities of extra-caldera (SMP1-e and CE1) samples investigated herein are marked.

Figure 2: SEM and light microscope images of the distal and proximal tephras. Y-3 tephra recovered from M25/4-12 in the Ionian Sea (a-f); (a) shard 40D, a 20µm ablation pit is observed left of a vesicle; (b) shard 29C, with two laser ablation pits (34 and 20 µm diameter); (c) shard 50E showing a 34 µm ablation pit; (d) shard 32D, a thin microlite is observed running through the glass shard, which demonstrates the benefit of preliminary SEM investigations prior to LA-ICP-MS analysis; (e) shard 51E; (f) shard 42D showing two ablation pits (34 and 20 µm); (g-h) the lower VRa, highly vesiculated white pumices (i) the upper VRa, less vesiculated, darker pumice; (j-l) SMP1-e (ZS98 262), highly vesicular and stretched pumices; (m) Lower CE1 (ZS

2506) pumice, vesicular and stretched glasses; (n-m) Upper CE1 (ZS 2507) pumices are less vesiculated than the stratigraphically lower CE1 pumices.

Figure 3: Major element bi-plots showing the Ionian Sea Y-3 tephra (M25/4-12) compared to the glass compositions of proximal intra-caldera Tufi Biancastri (Tomlinson et al., 2012) and extra-caldera deposits (SMP1-e, CE1; this Study) from Campi Flegrei. Glass data from cryptotephra TP 9.70 layer in Tenaghi Philippon, NE Greece (This study). Published distal compositions are also presented to assess distal-distal tephra correlations: (1) Tomlinson et al., (2012); (2) Bourne et al., (2010)*; (3) Vogel et al., (2010); Munno and Petrosino (2004); (5) Paterne et al. (1988) and (6) Zanchetta et al. (2008). Error bars represent 2 standard deviations of repeat analyses of the StHs60-G MPI-DING reference glass. (a) TAS classification after Le Bas et al. (1986). PRAD 1332* data was re-normalised assuming 0.5 wt.% of Cl (Cl not measured by Bourne et al., 2010) for comparative purposes, 0.5 wt.% being a typical value for phono-trachytic CF glasses.

Figure 4: Major and trace element compositional variation of glasses from the Y-3 tephra recorded in the Ionian Sea compared to potential proximal, medial and distal tephra correlatives. The Ionian Sea Y-3 glasses are dominated by two compositional end-members, whilst the Tenaghi Philippon tephra, NE Greece spans the full compositional range. Refer to Figure 3 figure caption for published data references.

Figure 5: Trace element bi-plots showing the glass compositions of the Ionian Sea Y-3 tephra (M25/4-12) compared to the glass compositions of proximal intra-caldera Tufi Biancastri and extra-caldera deposits (SMP1-e, CE1; this study) from Campi Flegrei. Distal tephras TP 9.70 from Tenaghi Philippon, NE Greece and PRAD 1332, Central Adriatic are also presented (this study) along with published distal data from LGdM

TM-15 and Oh-876 (Zanchetta et al., 2008). Error bars represent 2 standard deviations of repeat analyses of both the StHs60-8G and ATHO-1 reference glasses.

Figure 6: Major and trace element bi-plots showing the compositions of the Ionian Sea Y-3 tephra (M25/4-12) compared to proximal glasses of Campi Flegrei (Tomlinson et al., 2012), Somma-Vesuvius (Tomlinson et al. unpublished¹) and Ischia glasses (Tomlinson et al., in prep). (a-b) Y-3 glasses compared to the overall compositional fields of the Neapolitan volcanic centres (c) Y-3 glass compositions plotted against the pre- and post-Campanian Ignimbrite series (Tomlinson et al., 2012). Error bars represent 2 standard deviations of repeat analyses of the StHs60-G reference glass.

¹ Vesuvius glass data used to evaluate potential geochemical links and to generate this compositional field is available on the RESET database (<https://c14.arch.ox.ac.uk/login/login.php?Location=/resetdb/db.php>)

Figure 7: The revised dispersal and distribution of the Y-3 tephra both across the central and eastern Mediterranean regions.

Figure 8: Posterior probability density function generated for TP 9.70, the Tenaghi Philippon cryptotephra layer. The brackets at the base of the distribution represent the 95.4% and 99.7% probability ranges.

Figure 9: Comparison of the Tenaghi Philippon (TP-2005) and Lago Grande di Monticchio total tree pollen percentages. The age model for Tenaghi Philippon is described in section 3.2, and the Lago Grande di Monticchio chronology follows Brauer et al. (2007). The position of the Y-3 tephra in both records is also shown. Greenland Interstadial labelling follows those outlined in Fletcher et al. (2010) and Müller et al. (2011).

Figure 10: Climatostratigraphic context of the Y-3 tephra at Tenaghi Philippon, NE Greece.

Shown from left to right: (a) Marine Isotope Stage (Svensson et al., 2006; 2008); (b) The INTIMATE event stratigraphy (Lowe et al., 2008; Blockley et al., 2012). (c) The NGRIP oxygen isotope record based upon the GGIC05 timescale from Andersen et al. (2006) and Svensson et al. (2006). (d) Calibrated age ranges for Heinrich Event 3 from western European records (Bard et al., 2000; de Abreu et al., 2003) (thin line) and calculated ages (Thouveny et al., 2000) (black box). (e) Tenaghi Philippon (TP-2005) total tree pollen percentage curve and the stratigraphic position of the Y-3 cryptotephra. (f) The age–depth model (at 95.4 % probability range) and radiocarbon ages on which it is based are also shown (green) alongside the original Müller et al. (2011) chronology (grey green line). Note all data have been adjusted to a yrs BP (1950) timescale.

Table Captions

Table 1: Reported occurrences of the Y-3 tephra and proposed correlatives from across the Central Mediterranean region. Dispersal is given relative to Campi Flegrei caldera. Presented are ages associated with these tephras. Terrestrial and marine radiocarbon ages ~~are~~ have been calibrated using atmospheric and marine data sets respectively incorporated within IntCal09.

Table 2: Representative grain-specific major, minor (EMPA) and trace element (LA-ICP-MS) glass data from the Ionian Sea Y-3 tephra (M25/4-12). Also given is grain-specific glass data for the extra-caldera deposits (SMP1-e and CE1) and other distal tephras considered as potential correlatives of the Y-3 tephra including TP 9.70 (Tenaghi Philippon, NE Greece) and PRAD 1332 (PRAD 1-2, Central Adriatic). (LA, LA-ICP-MS analyses). A full grain-specific glass data set is presented in the supplementary information.

Table 3: Diagnostic concentrations and ratio for geochemical fingerprinting of the Y-3 tephra, errors are 2 standard deviations. TAS classification is based on (Na₂O + K₂O) versus SiO₂ using Le Bas et al. (1986). * is a bulk glass separate analysis of 896-Oh Lake Ohrid (Zanchetta et al., 2008), not a grain-specific trace element analysis.

Tephra/Archive	Depth (cm)	Thickness	Dispersal	Independent dating method	¹⁴ C (uncal)	Age cal.yrs BP	Reference
<i>Ionian Sea (type locality)</i>							
Y-3 , Ionian Sea (RC191)	245-244	1	SE	-			Keller et al. (1978)
Y-3 (M25/4-13* , M25/4-12)	117-118	1	SE	¹⁴ C interpolation age		22300-28300	Kraml (1997)
<i>Distal 'Y-3' correlatives</i>							
<i>Marine</i>							
<i>Tyrrhenian Sea</i>							
A2 , Salerno Gulf core C-106	565-579	14	SE	AMS ¹⁴ C on foraminifera's 4 cm below the tephra	26030 ± 150	30190-30910 ^(b)	Munno and Petrosino (2004)
B2 , Salerno Gulf core C-45	380-383	3	SE	AMS ¹⁴ C on foraminifera's 3 cm below the tephra	25570 ± 110	29580-30320 ^(b)	Munno and Petrosino (2004)
C-7 , KET8004	264-274	10	S	-			Paterne et al. (1988); Zanchetta et al, (2008)
C-7 , KET8011	205	1	S	-			Paterne et al. (1988); Zanchetta et al. (2008)
<i>Adriatic Sea</i>							
920 , MD90-917	920	-	E	-			Zanchetta et al. (2008)
PRAD 1332 , PRAD1-2	1332	>1	NE	-			Bourne et al. (2010)
<i>Terrestrial (Italy/Balkans)</i>							
TM-15 , LGdM	1471.9	28.6	E	Varve Chronology		27260 ± 1360	Wulf et al. (2004, 2012)
S19 , SGM	665-700	35	SE	-			Munno and Petrosino (2007)
OT0702-4 , Lake Ohrid	617-620	3	E	AMS bulk ¹⁴ C on sediment directly above the tephra layer	25260 ± 210	29540-30500 ^(a)	Vogel et al. (2010)
PT0915-05 , Lake Prespa	616.8-617.8	1	E	-			Damaschke et al. (2013)
<i>Medial 'Y-3' correlative</i>							
SMP1-e Sorrentina Peninsula	-	40-50	SE	AMS ¹⁴ C on charcoal directly beneath the tephra	25820 ± 270	30310-31110 ^(a)	Di Vito et al. (2008)

Table 1

Sample	Y-3 Ionian Sea (117-118.5cm)				Extra-caldera, Tufi Biancastri					
Core/Locality	(M25/4-12)				SMP1-e (ZS 98 286)	CE1 Lower (ZS 2506)		CE1 Upper (ZS 2507)		
I.D	31C	29C	18B	28C	9	2	23	8	1	13
<i>Major, minor</i>										
SiO ₂	60.53	60.92	62.23	62.75	62.51	62.03	57.93	58.35	58.23	57.44
TiO ₂	0.40	0.36	0.34	0.34	0.36	0.41	0.53	0.51	0.54	0.59
Al ₂ O ₃	18.35	18.43	17.82	17.81	17.79	17.90	19.16	18.60	18.78	18.66
FeOt	3.77	3.27	2.77	2.82	2.79	3.01	4.53	4.65	4.37	4.88
MnO	0.11	0.12	0.10	0.08	0.12	0.14	0.15	0.11	0.15	0.21
MgO	0.83	0.74	0.35	0.45	0.43	0.40	1.16	1.06	1.26	1.36
CaO	2.63	2.60	2.28	2.10	2.03	2.22	3.70	3.67	3.98	4.27
Na ₂ O	2.98	3.27	4.50	4.33	4.57	4.76	3.67	3.72	3.43	3.58
K ₂ O	9.96	9.76	8.75	8.51	8.61	8.32	8.38	8.47	8.42	8.22
P ₂ O ₅	0.14	0.14	0.05	0.09	0.10	0.09	0.28	0.34	0.30	0.30
Cl	0.30	0.38	0.81	0.71	0.71	0.72	0.52	0.52	0.55	0.50
Analytical Total	95.26	97.79	98.59	94.91	95.87	94.06	93.93	95.11	99.02	98.32
<i>Trace</i>										
<i>Spot size</i>	34 µm	34 µm	34 µm	20 µm	34 µm	34 µm	34 µm	34 µm	34 µm	34 µm
<i>Method</i>	LA	LA	LA	LA	LA	LA	LA	LA	LA	LA
V	68.9	56.3	29.8	31.1	31.7	30.4	106.0	110.9	121.3	127.3
Rb	268	276	344	355	356	324	326	309	317	314
Sr	597	508	138	134	128	123	697	701	799	795
Y	19.2	22.0	31.5	29.8	29.7	29.9	25.8	26.4	26.4	25.0
Zr	172	223	370	370	358	354	277	273	281	264
Nb	30	38	53	55	56	53	45	44	43	41
Ba	801	636	24	32	26	26	1176	1194	1354	1376
La	43	48	71	67	65	66	69	66	65	63
Ce	79	96	134	131	129	128	130	129	132	126
Pr	8.4	10.0	13.9	13.3	13.2	12.7	13.6	13.4	13.6	12.9
Nd	31.1	37.2	49.3	48.8	47.7	48.6	51.9	48.4	50.2	47.8
Sm	6.1	6.3	8.3	10.1	8.3	9.2	9.2	9.3	9.5	9.1
Eu	1.9	1.8	1.6	1.5	1.6	1.6	2.2	2.1	2.2	2.1
Gd	4.5	5.0	6.0	8.1	6.3	6.5	6.7	6.5	6.6	6.7
Dy	3.6	4.9	5.6	5.7	5.0	5.3	5.3	5.2	5.1	4.9
Er	1.8	2.3	3.1	3.1	2.9	3.1	2.7	2.7	2.6	2.4
Yb	1.7	2.3	3.3	2.9	2.9	3.0	2.5	2.7	2.3	2.3
Lu	0.27	0.28	0.45	0.49	0.39	0.39	0.43	0.40	0.38	0.36
Ta	1.5	1.9	2.7	2.8	2.7	2.4	2.4	2.2	2.1	2.1
Th	13.2	16.7	30.7	29.9	28.7	28.6	27.3	26.3	25.9	24.7
U	4.4	5.8	9.9	10.1	9.6	8.8	9.1	8.6	7.9	7.9

Table 2

TP 9.70 Tenaghi Philippon, Greece				PRAD 1332 Central Adriatic			
TP-2005				PRAD 1-2			
384_22	384_21	334_5	332_14	0068_107	0068_8	0068_6	0068_113
				Component 1		Component 2	
				See Bourne et al. (2010)			
60.54	61.59	62.73	62.83				
0.35	0.31	0.36	0.38				
18.71	18.29	18.16	18.36				
3.63	3.19	2.78	2.94				
0.10	0.09	0.09	0.12				
0.81	0.55	0.49	0.42				
2.71	2.30	2.33	2.14				
2.66	3.67	3.87	4.16				
9.96	9.31	9.08	8.59				
0.18	0.13	0.10	0.06				
0.34	0.55	–	–				
98.47	97.58	97.15	94.99				
5 µm	5 µm	34 µm	5 µm	25 µm	25 µm	25 µm	25 µm
SIMS	SIMS	LA	SIMS	LA	LA	LA	LA
77.0	40.1	41.9	38.2	128.4	136.1	90.1	75.7
216	272	347	334	330	310	321	337
599	415	341	168	742	723	639	609
17.5	23.6	27.9	27.1	24.6	24.1	23.8	24.1
168	250	307	348	257	237	256	267
22	38	48	51	40	37	40	41
880	315	182	47	1296	1257	1064	1051
41	45	63	56	50	48	50	51
78	89	116	122	97	94	99	97
-	-	12.8	-	11.0	9.9	10.2	10.4
25.9	31.5	43.9	48.8	40.3	39.5	39.4	38.5
4.3	4.7	8.3	8.4	7.8	7.9	6.8	6.4
1.3	1.4	1.9	1.7	2.0	1.9	1.9	1.7
3.7	3.8	7.2	6.5	5.5	5.9	5.7	5.5
3.5	3.8	5.3	5.3	4.9	4.6	4.7	4.3
2.0	2.2	2.7	2.9	2.4	2.5	2.4	2.3
1.8	1.7	2.8	2.7	2.3	2.5	2.4	2.2
-	-	0.32	-	0.34	0.38	0.34	0.32
-	-	2.2	-	1.8	1.9	2.0	2.0
12.1	22.3	25.7	30.5	21.2	20.1	23.6	23.1
3.5	6.3	8.9	8.9	7.3	7.2	8.0	8.0

Table 2 Continued

Sample Locality TAS classification	M25/4-12 117.5-118.5cm – Y-3 Ionian Sea (This Study)		VRb Verdoline Valley Trachyte	VRa Verdoline Valley Phonolite-trachyte Trachyte		C.I. (Fall) Voscone & Aquafidia Phonolite to Trachyte	C.I. (Main flows) Mondragone Phonolite to Trachyte	C.I. Upper Flow Mondragone Trachyte
	(This Study)			Tomlinson et al. (2012)				
FeO/CaO	1.3 ± 0.1	1.3 ± 0.1	1.2 ± 1	1.3 ± 0.1	1.3 ± 1	1.6 ± 0.2	1.8 ± 0.1	1.3-2.2
Cl (wt. %)	0.36 ± 0.06	0.72 ± 0.11	0.45 ± 0.06	0.42 ± 0.05	0.49 ± 0.11	0.63 ± 0.06	0.85 ± 0.07	0.24-0.62
V (ppm)	63 ± 10	31 ± 1	51 ± 8	121 ± 14	38 ± 5	16 ± 4	14 ± 2	15-64
Nb/Th	2.1 ± 0.2	1.8 ± 0.1	1.9 ± 0.3	1.9 ± 0.1	1.9 ± 0.1	2.4 ± 0.1	2.4 ± 0.2	2.1-2.5
Zr/Th	13.1 ± 0.6	11.9 ± 0.5	11.2 ± 1.1	12.0 ± 0.4	12.2 ± 0.3	13.4 ± 0.6	12.7 ± 0.6	11.8-13.4
Ta/Th	0.10 ± 0.02	0.09 ± 0.01	0.09 ± 0.01	0.09 ± 0.003	0.09 ± 0.01	0.11 ± 0.004	0.11 ± 0.01	0.16-0.19
Nb/Zr	0.16 ± 0.02	0.15 ± 0.01	0.17 ± 0.01	0.16 ± 0.004	0.15 ± 0.01	0.18 ± 0.01	0.19 ± 0.01	0.10-1.13
Y/Th	1.41 ± 0.12	1.00 ± 0.03	1.01 ± 0.1	1.15 ± 0.04	1.06 ± 0.1	1.04 ± 0.1	1.06 ± 0.06	1.0-1.5
La/Yb	24.5 ± 3.6	22.7 ± 2.7	25.5 ± 1.4	22 ± 1.7	23.1 ± 1.5	22.8 ± 1.7	23.2 ± 2.1	23.6 ± 2.1
Sample Locality TAS classification	SMP1-e SMP1-e CE1 Trachyte Phono-Trachyte		TM-15 LGdM Trachyte	PRAD 1332 PRAD1-2 Trachyte (1) Trachyte (2)		Tenaghi Philippon TP 970 Phonolite to Trachyte	Lake Ohrid 896 - Oh* Phonolite to Trachyte	
	(ZS 98262)	(ZS 2506)	(ZS 2507)	Tomlinson et al. (2012)	(This Study)		(This Study)	(Zanchetta et al., 2008)
FeO/CaO	1.4 ± 0.1	1.2 ± 0.1	1.2 ± 0.1	1.3 ± 0.1	1.2 ± 0.1	1.2 ± 0.1	1.3 ± 0.1	1.3 ± 0.1
Cl wt. %	0.71 ± 0.08	0.54 ± 0.06	0.50 ± 0.05	0.57 ± 0.21	-	-	0.54 ± 0.24	0.54 ± 0.28
V (ppm)	31 ± 3	107 ± 7	122 ± 10	40 ± 10	128 ± 16	87 ± 20	46 ± 23	70
Nb/Th	1.8 ± 0.2	1.7 ± 0.1	1.7 ± 0.2	1.8 ± 0.1	1.9 ± 0.1	1.8 ± 0.1	1.7 ± 0.4	1.6
Zr/Th	12 ± 1.0	10.4 ± 0.7	10.9 ± 1.3	12.2 ± 0.5	11.8 ± 0.7	11.6 ± 1.0	12.0 ± 1.8	11.3
Ta/Th	0.09 ± 0.01	0.08 ± 0.01	0.08 ± 0.02	0.09 ± 0.01	0.09 ± 0.01	0.09 ± 0.01	0.09 ± 0.02	0.10
Nb/Zr	0.15 ± 0.01	0.16 ± 0.01	0.16 ± 0.01	0.15 ± 0.01	0.16 ± 0.01	0.15 ± 0.01	0.14 ± 0.3	0.14
Y/Th	1.00 ± 0.09	0.99 ± 0.08	1.03 ± 0.08	1.09 ± 0.1	1.17 ± 0.07	1.04 ± 0.09	1.08 ± 0.40	1.40
La/Yb	22.5 ± 2.4	27.1 ± 3.4	25.5 ± 2.7	23.2 ± 2.9	21.0 ± 2.9	21.3 ± 2.9	23.9 ± 5.1	21.3

Table 3

Table 1: Reported occurrences of the Y-3 tephra and proposed correlatives from across the Central Mediterranean region. Dispersal is given relative to Campi Flegrei caldera. Presented are ages associated with these tephras. Terrestrial and marine radiocarbon ages have been calibrated using atmospheric and marine data sets respectively incorporated within IntCal09.

Table 2: Representative grain-specific major, minor (EMPA) and trace element (LA-ICP-MS) glass data from the Ionian Sea Y-3 tephra (M25/4-12). Also given is grain-specific glass data for the extra-caldera deposits (SMP1-e and CE1) and other distal tephras considered as potential correlatives of the Y-3 tephra including TP 9.70 (Tenaghi Philippon, NE Greece) and PRAD 1332 (PRAD 1-2, Central Adriatic). (LA, LA-ICP-MS analyses). A full grain-specific glass data set is presented in the supplementary information.

Table 3: Diagnostic concentrations and ratio for geochemical fingerprinting of the Y-3 tephra, errors are 2 standard deviations. TAS classification is based on ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) versus SiO_2 using Le Bas et al. (1986). * is a bulk glass separate analysis of 896-Oh Lake Ohrid (Zanchetta et al., 2008), not a grain-specific trace element analysis.

- Campi Flegrei Volcanics
- Somma-Vesuvius Volcanics
- Quaternary and active terrigenous sediments
- Mesozoic carbonate units
- Pliocene and Miocene terrigenous sediments
- Quaternary Volcanic Centres

- Faults
- Overthrusts
- Caldera margins

Distal tephra

◆ Y-3 M25/4-12
(Ionian Sea)

▲ TP 9.70cm
Tenaghi Philippon (Greece)

◇ TM-15 (LGdM)¹

✕ PRAD 1332 (Adriatic)

● 986-Oh (Lake Ohrid)²

Proximal Tufi Biancastri¹

--- VRb

■ VRa (30.3 ± 0.2 ka)

Medial (Extra-caldera)

▲ CE1 upper (ZS 2507)

● CE1 lower (ZS 2506)

■ SMP1-e (ZS 98262)

OxCal v4.1.7 Bronk Ramsey (2010); r.5

*Lago Grande
di Monticchio*

*Tenaghi Philippon
(TP-2005)*

Total Tree Pollen (%)