**Developing a robust tephrochronological framework for Late Quaternary marine records in the Southern Adriatic Sea: new data from core station SA03-11**.

**Matthews I.P**1**., Trincardi F**2**., Lowe J.J**1**., Bourne A.J**1\***., MacLeod A**1**., Abbott P.M**1\***., Andersen N**3**., Asioli A**3**., Blockley S.P.E**1**., Lane C.S**4ǂ**., Oh Y.A**4**., Satow C.S**1~**., Staff R.A**1$**., Wulf S.** 5

1 Centre for Quaternary research, Department of Geography, Royal Holloway University of London, Egham, Surrey, TW20 0EX, U.K.

2 ISMAR-CNR, Istituto di Scienze Marine-Consiglio Nazionale delle Ricerche, Via Gobetti, 101 40129, Bologna, Italy

3 Istituto di Geoscienze e Georisorse del C.N.R.- Sede di Padova, c/o Dipartimento di Geoscienze dell'Università di Padova, C.so Garibaldi, 37 35121 Padova, Italy

4 Research Laboratory for Archaeology and the History of Art, University of Oxford, South Parks Road, Oxford, OX1 3QY, U.K.

5 GFZ German Research Centre for Geosciences, Section 5.2 – Climate Dynamics and Landscape Evolution, Potsdam Germany

\*Present address: Department of Geography, College of Science, Swansea University, Singleton Park, Swansea, SA2 8PP.

ǂ Present address: Geography, School for environment, education and development, University of Manchester, Arthur Lewis Building, Oxford Road, M13 9PL.

~Present address: Faculty of Science, Engineering and Computing, Penrhyn Road, Kingston upon Thames, Surrey, KT1 2EE, U.K.

$Present address: Research Laboratory for Archaeology and the History of Art, University of Oxford, South Parks Road, Oxford, OX1 3QY

Key words: Tephra; tephrochronology; Central Mediterranean; Marine; Late Quaternary; Age modelling

***Abstract***

Tephra layers are assuming an increasingly important role in the dating and correlation of Late Quaternary marine sequences. Here we demonstrate this potential by reporting a new study of the sediment sequence of marine core SA03-11, recovered from the Southern Adriatic Sea, which spans the last c. 39 ka. A total of 28 discrete tephra layers are reported from this sequence, 10 of which are visible in the core and a further 18 are non-visible cryptotephra layers. These have been analysed using more than 1400 WDS-EPMA measurements of glass chemistry and results have been compared with published chemical measurements obtained from relevant proximal and distal sites which preserve eruptions dating to within the same time interval. The data show that a high proportion of the layers originate from the Campi Flegrei volcanic field but more distinctive layers are sourced from Vesuvius, the Aeolian Islands and Vulcano, and these provide key marker horizons. The results show that the sequence extends in time to the Campanian Ignimbrite at the base, that a number of the layers have robust age estimates that permit a better constrained age-depth model to be constructed for the sequence, and that the potential exists for importing terrestrially-based age estimates into marine contexts, thereby circumventing problems of incorporating reservoir uncertainties associated with marine radiocarbon dates. The WDS-EPMA dataset generated here also provides important new data that constrains key Late Quaternary tephra layers in the central Mediterranean region.

1. ***Introduction***

Tephra layers have long been used to underpin Late Quaternary palaeoenvironmental research in the Mediterranean region, including distal layers recovered from marine sediments that have been linked to specific eruption events in proximal volcanic settings (e.g. Keller, 1978; Paterne *et al.*, 1986; Rosi and Sbrana, 1987; Calanchi *et al*., 1998; Smith *et al.,* 2011). The results provide correlative time-equivalent marker horizons (‘isochrons’) between marine sequences and between marine and terrestrial records, as well as improved site chronologies where individual ash layers have been reliably dated (Bourne *et al*., 2010). A series of tephra layers common to different sediment sequences therefore provides a powerful independent means of testing age models derived using other means, such as radiocarbon dating, and biological or isotopic zonation schemes. These latter methods have their problems: radiocarbon dates obtained from marine deposits and their contained fossils are subject to variable marine reservoir effects (e.g. Ascough *et al*., 2005), while correlations based on biostratigraphic and/or isotopic zonation schemes (e.g. Fletcher and Sánchez-Goñi, 2008; Numberger *et al*., 2009) assume synchroneity of zone boundaries over large areas, an assumption that requires independent verification. As will be discussed in this paper, however, tephrochronology is also not free of significant practical difficulties and interpretational uncertainties; nevertheless, its strengths allow it to continue assuming increasing and widespread application in constraining models of rapid environmental change during the late Quaternary (Siani *et al*., 2004; Lowe *et al*., 2007; Bourne *et al*., 2010).

 Until relatively recently, Mediterranean tephrochronology has tended to focus on the identification of clearly visible ash layers in sediment sequences, which has limited both the geographical scope of the method as well as the number of individual ash layers that can be employed for correlation purposes in sequences located further from source regions . In recent years, however, it has been demonstrated that distal ash layers that are either extremely thin, and hence barely visible, or that are not visible at all (so-called ‘cryptotephra’ layers), can be traced over much greater distances from volcanic source, while increasing the number of layers that contribute to a local tephrostratigraphical scheme (Siani *et al.,* 2004; Wulf *et al.,* 2008; Lowe *et al.,* 2007; Bourne *et al.,* 2010). Indeed, in some marine sequences, the number of cryptotephra layers may significantly exceed the visible layers present, though they mostly go undetected by routine down-core scanning procedures; unless appropriate detection measures are adopted, therefore, the full tephrostratigraphical potential of some sedimentary sequences may not be realised (Bourne *et al*., 2010). Here we confirm this to be the case with respect to a set of marine cores obtained from core station SA03-11 located in the Southwestern Adriatic Margin (SAM), which contains a number of cryptotephra as well as visible ash layers, spanning the last c. 38,000 years. The methods used to detect, extract, chemically fingerprint and identify individual ash layers will be explained and evaluated, and the reliability of the results assessed. The implications of the results with respect to late Quaternary palaeoenvironmental reconstruction in the Adriatic region are also briefly examined.

1. ***Site and depositional context***

The sediment core sequence reported here, extracted in 2003 from core station SA03-11 (41°22N; 17°17E) by ISMAR, Bologna, is located in the SAM, a small sub-basin situated to the east of the Gargano promontory in the Adriatic Sea, from a water depth of 1125.9m (Figure 1). A multibeam bathymetric map (Figure 1, upper left) reveals the sea-floor relief in the southern Adriatic, and notably the Dauno Seamount with a deep channel (‘moat’) flanking its northern edge. Mud waves created by Dense Shelf Waters (DSW) cascading downslope have led to the accumulation of continuous sediment mud layers, reflected in the sonar cross-profiles (Trincardi et al., JGR 2007; Foglini *et al.* Marine Geology submitted; Benetazzo et al., Progress in Oceanography *in press*). Core SA03-11 was obtained from a location where the sediments are least disturbed, avoiding areas of sediment sliding, especially in the vicinity of the Gondola Slide (GS), and close to the moat. However, some minor disturbances caused by DSW flow, particularly during intensified events, cannot be ruled out, and may be responsible for recycling of sediment layers from shallower parts of the outer shelf or upper slope. The moat and sediment drifts plastered against the northern wall of the Dauno Seamount (on the right of the profiles) resemble many other examples of contourite deposits described in the literature (e.g. Faugeres et al., 1999) and define an area where DSW flow impacted more vigorously on the sea floor. The velocity of such bottom currents measured by a mooring station recently set up in this part of the sea floor exceeded 50 cm/sec during an extreme DSW cascade event in April 2012 (Chiggiato et al., submitted). The sedimentary context combined with the coherent isotopic and biostratigraphic data for SA03-11 (Figure 2) demonstrates that a stratigraphically-continuous sediment pile with low bedding gradient and no evidence of distorted or truncated sedimentary structures. Measuring 15.98m in its complete length, the core sequence mainly consists of grey to brown bioturbated muds that show little evidence of turbidite structures or breaks in sedimentation (Figure 2). A series of 12 visible ash layers, as well as foraminiferal and isotopic stratigraphy, suggest that the core sequence accumulated over approximately the last c. 39 ka (Piva *et al.,* 2008; Ariztegui *et al.,* 2000; Asioli *et al*., 2001; Sangiorgi *et al*. ,2003; Favaretto *et al*., 2008). On that basis, we present the tephrostratigraphical data obtained from core sequence SA03-11 in three broad periods:

1. ***Present day to c. 9.25 cal ka BP***. This encompasses the period spanning the top of the core sequence to the base of Sapropel Layer 1 (S1 - Sangiorgi *et al.* 2003). This time-span consists of foraminiferal ecozones I-III of Piva *et al*. (2008), extending from 0 to 370 cm in the SA03-11 sequence. It also includes the horizon of the last common occurrence (LCO) of foraminiferal species *G. sacculifer* and *G. inflata,* believed to have occurred at c. 0.55 and 6.00 ka BP respectively, and recorded in the SA03-11 sequence at 20 and 200 cm depth respectively (Piva *et al*. 2008). Other important stratigraphical markers previously identified are the upper boundary of Sapropel 1 (S1 at c. 250cm), the age of which is not known precisely, but is estimated at around 6.5-7.0 cal. ka BP, and a distinctive 500-year break/ interruption within the S1 layer, separating it into two phases, S1a and S1b; the break between S1a and S1b is estimated to centre around 8.0 cal ka BP (Ariztegui *et al*. 2000; Sangiorgi *et al*. 2003).
2. ***The last glacial to interglacial transition (LGIT)***. The base of this interval (370-640cm in SA03-11) is defined by a distinct shift to more negative oxygen isotope values, while the upper boundary is marked by the base of S1. The approximate age span of this interval is c. 14.50 – 9.25 cal ka BP on the basis of (*inter alia*) distinctive biozones, identified as regional ecozones IV-VI by Asioli *et al.* (2001) and Favaretto *et al*. (2008).
3. ***Base of the LGIT to the base of the core sequence***. The remainder of the sequence, below the base of the LGIT, spans Termination 1, MIS-2 and the final phase of MIS-3, according to the published biostratigraphical data (regional ecozone VII of Asioli *et al.,* 2001).

On the basis of the biostratigraphic and isotopic zonation, it was assumed that the sequence did not extend as far back in time as the age of the Campanian Ignimbrite, a tephra widespread in the Mediterranean and eastern Europe, and dated to c. 39 ka BP (Di Vivo *et al*., 2001; Pyle *et al*., 2006). The new tephrostratigraphical data presented here offer a means of testing this assumption, as well as an independent check on the overall chronology of events summarised above.

1. ***Laboratory Methods***

Except in the case of thick visible volcanic ash layers that consist almost entirely of glass shards, it is essential to analyse the entire sediment column in order to establish quantitatively the full tephrostratigraphical record preserved in a sequence. The resulting data can provide information that is critical for establishing the total number of individual ash layers represented, the sedimentary processes that may have influenced ash deposition and the horizons within ash layers that may equate with the eruption event from which they originated. The analytical procedures employed should also include steps for quantifying the number of cryptotephra shards present. To achieve this, floatation procedures have been employed that use liquids of fixed densities designed to remove non-glass components and to isolate and concentrate glass shards (Turney, 1998; Blockley *et al.,* 2005). Since some cryptotephra layers in lake and marine sediments may be only a few mm thick and consist of shards smaller than 50 μm, the sediment column was sub-sampled contiguously to ensure that the full tephrostratigraphical record was captured (see e.g. Bourne *et al.,* 2010; Lane *et al.,* 2011).

***3.1 Core sampling***

Following cleaning of core surfaces, contiguous strips of sediment two centimetres wide and 10 centimetres long were cut from each core-length. These were examined in 3 stages as follows. First, thin strips measuring 10 x 0.5 x 0.5 cm were cut from the larger strips, homogenised and examined for the presence of tephra. For this preliminary or scanning stage, glass shard numbers were counted to reveal the quantitative distribution of shards per gram of dry sediment at 10 cm vertical resolution. Second, those samples that revealed some glass content but which did not match up with visible ash layers were then examined at 5 cm and, where necessary, 1 cm vertical resolution using new thin strips or spot samples cut from the original thicker samples. These procedures allowed the full vertical variation in glass shard content and the precise positions of peak glass shard concentrations to be determined. Samples of glass were extracted from all distinctive peaks for geochemical analysis, but also from some horizons with lower shard concentrations in order to test for ‘background’ input of glass and to resolve ‘outliers’ in the geochemical data obtained from tephra peaks.

***3.2 Extraction of glass shards***

The sodium polytungstate (SPT) floatation procedure of Blockley *et al*. (2005) was adopted for glass shard extraction with two modifications: (1) use of a larger sieve mesh size (125 μm) to retain tephra shards larger than those found in distal lake sites, for which the protocol was initially developed; and (2) a lower density SPT ‘cleaning’ solution (1.95 g-cm-1) to capture highly vesicular shards. The extracted glass shards were mounted in Euparal on glass slides and examined using an Olympus CX-41 microscope fitted with cross-polarising filters. Tephra shards were initially classified by optical properties (colour and morphology) into two types: (a) ‘colourless’, which tended to be vesicular and to contain mineral inclusions; and (b) ‘brownish’, ranging from yellowish-brown to olive-brown but varying in form between fluted, vesicular and blocky.

***3.3 Geochemical analysis***

Samples were prepared for chemical analysis following the method outlined in the supplementary information. Wavelength Dispersive Spectrometry – Electron Probe Micro-Analysis (WDS EPMA) measurements were obtained using three different systems. Firstly, a JEOL JXA8800R, housed at the Department of Earth Sciences, Oxford University with four spectrometers, an accelerating voltage of 20 keV, beam current of 10 nA and an operational beam diameter of 10 µm with a diffuse spot was used. Secondly, a JEOL 8600 probe housed at the Research Laboratory for Archaeology and the History of Art, Oxford University. This also had 4 spectrometers, an accelerating voltage of 15 keV, beam current of 10 nA and an operational beam diameter of 10 µm. Some layers containing very small shards presented particular challenges, especially if vesicular in shape or rich in microlite inclusions (crystalline impurities), where it was difficult to focus the beam on flat surfaces of pure glass. Some material was therefore analysed using a Cameca SX100 microprobe (housed at the University of Edinburgh) with a 5µm beam, operating with an accelerating voltage of 15 keV, beam current of 2 nA for Na, Al, Si, Fe, K, Ca and Mg and a beam current of 80 nA for F, Mn, Cl, P, S, and Ti (Hayward, 2011). All EPMA systems were calibrated using standard calibration blocks and vitreous secondary standards (MPI-DING StHs6/80-G; NIST612; an internal Lipari Obsidian standard; ML3-B; KL-2; and the Hunt and Hill (1996) Lipari Obsidian to monitor accuracy (see supplementary data Table S1). Count times were 15 seconds, with sodium measured first to minimise sodium mobilisation (Dugmore *et al.* 1995). Details of which samples were analysed with which microprobe are provided in the Supplementary data.

The resulting geochemical data were screened by first scrutinising the secondary standard results to check for machine drift, and any affected data were rejected. Of the data that met this criterion, those with analytical totals less than 95% were also excluded, except for those samples that consistently returned analytical totals in the region of 93-95% without trends suggesting inadequate analyses (samples 171, 247, 760 and 950cm). Finally, the data were screened for outlier values and representation of non-glass material and, where suspected, these data were also excluded from the final data-sets used to classify and correlate individual ash layers. Note that the data used here have not been normalised except when used in TAS classification plots (Le Bas, *et al.* 1986) or when necessary for making unbiased comparisons with other published records; for such cases the data transformations adopted are specified in the figure caption.

***3.4 Chemical classification and correlation procedures***

The chemical spectra of analysed samples were assessed systematically using the following steps: (1) Filtering of the data as outlined in section 3.3; (2) Classification using the TAS system (Le Bas, *et al.* 1986); (3) Biplot comparisons of selected major-oxide ratio plots in order to test for single or multiple geochemical populations within individual samples.

The chemical data generated from all of the SA03-11 tephra layers were in the first instance compared to regional reference data populated exclusively by measurements obtained by WDS-EPMA and checked for data quality. This incorporates: (a) the large data-set generated by Wulf *et al*. (2004, 2008) for the Lago Grande di Monticchio (LGdM) tephrostratigraphical record, a regional distal tephra stratotype for central-southern Italy; (b) various proximal data-sets from European volcanic (e.g. Turney *et al*. 2008; Smith *et al*. 2011; Tomlinson *et al*., 2012); and (c) data from other distal sites where multiple tephra have been preserved and geochemically analysed (e.g. Bourne *et al*.2010). These data were supplemented with information from the RESET database (<https://c14.arch.ox.ac.uk/login/login.php?Location=/resetdb/db.php>) where available. Layers for which the chemical matches remained unclear are classified as ‘unknown’, pending further investigation.

1. ***Results***

A total of 40 peaks in glass shard concentration have been recognised (Figure 3), of which 26 yielded robust geochemical information based on 1433 individual WDS-EPMA measurements generated from 56 analysed samples (see Supplementary Information Table 2 for raw data). This represents one of the most comprehensive data-sets of single-grain WDS-EPMA measurements obtained from distal tephra layers in the SAM. Not all of the layers show isolated peaks, however, as some zones of high shard concentration extend vertically over several tens of centimetres.

Samples with single chemical clusters are labelled by depth alone; samples displaying more than one chemical cluster are labelled by depth and an alphabetical letter for each individual cluster. Thicker layers of tephra, vertically covering several tens of centimetres, are particularly difficult to interpret, as they could reflect reworking of tephra by sedimentary or biological processes, or composite deposits of mixed tephra derived from different eruption events. These alternatives are considered below for relevant layers.

***4.1 Ash layers between present time and 9.25 ka BP***

Within the part of the SA03-11 sequence assigned by previous research to the last 9.25 ka, two broad zones of tephra shard deposition were detected between 85-153cm and 280-363cm, while five discrete tephra peaks are confined to between 10-12cm, 39-41cm, 161-162cm, 170-171cm, and 245-246 cm. The upper two of these peaks as well as the intervals between 140 and 153 cm and between 362 and 363 cm consist of visible ash layers. Because the top of the SA03-11 core sequence was distorted and compressed during the coring process, a duplicate short core (SA03-12SW) was obtained from an adjacent borehole. Magnetic susceptibility data revealed two tephra peaks at 15-20 and 75-80 cm that could be equated with those at 10-12 and 39-41cm in the main SA03-11 core. The geochemical data reported here were obtained from the SA03-12SW sequence, but to avoid confusion the data are assigned to corresponding SA03-11 depths. The data obtained from each of the tephra layers (denoted by T and the corresponding depth of peak tephra shards in the labels below) dating to within the last 9.25 ka are listed in Table 1 with additional criteria used to classify each tephra summarised below.

*SA03-11 T12 cm*  The trachytic composition suggests a source in the Campi Flegrei (Figures 3 and 4) and its position in the core, just above the last appearance of *G. sacculifier* (dated to c. 550 years ago) suggests an attribution to the Monte Nuovo eruption of AD 1538 could be plausible (cf. di Vito *et al.,* 1987). However, this is not supported by the very small amount of chemical information available for T12, which shows a weak match with the proximal Monte Nuovo data currently available (Figure 5) (Smith et al. 2011). At present the source of this layer is unknown.

*SA03-11 T41 cm* T41 is a visible black coloured tephra layer in the core sequence. Geochemical analysis produced a heterogeneous shard population for which 29 chemical analyses are available. A single rhyolitic outlier value was discounted due to a lack of supporting data (Figure 5). The first chemical grouping is tephri-phonolitic in composition with SiO2 values ranging from 48.08 to 52.54 wt% (Figure 3), most likely deriving from Vesuvius. This layer also had abundant associated volcanic minerals (unique within SA03-11), the composition of which are consistent with leucite and clinopyroxene. This chemical signature and associated mineral information best matches the available data for the AD 472 eruption of Vesuvius, known to have been dispersed eastwards (Rolandi *et al.,* 2004; Wulf *et al*., 2004; Sulpizio *et al*., 2005; Santacroce *et al*., 2008). The AD 472 eruption is detected in LGdM as layer TM-2b (Wulf et al., 2012) and in Lake Ohrid core Co1202 as layer OT0702-1 (Vogel et al., 2010, Sulpizio et al., 2012) (Figure 5). The chemical match between T41 and examples of the AD 472 tephra is not complete and it is possible this visible layer relates to a different inter-plinian eruption of Vesuvius. If this is the case it represents a far travelled layer from Vesuvius not previously recognised in the Southern Adriatic. However, the correlation to AD 472 is preferred here due to its presence in the LGdM record. The other chemical grouping is indicative of a source in the Campi Flegrei, and is similar to both T12 stratigraphically above T41 and the TM-5/AMST tephra chemistries reported for LGdM (Figure 6). However the correlation of the other geochemical population to the AD 472 eruption suggests the AMST-type chemistry either relates to a previously unrecognised and unreported eruption of the Campi Flegrei or to reworking of an underlying tephra layer.

*SA03-11 T153 cm* This visible layer within the tephra zone 153-85 cm displays three distinct colour changes with units ranging from sandy grey to light grey to dark grey up the core, the contacts between units being diffuse and gradational. Several peaks in tephra shard concentration occur throughout this broad zone (Figure 2.f), with the greatest concentration (estimated at >2.2 million shards-g-1) detected between 150-151 cm. Several intervals within the zone were selected for geochemical analysis (Table 1) in order to establish whether this protracted episode of ash deposition reflected multiple eruption events or reworking of the highly concentrated ash near the base of the zone. 184 analyses were obtained from six distinctive peaks in shard concentration, predominantly of phono-trachytic composition consistent with layers derived from the Campi Flegrei volcanic field during epoch III (Figures 3 and 4). Since no significant differences were detected in major element composition between the six peaks, it is suggested that tephra deposition within the 153-85 cm zone reflects prolonged reworking through DSW currents (see section 2). The closest chemical match to these layers is TM-5 (and sub layers a-d) of the LGdM sequence, linked with the AMST-Astroni eruptions in the Campi Flegrei (Wulf *et al.,* 2008), the base of which is 14C dated to 4.69–4.30 cal ka BP (Blockley *et al.,* 2008), possibly providing an indicative age for T85-153 cm (Figure 6). Although a cautious assignment of T153 to the AMST-Astroni group is proposed, a more robust correlation might be possible in the future using trace element analysis. Smith *et al*. (2011) have generated proximal geochemical data for the AMST complex, showing that compositional gradients in both major and trace elements occur over time. The data from T153 show strong similarities, especially in low Fe and Ca values, slightly elevated Na and depleted Mg, with the Smith *et al.* (2011) data for the lower layers in the series (Figure 6).

*SA03-11 T162 cm* This discrete peak underlies the large visible ash layer described above. The layer is chemically identical to the data presented for T153, but the peak in shard concentration is clearly separated from that layer (Figure 2 and 6). This may represent an isolated eruption from the Campi Flegrei that pre-dates the main AMST-Astroni group. De Vito *et al*. (1999) provide evidence for 9 Campi Flegrei eruptions that pre-date the AMST-Astroni group within the epoch series. The close proximity of T162 to the overlying layer that is equated with the start of the epoch III series indicates its most likely correlative to be either the Paleoastroni-1 or -2 eruptions (Orsi *et al.* 1996), although the best match with available chemical data, including new data from the Campi Flegrei provided by Smith *et al*. (2011), is with the Averno-1 event. The large overlap between the chemical data in these layers means, however, that T162 cannot currently be assigned to a single eruption event.

*SA03-11 T171 cm* This small peak displayed considerable morphological variability in shards with long axes generally less than 25 µm. The WDS data suggest a mix between two distinct chemical populations (Table 1), 4 displaying sub-alkali rhyolitic chemistry (T170a) and 3 with trachytic/trachy-dacitic affinity (T170b) (Figure 3). This mixed chemical signature suggests two sources for this layer, the rhyolitic component derived from the Aeolian Islands (Lipari being the most likely source) and the trachytic/trachy-dacitic component derived from Ischia, but with such a small amount of data it is difficult to judge whether the mixed signals represent two closely-spaced volcanic eruptions or some reworking (Figure 7). Since no eruptions in the Aeolian Islands are known from this time and the lower tephra layer T247 (described below) shows a strong rhyolitic signal, the likely source is reworking from this lower layer, however, thie possibility of a previously unreported tephra cannot be wholly excluded. The chemical data with affinity to an Ischia source may relate to the Piano Liguori eruption dated to c. 6.00-4.95 cal. ka BP (Orsi *et al.,* 1996; date recalibrated in this study using IntCal 13 within OxCal v4.2, BronK Ramsey, 2008; Reimer et al., 2013).

*SA03-11 T247 cm* This small peak, which lies just above the termination of S-1, consists of shards with considerable morphological variation and long axes generally less than 40 µm. Sixteen WDS measurements were obtained that indicate two distinct chemical populations, 6 displaying sub-alkali rhyolitic chemistry (T247a), chemically identical to those obtained from T171a and to a tephra layer detected by Siani *et al.* (2004) in SAM core MD90-917, and 10 with phono-trachytic chemistry (T247b) (Figure 3). Only one early Holocene eruption with sub-alkali rhyolitic chemistry from the central Mediterranean has been detected in distal settings, the Gabellotto-Fiumebianco unit from Lipari in the Aeolian Islands, which is thought to correspond with marine tephra layer E-1, dating to 8.73-8.40 cal ka BP (Paterne *et al.,* 1988; Zanchetta *et al.,* 2011). However, the E-1 layer falls within S-1 while the SA03-11 layer lies 4 cm above the upper S-1 boundary, so they are unlikely to be linked. The heterogeneous shard populations within this layer therefore suggest either reworking of older tephra or derivation from a previously undetected eruption that post-dates S1. T247b has a close chemical affinity with TM-5 of the AMST-Astroni group, but underlies by c. 1m other SA03-11 tephra layers already assigned to this group (see above). Its stratigraphic position just above the termination of S-1 and 46cm below the Last Occurrence (LO) of *G.inflata,* suggests an age of c. 6.00-7.50 ka BP, during a period of volcanic quiescence, when the P3 palaeosol developed throughout the Campanian region (palaeosol B in Di Vito *et al*., 1999). New data reported by Insinga *et al.* (2006) and Fedele *et al*. (2011) suggest that this period may not have been so quiescent after all, but was interrupted by the Porto Miseno eruption at c. 6.49±0.10 ka BP, a possible correlative for T247b, though there is little reliable data for this eruption. The origin of the tephra shards in T247b therefore remains uncertain.

*SA03-11 T363 cm* This large zone of tephra deposition falls within the S-1 sediment unit. A thin (5 mm) visible ash layer occurs at the base (362.5-363cm) and this is listed separately in Table 1. The core section was analysed at 1 cm vertical resolution, which revealed significant variations in shard concentration, with 8 further peaks identified (Figure 2). Geochemical data were obtained from the visible layer and from the other peaks above it. Taking the visible layer first: 17 WDS measurements were obtained from this layer, the data matching most closely with TM6-b in the LGdM sequence, which is equated with the Pomici di Mercato eruption of Somma-Vesuvius, dated to c. 8.90 ± 0.11 cal ka BP (Rolandi *et al*., 1993; Andronico *et al*., 1995; Santacroce *et al*., 2008). T363 also closely matches the glass shard chemistry of proximal deposits of the Pomici di Mercato eruption (Santacroce *et al.,* 2008) (Figure 8).

A total of 246 WDS-EPMA measurements were obtained from the eight shard peaks identified above the visible layer (T285-T342). Collectively, the data show mixed chemical signals, with the majority showing a strong overlap with the Pomici di Mercato chemical cluster, while some data fall into two quite different clusters, one of Vesuvius-type and the other with a typical Campi Flegrei chemical composition (Figure 8). The Vesuvius-type chemistry most closely aligns with tephra layer TM-6a in the LGdM record (Wulf *et al.*, 2004). Wulf et al. (2004) also ascribe this layer to the Pomici di Mercato event (Figure 8), an assertion supported by match with layer OT0702-3 in Lake Ohrid (Figure 8) (Vogel et al., 2010; Sulpizio et al., 2012). However, sediment cores recovered from the Ionian Sea demonstrate multiple peaks in tephra shards with Vesuvius-type chemistry. They ascribe these to multiple eruptions during this period and this interpretation cannot be excluded when interpreting the SA03-11 data. Finally, the shards that show a Campi Flegrei chemical signal, although somewhat variable in composition, compare closely with the Agnano Pomici Principali (APP) tephra (Figure 8). The lack of contemporaneous eruptions from the Campi Flegrei during this period and the possible evidence for reworked Mercato tephra throughout the S-1 unit in the SA03-11 record suggest the most likely source of these shards is reworking of large T492 layer (see below).

***4.2 Ash layers within the last glacial-interglacial transition (LGIT)***

In the part of the SA03-11 sequence that is assigned to the LGIT, one discrete ash layer and two broad zones of ash deposition have been detected on the basis of tephra counts conducted at 1 cm resolution.

*SA03-11 T492 cm* A visible tephra layer that could be sub-divided into three distinct units based on colour variation was recorded between 480-492cm. Shards from all three colour bands were selected for WDS measurement, but all the data generated from this visible layer were trachy-phonolitic in composition with a source from the Campi Flegrei (Figures 3 and 4) and matched closely to the Pomici Principali tephra (Smith et al., 2011) and TM-7b in the LGdM sequence (Wulf et al., 2004) (Figure 9A). The Pomici Principali (PP) has been 14C dated to 12.08±0.95 cal ka BP (Smith *et al.,* 2011) and a correlation to the Pomici Principali seems plausible as it has been reported from a number of sites in the Adriatic (e.g. Lowe *et al*., 2007, Siani et al. 2004), while the visible ash layer in the SA03-11 sequence falls within the Younger Dryas stadial as defined by isotopic stratigraphy (Figure 2). The chemical data obtained from the non-visible ash peaks between 419 and 480 cm all have identical chemistry to the PP, and hence are likely to reflect reworked deposits from the visible layer, but attribution to different events with similar chemical composition cannot be entirely excluded.

*SA03-11 T531cm* This small cryptotephra layer with peak shard concentrations at 531 cm depth has a phonolitic chemistry (Figure 3) very similar to that of TM-7b/PP but is a discrete layer 40 cm below the visible layer at 480-492 cm and is chemically much less variable (Figure 9B). It does not appear to chemically match with any tephra in the LGIT interval of the LGdM (Wulf *et al*., 2004) or the PRAD1-2 (Bourne *et al*., 2010) sequences. T531 occurs at the onset of the Younger Dryas event in the SA03-11 sequence and a total of c. 20 eruptions are recorded for Italian volcanoes during this period, but none have been identified in the Adriatic so far (Di Vito *et al*., 1999). T531 shows a good chemical match to the composition of the La Pigna I eruption and while other candidates like Soccavo 1 may be possible, this layer is thought to occur slightly later in time than the period represented by T531 and here a correlation to La Pigna I is preferred (Di Vito *et al*., 1999; Smith *et al*., 2011; Albert *et al*., 2012).

*SA03-11 T640 cm* Peak shard numbers occur at 640 cm depth but high concentrations characterise the interval between 627 and 640 cm. Tephra from six levels within this interval were selected for WDS analysis, and a total of 197 measurements obtained. All the data matched the chemistry of TM-8 in the LGdM sequence, equated with the Neapolitan Yellow Tuff (NYT), and with other sites where the NYT has been analysed, such as in the PRAD 1-2 sequence (Bourne *et al*., 2010) (Figure 9A). The NYT has been dated to 14.9±0.4 ka via the 40Ar/39Ar dating method (Deino *et al*., 2004), more recently refined to 14.11±0.21 cal ka BP (Blockley *et al*., 2008). The relative merits of these conflicting ages are discussed in detail by Blockley *et al*. (2008) and the younger age has subsequently been supported in Lane *et al.,* (2011), hence we apply this age estimate to T640.

***4.3 Ash layers within MIS-2 and MIS-3***

In the part of the SA03-11 sequence that is assigned to MIS-2 and 3, 18 discrete ash layers have been detected of which 5 are visible ash layers whilst the rest are cryptotephra layers detected by floatation procedures. Oxygen isotope and biostratigraphic zonation (Figure 2) suggest that all of the layers post-date the Campanian Ignimbrite (c. 39 ka).

*SA03-11 T646 cm* A total of 19 shards chemically analysed from this small cryptotephra peak, these display a predominantly trachytic chemistry (Figure 3) that closely matches chemical data for TM-9 (Figure 10) in LGdM (c. 14.56±0.73 ka BP) (Wulf *et al*., 2004; Tomlinson *et al*., 2012). TM-9 was initially correlated to the GM-1 tephra layer (Andronico,1997) in the Tufi Biancastri series (Wulf *et al*., 2004). However, Tomlinson *et al*. (2012) dispute this correlation as a robust match cannot be made between the two layers with the available chemical data. The match of T646 to TM-9 is robust and this age estimate can be imported into SA03-11.

*SA03-11 T651 cm* Geochemical data from this small peak suggest a predominantly trachytic-phonolitic chemistry, consistent with a source in the Campi Flegrei (Figures 3 and 4). T651 is chemically similar to the tephra between 640-627cm, except for the wider range of SiO2 values associated with the latter. The best chemical match found for T651 is to the complex of tephra layers referred to by Wulf *et al*. (2008) as TM-10a-d, thought to relate to the Lagno Amendolare eruption (Figure 10). On the basis of the LGdM data, Wulf *et al*. (2008) contend that the Lagno Amendolare activity was not a single event but a series of eruptions derived from the Campi Flegrei and dated to between 15.55±0.78 and 15.03±0.75 ka BP. The closest chemical match to T651 is TM-10b, dated to 15.22±0.76 ka. However, the chemical data are relatively sparse for TM-10 (Figure 10). For the moment, therefore, the precise age of T651 is rather unclear, but it is provisionally considered to be within the age spread of the Lagno Amendolare series.

*SA03-11 T730cm* 17 chemical measurements from this non-visible peak suggest a trachytic chemistry identical to T646, which indicates a source for this layer in the Campi Flegrei (Figures 4 and 5). While the layer is identical to T646 and thus TM-9, the fact that it is stratigraphically below T651, which has been correlated with TM-10, precludes its correlation to TM-9 (Figure 11). This suggests that a series of eruptions with near identical major element chemical signatures were erupted from the Campi Flegrei between c. 17-14 ka BP. No correlation for this layer can be found in the LGdM or PRAD1-2 data-sets, but it displays strong similarities to the TLs member of the Tufi Biancastri proximal volcanic deposits in the Trefola quarry site (Pappalardo *et al.*, 1999). However, glass chemical data are only currently available for a small number of the Trefola quarry units (TLo and PRa) and these do not correlate with T730 (Figure 10) (Tomlinson *et al*., 2012). There is therefore an urgent need for WDS-EPMA determinations based on glass for the remaining unanalysed Tufi Biancastri deposits at Trefola Quarry, to firm up the provisional correlation made here.

*SA03-11 T760cm*  This small non-visible peak at 760 cm depth has a trachytic chemistry (Figure 3) with rather unusual alkali ratios (K2O:Na2O) of c. 1.2 (Figure 4). These values, combined with relatively high SiO2 and low Al2O3 and FeO values, are distinctive in SA03-11, and hence this layer has the potential to provide an important marker horizon in the Adriatic which pre-dates the NYT. No chemical match for T760cm could be found in either the LGdM or PRAD1-2 data-sets, but it is similar to the TLo member of the Tufi Biancastri deposits in Trefola quarry dating to 17.90±0.50 ka BP (Pappalardo *et al.*, 1999) (Figure 10). Recent investigations of glass shards within the TLo unit provide more robust chemical data for comparison (Tomlinson *et al.,* 2012). These indicate that while T760 is similar to the TLo eruption, T760 has slightly elevated potassium and marginally lower aluminium and sodium content (Figure 10B). This indicates that T760 may not correlate with the TLo, but with a hitherto undetected eruptive event. The origin of this distinctive ash layer is therefore only likely to be resolved through additional detailed glass chemistry of proximal material in key reference sites like Trefola quarry or Verdolino valley.

*SA03-11 T865 cm* This thin layer was visible in the core and on microscopic inspection consisted of volcanic minerals and glass shards with large and numerous microcrystalline inclusions, this made obtaining reliable chemical data problematic. However, the chemical data obtained on the glass fraction show it clearly to have an origin from Vesuvius, and the closest match obtained was with TM-12 in the LGdM sequence (Figure 11). TM-12 is correlated with the Greenish Pumice or Pomici Verdoline, derived from a sub-Plinian eruption of Vesuvius and dated to 15.97±0.70 14C ka BP (21.24-17.85 cal. ka BP) from charcoal underlying proximal deposits (Siani *et al*., 2001), while Santacroce *et al*. (2008) consider the maximum age for this eruption to be 19.27±0.11 cal. ka BP. This eruption has an ENE dispersal pattern and has already been detected in cores recovered from the Adriatic (Cioni *et al*., 2003; Siani *et al*., 2004; Bourne *et al*., 2010).

*SA03-11 T950 cm* A 4cm-thick visible tephra layer occurs within this interval consisting of an upper 2 cm that is black in colour, while the lower 2 cm is of a coarser grain size and grey in colour. A sample for WDS EPMA analysis was prepared from both units. A total of 33 chemical analyses from the lower unit show a tightly clustered trachytic composition, while a further 23 analyses from the upper black unit range widely in composition through basaltic-trachy-andesite and trachy-andesite to tephri-phonolite composition (Figure 3). On the basis of their chemical composition and correlation to other tephra deposits, the two units are thought to reflect earlier and later phases of the same eruptive event. The two units closely match TM-13 from the LGdM sequence, which is correlated with the Pomici di Base tephra derived from a Plinian eruption of Vesuvius, dated to 18.30±0.18 14C ka BP (22.24–21.15 cal ka BP) (Andronico *et al*., 1995; Bertagnini *et al*., 1998; Landi *et al*., 1999), consistent with an independent age estimate of 22.52±1.0 ka BP based on K-Ar dating of sanidine (Capaldi *et al*., 1985). A close chemical match can also be observed between T950 and proximal glass chemistry (via EDS) from the Pomici di Base eruption (Santacroce *et al*., 2008) (Figure 11). Wulf *et al*. (2004) regarded TM-13 as the most distal occurrence of ‘Pomici di Base’, but its subsequent recognition within cores MD90-917 (Siani *et al*., 2004), PRAD1-2 (Bourne *et al*., 2010), IN68-9 (Calanchi *et al*., 2008) and now SA03-11 prompts a revision of that view. The new data also underlines the likely easterly airfall dispersal direction from this eruption, while the fact that this is the largest visible ash layer within MIS-2 in SA03-11 suggests that it may prove an important marker for correlating sequences across the Adriatic and perhaps over a wider area.

*SA03-11 T1026 cm* This peak in glass shards occurs at the base of a turbidite deposit. Close inspection of this layer via thin-section micromorphology indicates that the glass shards are unconformably deposited on earlier sediments, with the sediments stratigraphically above it being progressively sorted with respect to grain-size through density setting processes. Therefore it is most likely this reflects the re-suspension and deposition of an earlier ash layer brought about by the turbidity current. WDS-EPMA chemistry indicates a bimodal distribution between phonolitic and trachytic shards (Figure 3). Its chemical composition is consistent with products of the Campi Flegrei (Figure 4) and is remarkably similar to that of the c. 39 ka Campanian Ignimbrite layer identified across the region, and this suggests that T1026 may reflect a reworked tephra layer; this contention is supported by the lack of a correlative within other regional records. However, the possibility of a previously unrecognised eruption from the Campi Flegrei with identical chemistry to the Campanian Ignimbrite cannot be fully excluded at this time.

*SA03-11 T1226, T1327 and T 1426 cm* Three visible ash layers were identified at T1226, T1327, and T1426cm. They are discussed together as they have similar major element chemical compositions and occur during a period for which several possible correlatives exist. Each of the three layers were chemically analysed and display chemical compositions consistent with eruptions from the Campi Flegrei. 28 measurements obtained from T1226 suggest a bimodal population of trachytic and phonolitic shards (Figure 3). When compared with the LGdM sequence, no clear correlative is evident but the data match the chemistry of PRAD1332 (Bourne *et al*., 2010). PRAD1332 has previously been correlated with the Y3 ash layer (Figure 12), widely reported from core sequences across the central Mediterranean. Albert *et al*. (2014) have re-investigated the distal occurrences of the Y-3 and conclude that the PRAD1332 represents the VRa eruption of the Campi Flegrei and not the Y3. A correlation is made here between T1226 and PRAD1332, and hence also to the VRa which has been argon-argon dated to 30.3±0.2 (1σ) ka BP (Pappalardo *et al*., 1999).

30 successful WDS measurements obtained for T1327 show it to consists of shards with trachytic chemistry (Figure 3) which can be securely matched with TM-15 in the LGdM sequence (Wulf *et al.,* 2004), and thus with the Y3 ash layer described in the Ionian Sea (Keller, 1978; Albert *et al*., 2014), which equates with the C-7 ash layer (Paterne *et al*., 1986; 1988) (Figure 12). Recent identification of the Y3 tephra in Tenaghi Phillipon (Albert *et al*., 2014) provides a robust age of 29.42-28.68 cal ka BP for this layer in SA03-11. This age is younger than the argon-argon age provided by correlation to the VrA for T1226 and suggests that the latter may be inaccurate. The rejection of the argon-argon age is based on the fact that to accept this age multiple radiocarbon determinations from the terrestrial Tenaghi Phillipon site would have to be rejected. These seemingly robust dates occur in a sequence alongside robust palaeoevironmental data and therefore are preferred to the single argon-argon determination.

The ash layer detected at 1426 cm yielded 23 successful analyses that indicate a predominantly trachytic chemistry with some phonolitic shards (Figure 3). The layer is chemically distinguishable from both 1226 cm and 1327 cm, as it has a wider chemical range, lower MgO and higher TiO2 percentages. The layer is a good match in terms of stratigraphic position with PRAD1474 (Bourne et al., 2010) and new chemical data confirm this match (Figure 12 and Supplementary table S2.). We hypothesise this layer represents a previously unreported eruption from the Campi Flegrei dating to between ca 30-34 ka BP.

*SA03-11 T1463 cm* A 1cm- thick visible tephra layer occurs at the base of an interval of high shard concentrations between 1463-1456 cm. 12 WDS-EPMA measurements were obtained from the visible layer and the zone of high shard concentrations at 1456cm, the number limited by microcryst inclusions. The visible layer and high concentration sample glass compositions span the trachytic, phonolitic and tephri-phonolitic fields (Figure 3). Biplots of major oxides suggest that T1463 matches TM-16b in the LGdM record and also with PRAD1494 in the PRAD1-2 sequence (Figure 11). TM-16b and PRAD1494 have been correlated with the Codola eruption. The Codola eruption is dated by radiocarbon to 25,100±400 14C yr BP (30.31-28.37 cal ka BP) (Santacroce, 1987; Alessio *et al*., 1974), while Giaccio *et al*. (2008) suggest its age to be closer to 33-34 ka, because it is correlated with the C-10 tephra in the Tyrrhenian and Adriatic seas, and which in turn is associated with a well-dated Palaeolithic archaeological sequence in Paglicci Cave. This older age is in good agreement with the age estimate suggested for the overlying Y3 tephra (equivalent T1327) and is preferred here.

*SA03-11 T1522 cm* This cryptotephra peak in shard concentrations is composed of trachytic shards with a chemical signal consistent with the Campi Flegrei and consistent with the Campanian Ignimbrite (CI). The stratigraphic position of this layer exclude the CI as a possible correlation and potentially this layer reflects either reworking of an earlier eruptive event or the occurrence of a previously unrecognised tephra layer. At present there are no known candidates for correlation.

*SA03-11 T1535 cm* This cryptotephra layer contained a mix of trachytic and rhyolitic chemistry (Figure 3). The rhyolitic component of T1535 (part a) is chemically consistent with the E-11 tephra layer identified in cores KET8003 and KET8011 recovered from the Southern Tyrrhenian Sea (Paterne *et al.*,1988) (Figure 13). E-11 is thought to lie above the C-13 ash layer, correlated with the c. 39ka Campanian Ignimbrite, and below the C-10 ash layer, correlated with the Codola eruption, and is the only rhyolitic ash reported for this period. Paterne *et al*. (1988) suggest its age to be c. 37.7 ka, although this is based on oxygen isotope profile matching and is therefore considered approximate. The trachytic component of T1535 is chemically identical to TM-18 in the LGdM sequence and with the Campanian Ignimbrite, but due to its stratigraphic position and association to the rhyolitic component a link to this eruption is implausible. A second layer with identical chemistry to both T1535a+b has recently been reported in the Ionian Sea (Insinga *et al*., 2014) where the rhyolitic and trachytic chemical signature makes it a distinctive layer (Figure 13). They ascribe an astronomical age to this layer of 34.1 ka which is also consistent with the age produced by the SA03-11 age model (Table 2).

*SA03-11 T1567 cm* T1567 is a morphologically distinctive tephra layer as the glass shards are predominantly brown in colour with a blocky morphology. The layer was difficult to chemically analyse as it frequently yielded analytical totals below acceptable values, but 15 reliable analyses were obtained which indicate a shoshonitic chemical composition (Figure 3) with high FeO, CaO, and MgO content. This chemical composition is unique within SA03-11 and rare across the central Mediterranean. No direct match for the chemistry could be found within the PRAD1-2 or LGdM tephra records, or from proximal records. The layer is similar to the TM-14b ash layer in the LGdM record which has been correlated with the eruption at c. 20 ka of the Solchiaro tuff ring on the Isle of Procida (Alessio *et al.*, 1976; Wulf *et al*., 2004), which is too young for this SA03-11 layer (Figure 14). While a link to a previously unidentified eruption of Procida is possible, a more robust match of the chemical signal displayed by T1567 is to Tufi di Grotte dei Rossi (TGR) described on the island of Vulcano (De Astis *et al.,* 1997) with chemical information recently reported by Albert *et al.* (2012) (Figure 14). A direct correlation to this layer is implausible as the age of the TGR event is thought to be 7.7±1.1 ka and hence is too young to be T1567, however, based on the tephra chemical data available it is likely T1567 relates to an older eruption of Vulcano. This would represent the first identification of a Vulcano shoshonitic chemistry of this age identified in a distal setting, although shoshonite tephra from Vulcano and dating to c. 18 ka has been identified in the Ionian Sea (Insinga *et al*., 2014). The distinctiveness of the T1567 chemical signal makes it a potentially useful marker layer for correlating sediment sequences in the Southern Adriatic.

*SA03-11 1598 cm* The basal 5cm of the core sequence shows downwardly-increasing shard concentrations suggesting that the base of the recovered core rests directly on a thick ash layer. 20 WDS measurements from the lowermost centimetre mostly show a trachytic chemical composition, while three indicate a trachy-andesitic composition (Figure 3). When compared with the LGdM and PRAD1-2 records, a clear correlation can be made with the Campanian Ignimbrite (Figure 13) which, if correct, suggests that the base of the SA03-11 sequence marks the end of Campanian Ignimbrite influx into the sediment basin, providing a basal date for the sequence of no more than 39.28 ± 0.11 ka (De Vivo *et al.*, 2001).

***5. Discussion***

***5.1 Integrity of tephra identifications***

The primary aim of this investigation was to establish an independent basis for refining the chronology of environmental changes in the Adriatic region using tephra isochrons. For this approach to be successful, individual tephra layers need to be chemically distinctive, well-dated and undisturbed (e.g. largely unaffected by reworking or bioturbation). The 28 tephra layers identified in the SA03-11 sequence (defined in section 4 and Table 1) range widely in thickness, shard numbers and chemical homogeneity, while some have been affected by reworking processes. These reworking processes appear to include some *in situ* bioturbation but also include sediments eroded, re-suspended and deposited during periods of enhanced DSW conditions. The biggest challenges with resolving the sequence into discrete volcanic eruption events, however, is the dominance of ashes originating from the Campi Flegrei volcanic cluster in Campania, the majority of which have very similar major element and trace element chemistries (Wulf *et al*., 2004; 2008; Tomlinson *et al*., 2012). The late Holocene AMST-Astroni complex (section 4.2) serves as a prime example of the extent of the problem, where repeated volcanic activity over a period of 800 years has deposited several ash layers with near identical chemical signatures (Smith *et al*., 2011). In an attempt to resolve matters, recourse has been made in section 4 to the use of other stratigraphic information (e.g. isotopic, bio- and sapropel stratigraphy) to help assign individual tephra layers to specific eruption events. This can lead to circularity of argument, where the aim is to employ tephrostratigraphy as an independent chronological tool for testing other stratigraphic schemes; but this more iterative approach is difficult to avoid at present, because much remains unclear about the chemical integrity and absolute ages of late Quaternary distal ash layers in the central Mediterranean (Di Vito *et al*., 2008; Zanchetta *et al*., 2008; Smith *et al*., 2011). In some cases, trace-element data have provided further criteria for correlation or subtle distinction of compositionally similar Italian tephra layers (Smith *et al.,* 2011; Albert *et al*., 2012; Tomlinson *et al*., 2012). Trace element analysis was beyond the scope and resource constraints of the present study, but is planned for the future in order to refine some of the correlations made in this article. Nonetheless, the new SA03-11 data contribute to the development of a more reliable tephrostratigraphic framework for the Adriatic region by: (a) confirming the importance of several key widespread marker tephra layers; (b) identifying new tephra layers which can be used to constrain climatic events; and (c) highlighting the problematic issues worthy of further focused research.

***5.2 Key tephra markers***

The most useful ‘marker’ tephra layers in the present study are those that originate from volcanic centres outside of the Campi Flegrei cluster, such as the Aeolian Islands, Ischia and Vesuvius, or where bimodal chemical distributions occur within the same sample. The Mercato, Verdoline, Pomici di Base and Codola tephras (Table 1) fall into this category, as they represent isolated, well-spaced discrete layers that are thought to reflect single large eruption events and that we predict will be found more regularly in future investigations of Central Mediterranean sediment archives that adopt the sampling procedures implemented here. Their chemical compositions are distinctive both with respect to each other and from eruptives sourced in the Campi Flegrei; as such, they provide robust tie-points for grouping the Campi Flegrei layers to within narrow time periods. Other important markers in this respect are the T760 layer, provisionally assigned to the Tufi Biancastri series (Pappalardo *et al.,* 1999), and the T531 layer, which closely matches the distinctive chemistry of the La Pigna 1 tephra (Campi Flegrei). The latter is a new important discovery of a distal marker that occurs stratigraphically close to the onset of the Younger Dryas cooling event. Also potentially important as a regional marker is T1567, which is the most chemically distinctive of the SA03-11 tephra layers, and which is most likely to have been derived from Vulcano. As this layer is close to the base of the SA03-11 sequence, it probably dates to shortly before c. 35 ka BP (see below); no eruption event has yet been reported from Vulcano for close to this time, but this does not preclude the use of this distinctive tephra as a regional marker horizon, providing that it can be traced to other core sequences.

More work is required to test and strengthen the tephrostratigraphic scheme outlined above. For example, the allocation of two SA03-11 layers to the Tufi Biancastri series is tentative because the proximal chemistry for those events (obtained from Trefola Quarry in the Campi Flegrei) are largely based on whole-rock analyses, and not glass. But the stratigraphic position of these layers, which lie below both the Neapolitan Yellow Tuff and the Lagno Amendolare, but above the Greenish (Verdoline) layers, gives some credibility to this interpretation. Indeed, the overall order of superposition, chemical composition and estimated ages of the marker layers detected within SA03-11 accords with other tephrostratigraphic schemes from the central Mediterranean (Table 1), indicating that a fairly continuous record of tephra deposition is preserved in the mid-Adriatic over the course of the last 39,000 years.

***5.3 Limitations with current chemical data-bases***

The limitations of the tephra chemical ‘fingerprinting’ approach used to correlate tephra layers and to assign them to specific eruption events are well rehearsed (Lowe, 2011), and in this region it is only in a minority of cases that comprehensive, standardised chemical information is available from both proximal and distal deposits derived from the same eruption event (see Smith *et al*., 2011; Albert *et al*., 2012). There is therefore very limited information on which to assess the degree of chemical gradation or variations that may characterise proximal-distal transects. An inability to assign individual tephra layers to specific eruption events may therefore reflect paucity of relevant data in the literature, which frequently frustrates the tephrostratigraphical correlation process.

Of the 28 tephra layers defined for the SA03-11 sequence where primary deposition can be determined (Table 1), 4 have been classified as ‘unknown’, because they could not be assigned to specific eruptions within the chemical clusters defined in the existing RESET data-base. Detailed cryptotephra investigations carried out on the PRAD 1-2 sequence and other records in the Adriatic (Bourne *et al*., 2010; Bourne, 2012) have generated similar results. Whether these also reflect gaps in the chemical training set or in the records of eruption events (for example, eruptions not represented in proximal records) is difficult to judge, but clearly merits further attention, as this may amplify the volcanic history of the region. For example, several distal ash layers that match Campi Flegrei chemistry have now been identified within the period approximately 33-28 ka, which encompasses the Y3 layer (Albert *et al*., 2014), and while these cannot yet be firmly matched with proximal deposits, there is growing evidence that indicates that the Campi Flegrei was more active during that period than previously realised.

***5.4 Implications for future tephrochronological studies***

While expansion and further exploration of proximal tephra data-sets and their links to distal settings in the central Mediterranean must remain the priority for future tephrochronological research in this region, it is clear that due to the factors outlined above, these resources are unlikely to be able to identify and confidently assign correlations to all distal ash layers in the near future. Even if comprehensive records of all eruptions can be collated it is also likely that the products of some eruptions will not be able to be divided based on their major-element chemical signatures, while the small and highly vesicular shards reported here (with available analytical surfaces frequently less than 10µm in size) make obtaining trace element data problematic (Tomlinson *et al*., 2010; Pearce *et al*., 2011). In sections 4 and 5.2 we have identified key marker layers (the Plinian eruptions of Vesuvius) and then used these to provide a delimiting framework for the SA03-11 sequence. We suggest that in future tephra studies in the central Mediterranean, one of the most important factors when attempting correlations should be the formal consideration of the order in which ash layers are detected, utilising well-dated, chemically distinctive ash layers from less productive volcanic systems (the key marker tephras), and their relationships to chemically similar and thus less distinctive ash layers. We suggest that the Plinian eruptions of Vesuvius hold this potential as do the Solchiaro (Procida Island) and Biancavilla (Etna) layers. However, two periods in the timeframe of this study appear to hold few robustly characterised key marker layers and thus are in need of further refinement: a) the period 9-0 ka, and b) the period between the Campanian Ignimbrite and Codola eruptions (c. 39-33 ka). It is possible that during the more recent period specific eruptions from Ischia, the Aeolian Islands, and the sub-Plinian eruptions of Vesuvius will be critical for the discrimination of Campi Flegrei ash layers, while in the older period the layers identified here that are thought to relate to the Aeolian Islands (Lipari and Vulcano) may be crucial. Both time periods require further study before this potential can be fully realised.

***5.5 Implications of the SA03-11 Tephrochronology***

An age model for the SA03-11 sequence was constructed using Oxcal v4.2 (Bronk Ramsay, 2008 2009, Bronk Ramsey and Lee 2013) based on the tephrostratigraphical results outlined in earlier sections of this paper (Figure 15). The model was constructed using an ‘event-free’ stratigraphic approach where any turbidite structures were removed from the total stratigraphic depth. This was undertaken as these were considered to represent geologically instantaneous deposition and thus would skew the modelled age-depth relationship produced. The original and ‘event-free’ depths for each layer are presented in table 2. The details of the specific age model construction are supplied in the supplementary information. In the cases of cryptotephra layers, corresponding eruption events included within the model align with the position of peak tephra content in each layer, and for visible ash layers the eruption events equate with the base of each layer. The ages assigned to each tephra layer used in the age model are what were judged to be the most robust age estimates reported in the literature for each eruption event (Table 2 and discussed in section 4), with preference given to dates obtained from terrestrial settings to avoid such problems as marine radiocarbon reservoir effects. Where no prior dates exist for an identified tephra layer, a posterior age estimate was interpolated from the final age model (Table 2).

Nine radiocarbon dates obtained from planktonic foraminifera extracted from the SA03-11 core sequence have been incorporated into the model. Their ages were calibrated using the Marine13 calibration curve (Reimer *et al*., 2013) with the specific local marine reservoir offset (R) calculations of Siani *et al.* (2001), who used many of the same ash layers as those reported here to calculate reservoir offsets specific to the Southern Adriatic. There is good agreement between the SA03-11 radiocarbon dates with marine reservoir correction and the tephra-derived dates back to 21 cal ka BP (the age of the Pomici di Base tephra and the lower limit of Siani *et al*.’s data). Below this level, mean R calculations for the Adriatic were employed (R = 73±34), but there is some divergence between the independent tephra-based ages and the radiocarbon dates older than 33ka. If the SA03-11 radiocarbon determinations are robust, then these new results suggest that R variations in the Adriatic for the period c. 40-33 ka were of a similar magnitude to those determined by Siani et al. (2001). R values were most likely lower than the present day (*i.e*. closer to atmospheric values) for the period 35-33 ka BP.

1. ***Conclusions***

The tephra data derived from SA03-11 demonstrate that there are significant advantages to undertaking cryptotephra studies when attempting to construct chronologies for palaeoenvironmental records, particularly those derived from marine sequences. Our new data confirm the findings of previous investigations that have included procedures for the detection of cryptotephra layers (e.g. Bourne *et al*., 2010): a significantly greater number of tephra layers is available for correlation purposes than has previously been recognised. What is more, some cryptotephra layers have distinctive chemical fingerprints and, where available, robust ages can be imported from terrestrial to marine sequences, thereby bypassing the reservoir problems that afflict marine-based radiocarbon dates.

In summary, the key outcomes of the data reported in this contribution are as follows:

* 40 peak concentrations in glass shard concentration have been identified which represent 28 discrete tephra layers, from which a total of 1445 individual chemical measurements have been obtained. Ten of these layers are visible in the core, but 18 are cryptotephra layers. This significantly adds to the number of tephra layers previously recognised in the Southern Adriatic and demonstrates the value of including procedures for the detection of cryptotephra layers in studies of marine records in the Mediterranean.
* The new chemical data reported here augment the collective chemical data-base that supports the interpretation and correlation of Mediterranean tephra layers; the new data are available to the wider community via the RESET database (http://c14.arch.ox.ac.uk/reset/).
* The majority of the ash layers reported in this study originated from the Campi Flegrei volcanic centre, which are difficult to discriminate on the basis of chemical analysis. More distinctive marker layers were sourced from Vesuvius and the Aeolian Islands, while a distal occurrence of a shoshonitic tephra layer from Vulcano (T1567) dated to c. 35,000 cal. BP is also reported. These offer greater potential for the establishment of a regional tephra lattice, to underpin marine core correlations.
* The tephra results underpin a revised age-depth model for the SA03-11 record, using the most precise chronological data available. The most robust part of the revised chronology is that for the last glacial-interglacial transition (LGIT), for which centennial-scale resolution is achieved. The chronological uncertainties for the older part of the sequence are of millennial scale, as fewer of the older ash layers have robust ages, while some appear to be unreliable (e.g. VrA).
* This research demonstrates how temporally-varying R values can be derived for marine sectors to improve the radiocarbon chronology of marine events. It also shows the potential of importing terrestrially-based radiocarbon age estimates into marine sequences using tephrostratigraphical correlations. This may provide a more secure basis for dating marine sequences within the limits of the radiocarbon timescale.

***Acknowledgements***

The initial research (2004-2005) was funded by the Consiglio Nationale delle Ricerche, ISMAR, Bologna (project source ref. 339/D), while research carried out post-2009 was funded mainly via the UK Natural Environment Research Council (NERC)-funded RESET consortium project, code: NE/E015670/1. We would like to extend thanks to Victoria Smith and Norman Charnley of Oxford University and Christopher Hayward of the University of Edinburgh for access to, and assistance with, EPMA chemical analysis.

***Table Captions***

Table 1. Summary of tephra layers identified within SA03-11 including: quantified shard numbers; number of EPMA data points obtained; identified volcanic source region; chemical classification of shards, where possible (based on Le Bas et al., 1986); correlations that have been made in relation to published literature – marine (MD90-917, Siani et al. 2004; and PRAD1-2, Bourne et al. 2010) and/or terrestrial (Lago Grande di Monticchio, LGdM, Wulf et al. 2004) equivalents – and the most likely proximal correlative. Volcanic source region coding: AI: Aeolian Islands, CF: Campi Flegrei, I: Ischia, S-V: Somma-Vesuvius. Chemical classification coding: B: Basaltic, L: Latite, TP: Tephri-phonolite, Tr: Trachyte, TrD: Trachydacite, P: Phonolite, R: Rhyolite, TA: Trachy-andesite, TP: Trachy-phonolite, Sh: Shoshonite. Data entries in italics reflect peaks in glass shard numbers which were chemically characterised but were later determined to reflect re-working of the primary eruptive event.

Table 2 Summary of chemically characterised ash layers from SA03-11 and their proposed correlatives. The SA03-11 T code relates directly to the associated information in the text, whereas the event-free tephra depth has been calculated by removing event layers, such as turbidites, to provide a more robust age-depth relationship for the core. References for the published tephra ages can be found in the text associated with each tephra layer. Radiocarbon dates were calibrated using OxCal Version 4.2, Bronk Ramsey, 2008 (see supplementary data for details of age model construction) and the IntCal13 and Marine13 calibration curves (Reimer et al., 2013). Entries in italics are those which have no known correlative or, based on sedimentological and chemical data, are considered to represent deposition by secondary processes. \*Age range is based on extrapolation below the last independently-dated level and is likely to be too young.

***Figure Captions***

Figure 1. Chirp sonar cross-profiles (scale exaggeration is 34) of contourite deposits on the floor of the South Adriatic basin, from which Core SA03-11 was retrieved. Core penetration (19.5m from sediment surface) is shown as a red bar on both profiles. GS signifies an area of disturbed deposits caused by the Gondola Slide (Minisini et al., 2006). Both profiles illustrate how, with the exception of the GS, parallel sediment (mud) bedding reflects the flow of bottom-hugging currents against the northern flank of the Dauno Seamount (right side). Core SA03-11 was obtained from the part of the profile where the beds are most uniform. Note how the beds are attenuated in the moat which parallels the northern margin of the seamount. Multibeam bathymetric mapping (upper left) revealed the spatial distribution of the moat around the relief of the Dauno Seamount, which served to guide the positioning of the seismic profiles.

Figure 2. Stratigraphy, oxygen isotopes values, magnetic susceptibility and shard counts from SA03-11 and SA03-12SW. Shard counts are given as numbers of shards per gram of dry sediment and in section c. are limited on the diagram to a maximum of 10,000 shards in order to draw out the detail of the cryptotephra layers. The detailed shard counts and magnetic susceptibility values for SA03-12SW are presented in d-e, while total shard numbers for the three tephra zones identified above 500cm are presented in f-h.

Figure 3: Total alkali vs. silica plot (Le Bas et al., 1986) for SA03-11 tephra layers A)Ash layers between present time and 9.25 ka BP B) Ash layers within the last glacial-interglacial transition (LGIT); and C) Ash layers within MIS-2 and MIS-3.

Figure 4: Comparison of SA03-11 tephra layers with distinctive groupings of ash layers determined by alkali data. Volcanic system 1=Aeolian, 2=Campanian Volcanic Zone, 3=Ischia, 4=Pantelleria, 5=Etna, 6=Procida and 7=Alban Hills (Diagram reproduced from Paterne et al.,1988 and Wulf et al., 2004). A)Ash layers between present time and 9.25 ka BP B) Ash layers within the last glacial-interglacial transition (LGIT) and C) Ash layers within MIS-2 and MIS-3.

Figure 5: Comparison of T12 and T41 with the Monte Nuovo data of Smith et al., (2011) and the AD472 data of Santacroce et al. (2008) and layers correlated to the AD472 eruption by Wulf et al., (2012) (TM-2b) and Vogel et al. (2010) (OT0702-1).

Figure 6: Comparison of T41, T113-153 and T162 with the TM-5 data from LGdM (Wulf et al., 2004). This is compared to the field (light grey) of AMS from Smith et al. (2011).

Figure 7: Comparison of SA03-11 tephra layers T171 and T247 with distinctive groupings of ash layers determined by alkali data. Volcanic system 1=Aeolian, 2=Ischia, 3=Campanian Volcanic Zone. Within the Campanian Volcanic Zone 4=AMS eruption data from Smith et al., (2011) (Diagram reproduced from Paterne et al., 1988 and Wulf et al., 2004). Also shown are the data for TM-5-1 and TM-5-2 from Wulf et al. (2008).

Figure 8: Comparison of visible layer T363 and the 8 layers preceding it in SA03-11 with the TM-6a and TM-6b data of Wulf et al., (2004) and the Mercato proximal data from Santacroce et al., (2008). The Pomici Prinicapali field is compiled from Campi Flegrei proximal data from Tomlinson et al., (2012) and Smith et al., (2011) and from LGdM layer TM-7b (Wulf et al., 2004).

Figure 9: A) Comparison of layers T419 – T492 in SA03-11 correlated to the Pomici Principali eruption of the Campi Flegrei and the comparison of T627-640 with layers correlated to the NYT. B) Comparison of T531 with layers correlated to the La Pigna eruption. TM data from Wulf et al., (2004, 2008), PRAD-218 data from Bourne et al., (2010) and Pomici Princiali and La Pigna data from Smith et al., (2011).

Figure 10: Biplots showing the correlation of layers T646, T651, T730 and T760 to pre NYT eruptions from the Campi Flegrei.

Figure 11: Biplots showing correlation of SA03-11 tephra layers T865, T950 and T1463 to tephra layers present in Lago Grande di Monticchio that have been correlated to eruptions of Vesuvius (Wulf et al., 2004, 2008).

Figure 12: FeO vs CaO biplot showing the comparison on T1226, T1327 and T1426 to layers associated with the Y-3 Mediterranean marker layer. PRAD-1332 from Bourne et al., (2010), PRAD 1474 (this study), TM-14-3 and TM-15 from Wulf et al., (2004) and Wulf et al., (2012). SMP1-e data and Y-3 field from Albert et al. (2014) and Vra and Vrb data from Tomlinson et al. (2012).

Figure 13: Comparison of SA03-11 layers T1522, T1535 and T1598 with TM-18 (The Campanian Ignimbrite) from Wulf et al., (2004). Data from the E-11 eruption of Paterne et al. (1988) are shown for comparison with a population of T1535.

Figure 14: Comparison of T1567 with LGdM tephra layers corrected to Procida eruptions (Wulf et al., 2012) and with the Upper TGR eruption of Vulcano from Albert et al., (2012).

Figure 15: 95.4% confidence Highest Probability Density output for the Bayesian age/depth model for the SA03-11 sequence (run using a Poisson process model: see supplementary information for further details). The model was constructed using the best constrained age estimates for the tephra layers identified in the sequence (Table 1).

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