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TEPHROSTRATIGRAPHY OF MARINE CORE AD91-17 (ADRIATIC SEA) REVISED

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ABSTRACT: Revision of the tephrostratigraphy previously proposed for the marine core AD91-17 (Adriatic Sea), supported by energy-dispersive-spectrometry (EDS) chemical data, has allowed to challenge previous interpretation and proposed a core chronology on the basis of new tephrochronological data. Four different tephra layers were identified and correlated with known eruption from southern Italian volcanoes. The upper tephra layer was tentatively correlated with AD 1631eruption from Somma-Vesuvius, specifically using chemical composition of pyroxenes. The second one (actually represented by two distinct layers), due to pervasive alteration of glass shards, is difficult to be correlated even if is attributed to Somma-Vesuvius volcano. Close to sapropel S1 interruption a rhyolitic layer was correlated to E1/Gabellotto-Fiumebianco eruption from Lipari (Aeolian Islands). The lowermost tephra layers are correlated to the Mercato eruption (Somma-Vesuivus). This seems to confirm the multiple occurrence of Mercato distal deposits in distal areas, as testified by other findings in Mediterranean cores. This suggests that this eruption is probably more complex than previously hypothesised, and characterised by at least two phases fed by the same phonolitic magma.

Keywords: Tephrostratigraphy, Adriatic core, Holocene, Vesuvius.

1. INTRODUCTION

Tephrostratigraphy is a volcanology-Quaternary science cross-field method that deals with the detailed study of volcanic successions and ash layers in Quaternary archives and their correlation with parental eruptions or known distal tephra. The study of tephra layers in distal setting is an important source of information for the study of volcanic ash dispersion, for dating and correlating stratigraphic successions and events in paleoclimatology and archaeological researches (Lowe, 2011).

The Mediterranean region with a remarkable explosive volcanic activity characterised by an unique wide chemical compositional variability (Peccerillo, 2005), is an ideal area for tephrostratigraphic study (e.g. Keller et al., 1978; Paterne et al., 1988, 2008; Narcisi & Vezzoli, 1999; Siani et al., 2004; Sulpizio et al., 2010b; Zanchetta et al., 2011; Giaccio et al., 2012; Insinga et al., 2014).

The aim of this paper is to study the tephra layers found in AD91-17 core (Fig. 1), proposing an accurate correlation to parental eruptions and improving the core chronology proposed by Sangiorgi et al. (2003), partly based on stratigraphic position of the tephra layers in the core but not supported by tephra composition data.

2. STUDY AREA AND CORE DESCRIPTION

Core AD91-17 was collected in the south Adriatic Sea (40°52.17 N, 18°38.15 E), during the AD91 cruise, performed by the R/V Minerva from 5 to 21 March 1991, at a depth of 844 m below sea level. (Fig. 1). The area is well suited to recognizing explosive activity because of its downwind position and proximity to the southern Italian volcanoes (Siani et al., 2004; Caron et al., 2012). Indeed, in the central Mediterranean the dominant wind direction is W-E, and in some case W-ENE (Barberi et al., 1991; Sulpizio et al., 2008). The core has a total length of 330 cm (Fig. 2). It consists of olive-grey hemipelagic mud from the base to 200 cm, interbedded by two turbiditic layers (T1: 200-196 cm and T2: 318-307 cm). According to Giunta et al. (2003) T1 coincides with a hiatus, which probably comprises part of the Late Glacial, including the Younger Dryas. Instead, the Sapropel S1 is recognized from 190 to 125

Fig. 1 - Core location and position of other cores quoted in the text.

cm. It shows laminations and a grey colour. From 160 to 156 cm there is a massive lighter interval corresponding to the sapropel interruption and from 125 cm to the core top the lithology consists of olive-grey hemipelagic mud (Giunta et al., 2003).

Multiproxy studies have been carried out on the AD91-17 core (Jorissen, 1999; Capotondi and Morigi, 1996; Capotondi et al., 1999; Vigliotti et al., 2011). In the frame of this work it is useful to mention the palaeomagnetic study, which has included the magnetic susceptibility, natural remnant magnetisation (NRM) and the anhysteretic remanence (ARM) measurement (Vigliotti et al., 2011).

Chronology of the core has been based on five accelerator mass spectrometry (AMS) ^{14}C ages. Further indirect chronological constraints for the basal part of the core AD91-17, were based on its correlation with *Globigerina bulloides* δ^{18}O record from core MD90-917 (South Adriatic Sea) (Sangiorgi et al., 2003; Giunta et al., 2003), which was dated by means of a higher number of ^{14}C AMS dates (Siani et al., 2001). The same climatic expression and similar δ^{18}O were recognized in the two cores, which were collected very close to each other (Giunta et al., 2003). In the study of Sangiorgi et al. (2003) 3 tephra layers have been identified by visual inspection at a depth of 1, 170 and 195 cm. An additional tephra (A1 in Giunta et al., 2003) was closely dated by radiocarbon but no correlation was proposed. Based on their stratigraphic position and by comparison with other cores, the former three layers were attributed to known eruptions from the Campanian area. Considering the dispersal axis of the tephras and the ^{14}C dating, they have been correlated to the Agnano Pomici Principali eruption of Campi Flegrei (195 cm), to the Mercato-Ottaviano eruption from Somma-Vesuvius (170 cm) and to the AD 472 eruption of Somma-Vesuvio (1 cm). Two magnetic susceptibility peaks were found at 39 and 73 cm and have been associated respectively to “Avellino” eruption from Somma-Vesuvius (Sulpizio et al., 2010a) tephra and “Agnano Monte Spina” tephra from Campi Flegrei (e.g. Di Vito et al., 1999). However, none of these latter peaks were used as chronological tie points (Sangiorgi et al., 2003). From Figure 2 it is possible to observe that there is no an obvious correlation between tephra layers and the magnetic susceptibility peak and from a methodological point of view it is important to stress that the correlations were not based on any chemical analysis.

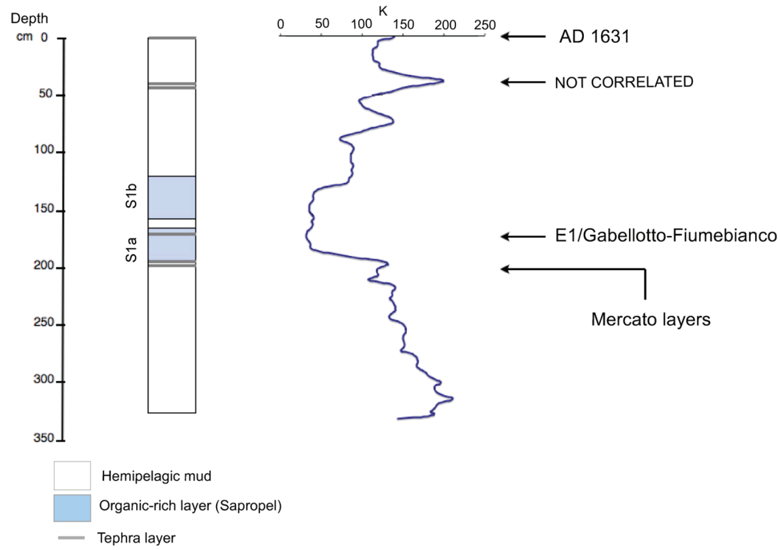

Fig. 2 - Core lithology, magnetic susceptibility (K, 10-5 SI units) and tephra position in AD91-17.

3. MATERIAL AND METHODS

For this work we used seven samples, previously sieved at 63 µm for micropaleontological studies, at 1 cm, 41 cm, 45 cm, 171 cm, 191 cm, 196 cm and 321 cm of depth. The samples were selected under binocular microscope on the basis of the observed glass shards, scoriae and lithic abundances. Then, the samples were embedded in epoxy resin, polished and screened for glass shards and micro-pumice fragments using scanning electron microscopy (SEM) coupled with an energy-dispersive-spectrometry (EDS). Chemical analyses of glass shards and micro-pumice fragments were performed using an EDAX-DX micro-analyser mounted on a Philips SEM 515 at the Dipartimento di Scienze della Terra, University of Pisa employing a 20 kV acceleration voltage, 100 s live time counting, 2100-2400 shots per second, and ZAF correction. The ZAF correction procedure does not include natural or synthetic standards for reference, and requires the results to be normalized to a given value (which was chosen at 100%). In particular two standards with chemistry accurately obtained using XRF analyses are routinely analyzed in the Pisa laboratory: a trachyte glass from Campi Flegrei (CR1) and an Albite (Marianelli & Sbrana, 1998). To avoid alkali loss, especially Na, a window spot usually with side ca 10 µm is used. Owing to the different shape and size of glass shard a smaller size can be used and this can influence analytical data (Hunt & Hill, 2001). However, this is minimized by the selection of the bigger shards and having the possibility to analyses many different shards from the same sample. Analytical precision is 0.5 % for abundances higher than 15 wt. %, 1 % for abundances around 5 wt. %, 5 % for abundances of 1 wt. %, and less than 20 % for abundances close to the detection limit (around 0.5 wt. %) (Marianelli & Sbrana, 1998). Several trials for comparing the performance of Pisa SEM-EDS with the wave dispersion spectroscopy (WDS) have been extensively discussed by Cioni et al. (1998), Marianelli & Sbrana (1998), Vogel et al. (2010), Sulpizio et al. (2010b) and Caron et al. (2010), indicating comparable performances on major elements. As basis for chemical correlation the data set of Santacroce et al. (2008), which is the collection of many years of analytical work on proximal deposits on Somma-Vesuvius, was used having the advantage to be produced in the Pisa laboratory with the same analytical equipment.

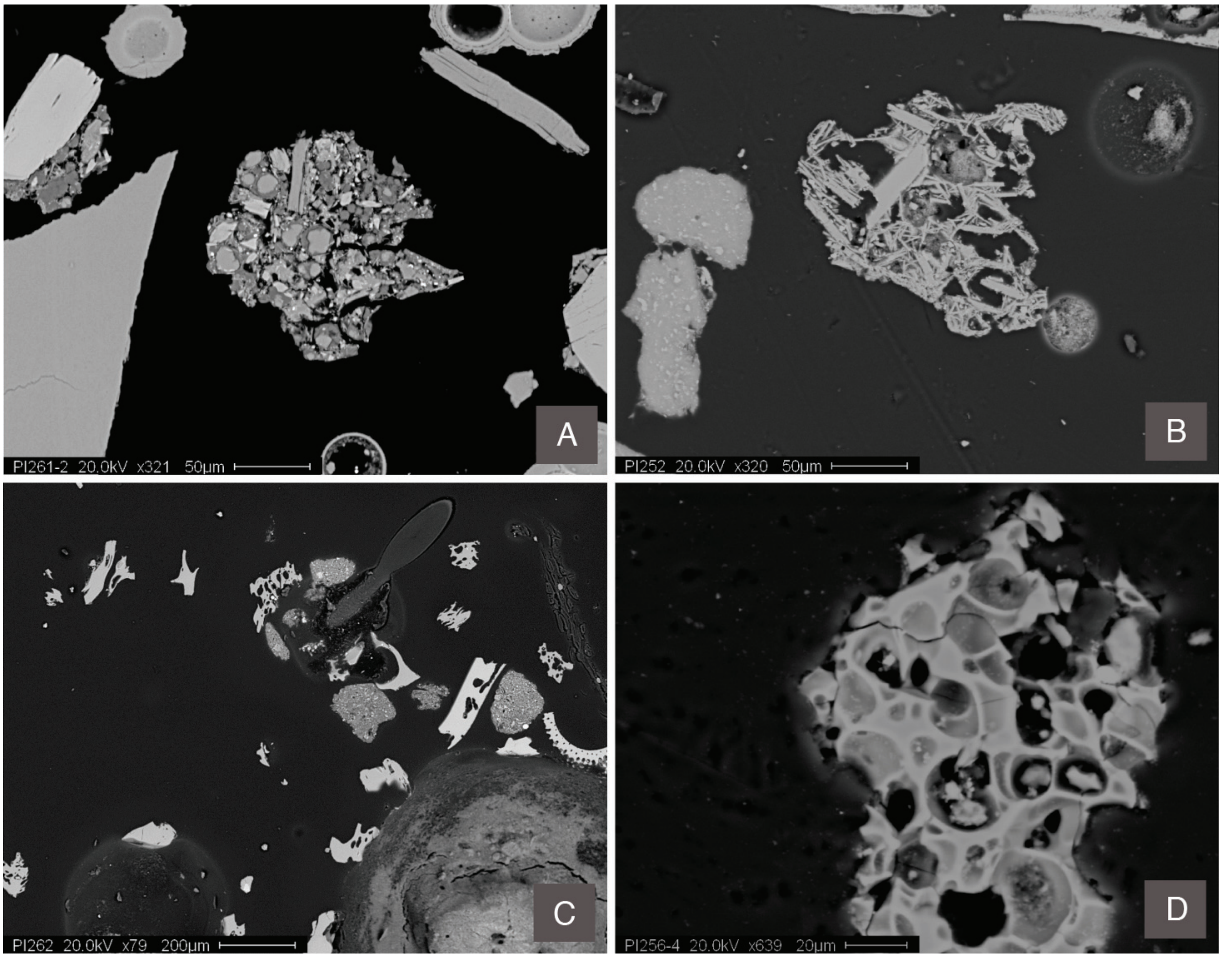

Fig. 3 -Tephra morphology by SEM-EDS. (A) Layer 0-1 cm, (B) layer 40-41, (C) layer 170-171 cm and (D) layer 190/195 cm depth.

4. RESULTS AND DISCUSSION

4.1 Tephra correlation

Tephra 1 cm depth

The topmost tephra layer does not contain any volcanic glass suitable for analyses. Morphologically, volcanic fragments were observed as an aggregate of minerals (Fig. 3A). Therefore, we analysed only mineral phases found in the samples, with particular attention to pyroxene crystals. The pyroxene compositions in the Wo-En-Fe diagram is shown in fig. 4 (Table 2). This compositional range is common to most of the pyroxenes from Somma-Vesuvius products. In particular, the geochemical data suggest a correlation to the field defined by the AD 1631 pyroxenes (Santacroce, 1987; Cioni et al., 1998; and unpublished data, Fig. 4). For comparison in the Figure 4 data from 1944 and 1906 eruptions from Somma-Vesuvius are shown along with the compositional field defined by AD 1631.

Tephra layers at 40-41 cm and 45-46 cm

The SEM observation for the two layers at 41 cm and 46 cm depth showed that glass phase was too altered (Fig. 3B) and it was not possible to perform any analysis on volcanic glass with confidence. However, analyses allowed to identify the presence of sodalite. Having no reliable glass compositions, a tentative correlation of this tephra layer, must be made making some consideration, such as the stratigraphic position of the layers and the aspect of the sediment seen with the optical microscope, albeit it is largely speculative. Sodalite is frequent in the Vesuvian products of the AD 472, Avellino, and/or the AP products (Santacroce et al., 2008; Zanchetta et al., 2011). However, this felspatoid is also reported in some lavas of Campi Flegrei and different magmatic rock from Ischia (Melluso et al., 2012,2014), but not in pyroclastic deposits.

Observations using the optical microscope, showed altered pumice of a very dark colour in both layers. This would suggest to attribute this layer to the Pollena AD 472 products rather than Avellino ones. Indeed, while the less evolved Avellino deposits are also described as dark pumices, they are very glassy also in distal deposit (Sulpizio et al., 2008, 2010a). On the contrary, the Pollena AD 472 deposits contain very dark juvenile fragments with a crystal rich matrix also on distal reaches (Sulpizio et al., 2010a; Vogel et al., 2010).

	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	ClO	Total
170-171 cm											
	74.71	0.17	13.69	1.50	0.10	0.14	0.69	3.64	5.08	0.29	100.00
	74.75	0.20	13.72	1.53	0.05	0.24	0.65	3.42	5.11	0.33	100.00
	74.24	0.09	13.76	1.52	0.04	0.15	0.81	4.00	5.10	0.28	100.00
	74.67	0.06	13.79	1.36	0.00	0.27	0.60	3.77	5.22	0.25	100.00
	74.62	0.00	13.46	1.33	0.00	0.25	0.78	4.03	5.25	0.29	100.00
	74.35	0.23	13.57	1.41	0.10	0.34	0.71	3.65	5.26	0.38	100.00
	74.59	0.11	13.59	1.43	0.00	0.24	0.72	3.99	5.04	0.30	100.00
	74.23	0.11	13.69	1.57	0.09	0.21	0.76	3.77	5.19	0.38	100.00
	74.24	0.15	13.54	1.48	0.16	0.29	0.75	3.95	5.20	0.24	100.00
	74.28	0.00	13.88	1.38	0.00	0.36	0.71	4.05	5.08	0.26	100.00
	74.49	0.05	13.90	1.30	0.00	0.26	0.67	4.02	5.05	0.67	100.00
190-191 cm											
	58.87	0.00	21.85	1.76	0.00	0.19	1.84	8.09	6.88	0.53	100.00
	57.66	0.31	21.80	1.81	0.32	0.42	1.68	8.60	6.82	0.57	100.00
	58.43	0.19	21.82	2.04	0.23	0.13	1.58	8.21	6.89	0.48	100.00
	58.57	0.16	21.86	1.75	0.16	0.18	1.62	8.23	7.01	0.48	100.00
	58.51	0.16	22.13	1.74	0.15	0.24	1.71	7.90	6.93	0.52	100.00
	58.90	0.00	21.99	1.63	0.08	0.35	1.72	8.02	6.82	0.48	100.00
	58.87	0.00	21.92	1.68	0.00	0.24	1.54	8.23	7.04	0.48	100.00
	59.40	0.00	22.13	1.66	0.10	0.22	1.90	8.23	5.92	0.43	100.00
	60.81	0.32	21.95	1.29	0.10	0.16	2.80	6.92	5.46	0.20	100.00
	58.06	0.16	22.53	1.51	0.18	0.35	1.64	8.67	6.40	0.50	100.00
	58.50	0.08	21.91	1.73	0.13	0.39	1.54	8.33	6.82	0.57	100.00
	57.80	0.23	22.18	1.62	0.18	0.32	1.14	8.77	7.18	0.56	100.00
	58.91	0.20	21.74	1.74	0.05	0.17	1.60	7.91	7.16	0.54	100.00
	58.30	0.18	21.74	1.82	0.29	0.26	1.72	8.24	6.88	0.56	100.00
195-196 cm											
	58.43	0.00	22.28	1.55	0.05	0.42	1.42	9.57	5.82	0.47	100.00
	58.90	0.13	21.93	2.07	0.09	0.41	1.83	6.41	7.63	0.61	100.00
	58.62	0.15	21.80	1.76	0.22	0.44	1.39	8.31	6.78	0.53	100.00
	58.83	0.19	22.03	1.70	0.31	0.45	1.56	8.22	6.68	0.48	100.00
	57.76	0.10	22.31	1.80	0.15	0.61	2.17	7.46	7.03	0.61	100.00
	58.40	0.00	22.96	1.51	0.00	0.37	1.73	8.07	6.50	0.47	100.00
	58.77	0.16	22.00	1.84	0.18	0.27	1.70	7.90	6.71	0.47	100.00
	58.57	0.24	22.19	1.71	0.21	0.44	1.67	8.18	6.38	0.40	100.00
	58.26	0.14	21.93	1.71	0.19	0.35	1.70	8.92	6.29	0.50	100.00
	58.53	0.19	21.90	1.66	0.11	0.57	1.59	8.30	6.64	0.51	100.00

Table 1 - Major-elements composition of pyroxenes from layer at 1 cm.

On the other hand the age model of Sangiorgi et al. (2003), indicates older ages suggesting the AP eruptions (Andronico & Cioni, 2002).

Therefore, at this stage we just tentatively propose a correlation with Pollena AD 472 for the layer at 45-46 cm. Due to their stratigraphic position, the second layer at 40-41 cm could be thus correlated with AD 512. However, the few data available make these correlations still speculative.

<u>Tephra layer at 170 cm</u>

This layer is rich in volcanic glass shards and micropumices (Fig. 3C) allowing a large number of analyses to be performed (Table 1). In the TAS diagram (Total Alkali Silica) data plot in the rhyolite field (Fig. 5a). Specifically, comparing this layer composition with the data in literature (Fig. 5c; Caron et al., 2012) the correlation to E1/Gabellotto-Fiumebianco deposit is evident. E1 tephra layer is widespread in Mediterranean (Paterne et al., 1988; Siani et al., 2004; Sulpizio et al., 2014) and has been correlated with the activity of Gabellotto-Fiumebianco source on Lipari Island. The age of this tephra has been constrained by radiocarbon dating at 7770 ± 70 yr BP (8730-8400 cal yr BP) by Siani et al. (2004) on a marine core and confirmed by subsequent studies (Caron et al., 2012).

<u>Tephra layers at 190-191 cm and 195-196 cm</u>

The layers found at 190-191 cm and 195-196 cm depth are similar and homogeneous in composition and thus were considered together. Both have abundant vesicular micropumice fragments with thick septa (Fig. 3D) on which several EDS analyses were performed (Table 1). On the TAS diagram these analysis plot in the phonolitic field (Fig. 5b), making it easy the correlation to the Mercato eruption of Somma-Vesuvius

Element	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Total
PI261-3-px	50.16	0.98	5.29	5.91	0.15	13.91	23.60	0.00	0.00	100.00
PI261-4-px	42.11	2.46	11.90	12.29	0.24	7.75	23.13	0.08	0.00	99.96
PI261-5-px	48.77	0.77	6.42	8.15	0.10	11.54	24.25	0.00	0.00	100.00
PI261-7-px	46.83	1.64	8.19	7.37	0.30	12.07	23.47	0.00	0.00	99.87

Table 2 - Major-elements glass chemistry of tephras recognised in core AD91-17.

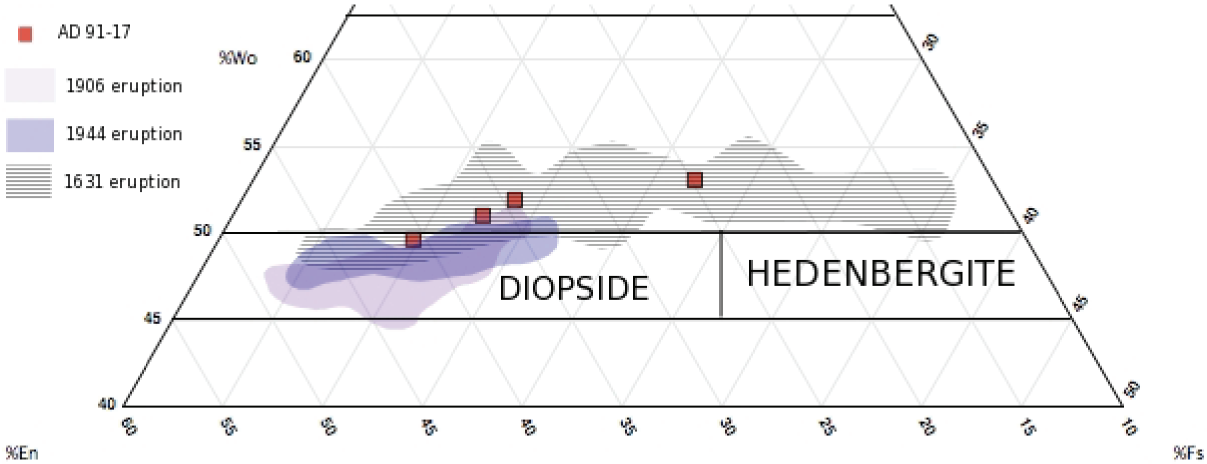

Fig. 4 -Wo-En-Fe ternary diagram of pyroxenes from layer at 1 cm. Data for comparison of 1906, AD 1944 and AD 1631 are also shown. Data from Santacroce, 1987, Santacroce et al., 1993, Cioni et al., 1998 and Marianelli et al., 1999.

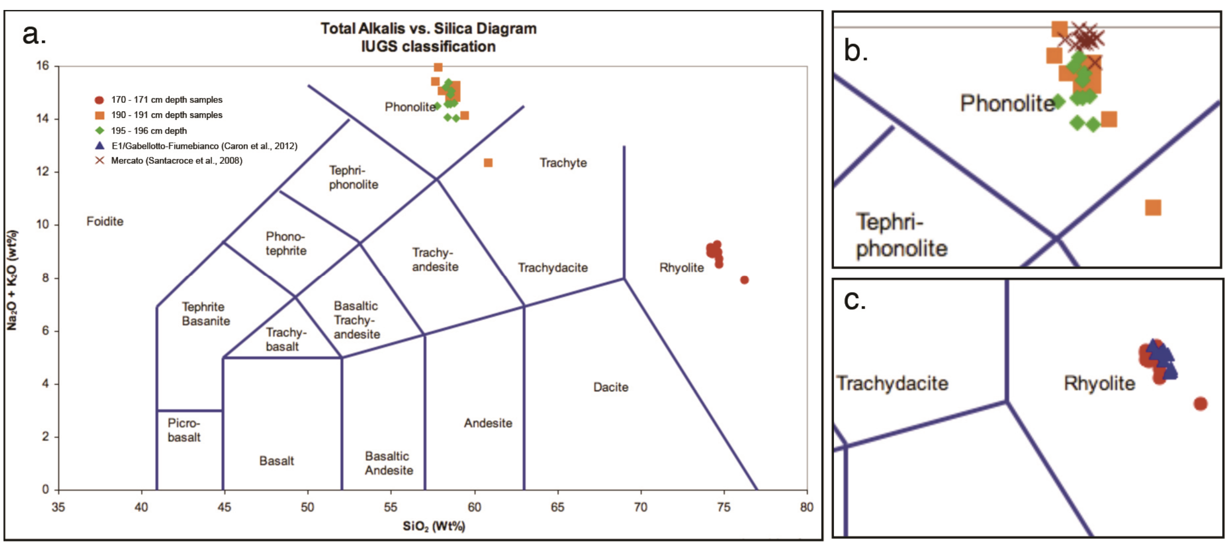

Fig. 5 - Total Alkaly- SiO2 diagram (Le Bas et al., 1986) for the studied tephra layers (a); Comparison with layers at 190-191 and 195-195 cm with Mercato chemical data (Caron, 2009; Caron et al., 2012) (b); Comparision with E1/Gabellotto-Fiumebianco tephra layers (Caron et al., 2012).

(Santacroce et al., 2008; Mele et al., 2011; Fig. 6b), radiocarbon dated at 7770 ± 40 yr BP (8630-8430 cal yr BP; Zanchetta et al., 2011).

4.2. Summary and general implications

Based on the glass and mineral composition as well as on the stratigraphic order of the tephras in the AD91-17 core (Fig. 2), we can propose the following correlations: i) 1 cm depth tephra, AD 1631 eruption of Somma-Vesuvius; ii) for the 41 cm and 45 cm depth tephra layers, no certain correlation can be proposed, but for the stratigraphic position and the presence of sodalite they could be related to the eruptions of AD 472 (Pollena) and AD 512 of Somma-Vesuvius, respectively; iii) 171 cm depth tephra layer, E1/Gabellotto-Fiumebianco eruption of Lipari Island, dated at 8730-8400 cal yr BP (Siani et al., 2004); iv) 191 cm and 195 cm depth tephra layers, Mercato eruption of Somma-Vesuvius dated at 8630-8430 cal yr BP (Zanchetta et al., 2011).

Beside the correlation of the tephra layers to the parental eruptions, it is worth noting that E1 tephra layer is placed just below the interruption in-between sapropel S1 (Fig. 2). This is consistent with the position of tephra E1 in MD90-917 (Siani et al., 2004) and MD90-918 (Caron et al., 2012). Therefore, the present data confirms that E1 tephra layer could be regarded as a good marker for correlating Tyrrhenian, Ionian and Adriatic Sea achieves during the sapropel S1 interruption (Zanchetta et al., 2011), which is correlated with the climatic deterioration recorded at ca. 8.2 ka (Siani et al., 2001).

The two layers sharing the composition of Mercato pyroclasts support the suggestion of Caron et al. (2012)

that in distal setting this eruption is represented by more than one layer. In core MD90-918 they occur at the base of the second sapropel layer (S1b) just above E1 and within the basal part of sapropel (S1a). The lower-most layer occur just below the S1a (Caron et al., 2012). In core AD91-17 one of the Mercato layers is at base of the sapropel S1 and the other one just below the sapropel. Both can correspond to two lower layers identified in Caron et al. (2012). Therefore, the core AD91-17 seems to confirm that at least two eruptive events with identical composition to the products from Mercato eruption are widespread in the Mediterranean archives.

On the basis of the new tephrostratigraphic data, it is therefore questioned the previous correlation proposed by Sangiorgi et al. (2003) of one of these layers to the Agnano Pomici Principali eruption from Campi Flegrei. The Agnano Pomici Principali tephra layer is a good marker of the Younger Dryas interval (Lane et al., 2011), whereas Mercato tephra layers are entirely within the Holocene.

Figure 6 illustrates the difference in age model compared to Sangiorgi et al. (2003). The age model proposed in this work contains the radiocarbon ages from Sangiorgi et al. (2003) and the ages of tephra layers discussed in this work with the exception of tephras at 40 and 46 cm, for which a secure correlation cannot be supported. All the radiocarbon ages are calibrated using updated Marine09 curve in CALIB 6 (Reimer et al., 2009). Differences can be appreciated for the top of the core and for the lower part of the records. The difference from the new age model and that of Sangiorgi et al. (2003), at ca. 190 cm, where the age of Mercato recently proposed by Zanchetta et al. (2011) is imposed to the age model, produces an increase of sedimentation rate and a shorter duration of the lower part of the sapropel S1. In the Sangiorgi's age model the age of this point is directly controlled by a radiocarbon ages, which yielded an older age. We have, however, to note that reservoir effect could be different during different time (Siani et al., 2001), and this can explain this difference. However, more data are necessary to clarify the succession and chronology of the event characterising the Mercato eruption(s). These differences highlighted the importance of tephra layers in improving ages model when tephras are well identified and dated, but also the work needed to improve our knowledge on tephrochronology of the Central Mediterranean.

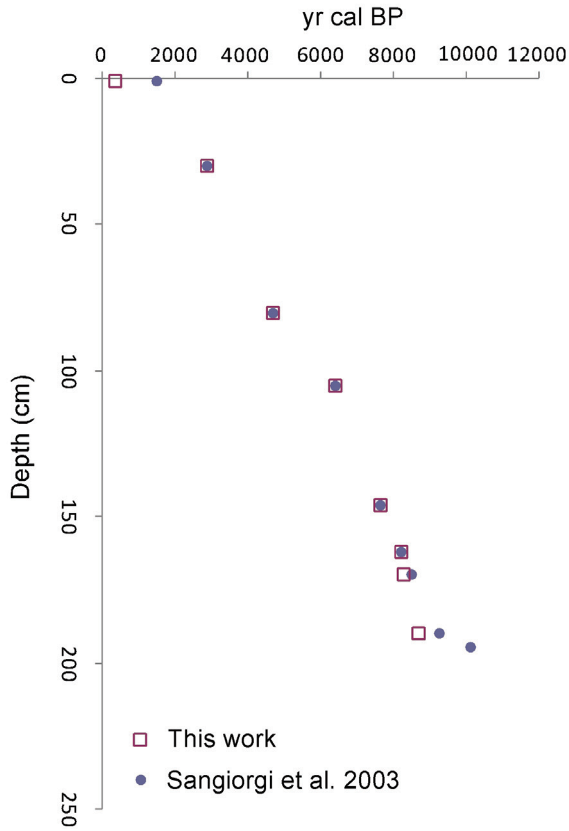

Fig. 6 - Age model from Sangiorgi et al., 2003 and this work. All the radiocarbon data were calibrated according to Reimer et al., 2009.

5. CONCLUSIONS

Data collected in AD91-17 confirm some previous tephrostratigraphic studies in the area, and details the occurrence of some peculiar tephra layers like Gabellotto-Fiumebianco (E1) and Mercato tephra layers. In particular, data of the present study are of particular relevance for the high-resolution Mediterranean tephrostratigraphy, because they confirm that there are multiple eruptive events compositionally indistinguishable from Mercato that occurred in different periods. This makes the chronological use of this tephra marker(s) more complex than suggested in the past and highlights the need to clarify the timing and stratigraphic succession of this eruption on proximal to distal reaches.

The tephra layer E1 is confirmed as an important marker for sapropel interruption, as suggested by Zanchetta et al. (2011) and Caron et al. (2012). In the future, a new detailed stratigraphy for the sapropel S1 interval can emerge and chemical and stratigraphic data will permit a very powerful correlation of the different parts of the sapropel S1 in different sector of Adriatic and Ionian seas.

Finally, this tephrostratigraphic study has questioned some of the previous proposed correlation for tephra from the core AD91-17, that have appreciable impact on the core age-model. More in general, this work indicates and confirms that tephrostratigraphy is a fundamental tool for reefing the chronology of marine cores but that no correlation can be attempted without robust chemical data.

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