

1 **Linking the Mediterranean MIS 5 tephra markers to the Campi Flegrei 109-92 ka**
2 **explosive activity (southern Italy) and refining the chronology of the MIS 5c-d**
3 **millennial-scale climate variability**

4
5 Monaco, L.^{1,*}, Giaccio, B.²⁻³, Palladino, D.M.¹, Albert, P.G.⁴, Arienzo, I.⁶, Conticelli, S.²⁻⁷, Di Vito, M.⁵,
6 Fabbrizio, A.⁸, D'Antonio, M.⁹, Isaia, R.⁵, Manning, C.J.¹⁰, Nomade, S.¹¹, Pereira, A.¹², Petrosino, P.⁹,
7 Sottili, G.¹, Sulpizio, R.¹³, Zanchetta, G.²⁻⁷⁻¹⁴.

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9 *1 Dipartimento di Scienze della Terra, "Sapienza" Università di Roma, Rome, Italy*

10 *2 Istituto di Geologia Ambientale e Geoingegneria, CNR, Rome, Italy*

11 *3 Istituto Nazionale di Geofisica e Vulcanologia, INGV, Rome, Italy*

12 *4 Department of Geography, Swansea University, Swansea, UK*

13 *5 Istituto Nazionale di Geofisica e Vulcanologia, INGV-Osservatorio Vesuviano, Naples, Italy*

14 *6 Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Florence, Italy*

15 *7 Istituto di Geologia Ambientale e Geoingegneria, IGAG-CNR, Rome, Italy*

16 *8 Institute of Petrology and Structural Geology, Faculty of Science, Charles University, Albertov 6, 12843 Prague, Czech Republic*

17 *9 Dipartimento di Scienze della Terra, delle Risorse e dell'Ambiente, Università degli Studi di Napoli Federico II, Naples, Italy*

18 *10 Department of Earth Sciences, Royal Holloway, University of London, Egham, UK*

19 *11 Laboratoire de Sciences du Climat et de l'Environnement, UMR 8212, CEA-UVSQ, IPSL and Université de Paris-Saclay, Gif-sur-*

20 *Yvette, France*

21 *12 Université Paris-Saclay, CNRS, UMR 8148 GEOPS, Orsay, 91405, France*

22 *13 Dipartimento di Scienze della Terra e Geoambientali, Aldo Moro-University of Bari, Bari, Italy*

23 *14 Dipartimento di Scienze della Terra, Università di Pisa, Pisa, Italy*

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27 **ABSTRACT**

28 **Explosive activity preceding the ~40 ka Campanian Ignimbrite (CI) eruption in the Neapolitan volcanic**
29 **area, Southern Italy, has long been speculated based on the occurrences of widespread tephra layers,**
30 **with a Campanian geochemical signature, such as the C-22, X-5, and X-6, preserved in Mediterranean**
31 **Marine Isotope Stage (MIS) 5 sedimentary records. However, previous studies of pre-CI pyroclastic**
32 **units occurring in close proximity of the Neapolitan volcanoes, including Campi Flegrei, Somma-**
33 **Vesuvius, Ischia and Procida islands, did not allow a conclusive identification of the near-source**
34 **equivalents of these tephra markers. Here we present a comprehensive characterisation of four**
35 **pyroclastic units from the Campanian Plain, comprising major and trace element glass compositions,**
36 **Sr-Nd isotopes and ⁴⁰Ar/³⁹Ar dating. Our data allowed the identification of the medial equivalents of**
37 **the MIS 5 tephra markers, including the widespread C-22, X-5, and X-6 tephra, and their assignment to**
38 **previously undocumented Campi Flegrei activity between 109-92 ka. In addition to substantially**
39 **extending Campi Flegrei explosive activity deeper in time, and thus providing the basis for a**
40 **reevaluation of its history, our findings provide new precise radioisotopic dating to better constrain the**
41 **chronology of the millennial scale climatic oscillations of the MIS 5c-d in the Mediterranean area and**
42 **possibly on a larger scale.**

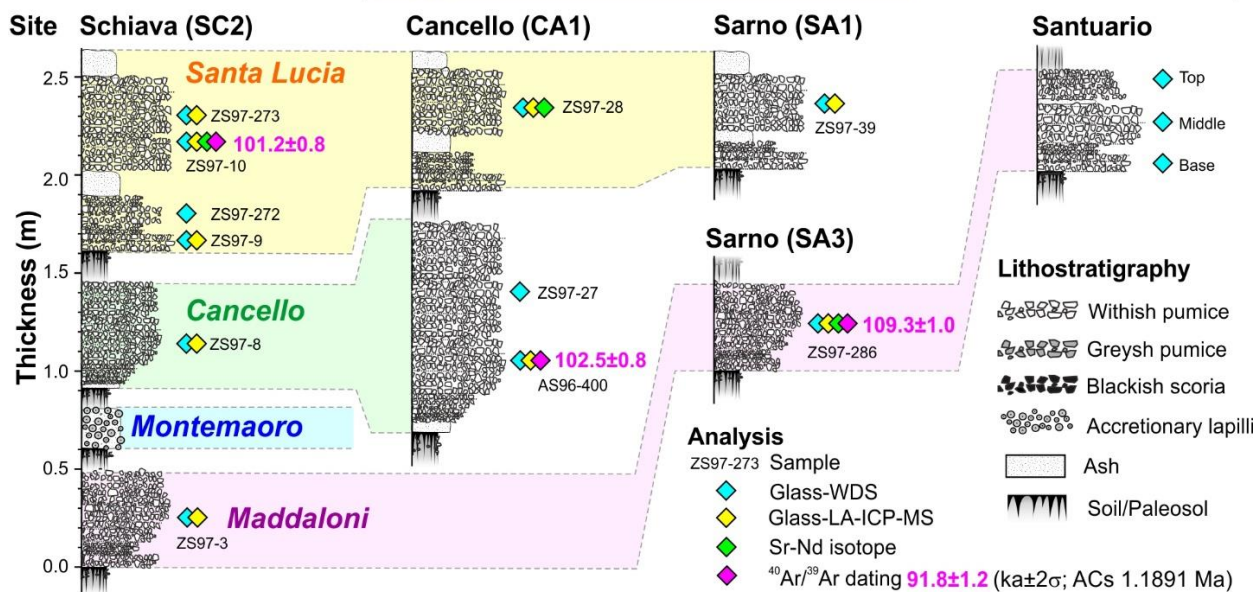
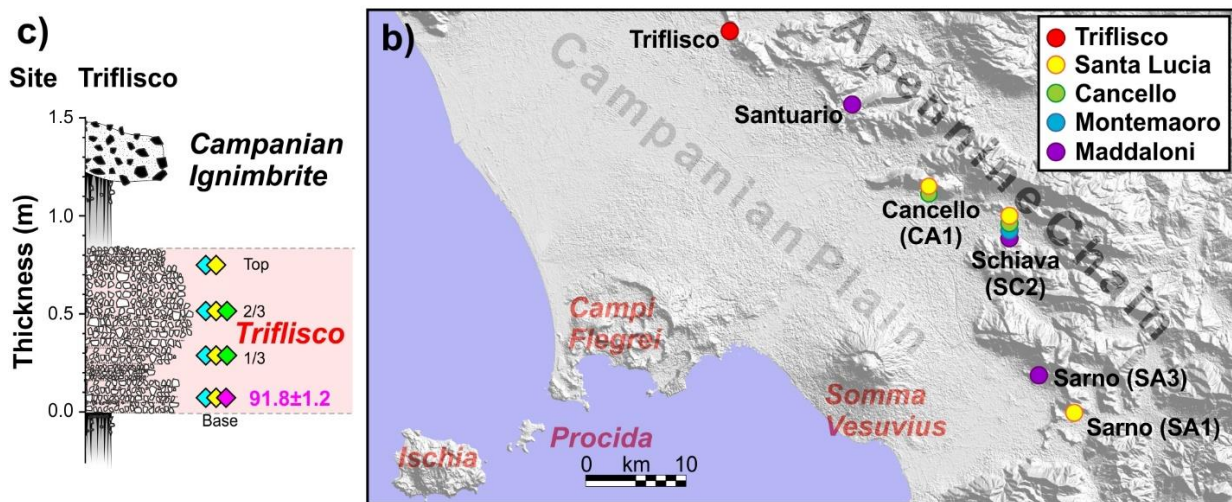
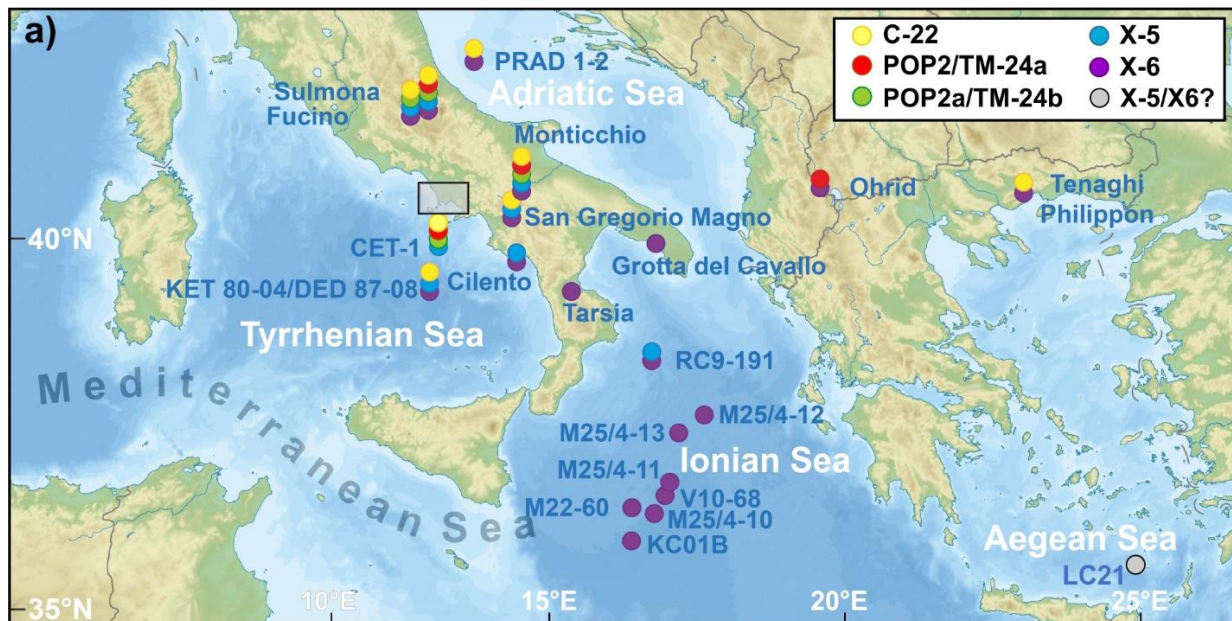
43 1. Introduction

44 Near-vent volcanic successions provide fundamental information for reconstructing the eruption history
45 and dynamics of volcanoes. Proximal exposures, however, often give only fragmentary records of the past
46 activity of a volcanic system, since deposits of older explosive events can be eroded, not preserved or, more
47 commonly, covered by products of younger eruptions. In contrast, tephra layers preserved in sedimentary
48 successions located far away from the volcanic source and characterised by a continuous sediment
49 accumulation history, can provide detailed and undisturbed records of explosive eruptions for a given volcano,
50 including events that are poorly represented or missing in near-vent sections (e.g., [Paterne et al., 1988](#);
51 [Monaco et al., 2021](#)).

52 This could apply to the Neapolitan volcanic area (Campania, southern Italy), including Campi Flegrei, Ischia,
53 Procida and Somma-Vesuvius ([Fig. 1b](#)), where the intense Late Pleistocene explosive activity (e.g., [Peccerillo,](#)
54 [2017 and reference therein](#)) made the earliest products barely accessible in proximal settings. However, these
55 activities are instead documented in distal sedimentary archives. Indeed, since the first discoveries of [Keller](#)
56 [et al. \(1978\)](#), several occurrences of widespread tephra layers with a Campanian geochemical signature
57 embedded within Marine Isotope Stage 5 (MIS 5) sedimentary successions suggested the occurrence of a
58 major explosive activity that, however, had never been documented in proximal sections of the Neapolitan
59 volcanoes. Among them, the C-22 ([Paterne et al., 1986](#)), X-5 and X-6 ([Keller et al., 1978](#)) tephra layers have
60 been traced widely across the central Mediterranean area in several terrestrial (e.g., [Wulf et al., 2004, 2008,](#)
61 [2012, 2018](#); [Marciano et al., 2008](#); [Sulpizio et al., 2010](#); [Giaccio et al., 2012, 2017a](#); [Lucchi et al., 2013](#);
62 [Regattieri et al., 2015](#); [Donato et al., 2016](#); [Leicher et al., 2016](#); [Zanchetta et al., 2018](#); [Petrosino et al., 2019](#))
63 and marine (e.g., [Paterne et al., 1986, 1988, 2008](#); [Bourne et al., 2010, 2015](#); [Insinga et al., 2014](#); [Iorio et al.,](#)
64 [2014](#); [Petrosino et al., 2016](#)) sedimentary archives. Moreover, at least two additional tephra, occurring between
65 the C-22 and X5 markers, with a similar Neapolitan geochemical signature, are also found in Mediterranean
66 MIS 5 records ([Giaccio et al., 2012, 2017a](#); [Wulf et al., 2012](#); [Leicher et al., 2016](#); [Petrosino et al., 2016](#)).

67 Over the last decades, these widespread tephra layers have been used as remarkable marker horizons for
68 dating, synchronizing, and correlating the MIS 5 Mediterranean sedimentary successions, the chronologies of
69 which would have otherwise been poorly determined. With this regard, tephra markers from Neapolitan
70 volcanoes arise as pivotal stratigraphic and chronological tools for paleoclimatic and archaeological
71 investigations at the regional scale (e.g., [Wulf et al., 2012, 2018](#); [Bourne et al., 2015](#); [Regattieri et al., 2015](#);
72 [Leicher et al., 2016](#); [Petrosino et al., 2016](#); [Giaccio et al., 2017a](#); [Zanchetta et al., 2018](#)).

73 Despite their great chronological importance, the lack of near-vent counterparts has left the specific volcanic
74 source of these marker layers still undetermined, leading authors to ascribe them either to an unspecified
75 Campanian volcanism (e.g., [Wulf et al., 2018](#)), or to an undefined Neapolitan volcanic area (e.g., [Giaccio et](#)
76 [al., 2017a](#)) or to the so-called “Campanian Volcanic Zone” (CVZ; [Rolandi et al., 2003](#)) (e.g., [Munno and](#)
77 [Petrosino, 2007](#)). Furthermore, in terms of tephrochronological applications, precise and accurate radioisotopic
78 ages are currently available only for two of these markers (i.e., X-5 and X-6), and their full geochemical
79 characterization (i.e., major, trace elements, and Sr-Nd composition) in near-vent outcrops is still pending.
80 Such remaining uncertainties on their origins and incompleteness of their geochronological and geochemical
81 characterization, prevent their use for any volcanological purposes and limit their tephrochronological potential.
82 In order to fill the knowledge gap about these tephra markers and exploit their full potential for both
83 volcanological and tephrochronological perspectives, we acquired stratigraphic, geochemical, and
84 geochronological data for five medial (30-60 km from the vent) pyroclastic units, preceding the Campanian
85 Ignimbrite (CI) eruption, outcropping around the eastern rim of the Campanian Plain ([Fig. 1b](#)). Four of these
86 units (Maddaloni, Montemaoro, Canello and Santa Lucia; [Fig. 1b](#)) were previously described ([Di Vito et al.,](#)
87 [2008](#)), while a fifth one (i.e., Triflisco) is recognised as a distinct, younger event in this study ([Fig. 1b](#)). The
88 new chemical, isotopic and geochronological data acquired in this study allowed confidently to correlate the
89 five medial fall units to the widespread X-6, X-5, TM-24b/POP-2a, TM-24a/POP2 and C-22 marker tephra,
90 attributing them to the 109-92 ka Campi Flegrei explosive activity. Our findings thus extend back in time the
91 explosive history of the Campi Flegrei volcanic field and provide new precise dating for refining the chronology
92 of the millennial-scale climatic oscillations of the MIS 5c-d in the Mediterranean area.
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Figure 1. Reference maps and stratigraphic logs of the investigated sections. a) Central Mediterranean sedimentary successions containing the MIS 5 tephras markers investigated in this study. b) Digital Elevation Map (DEM) of the Campanian Plain with location of the Neapolitan volcanoes and the investigated pyroclastic successions (Canello-SEMAC Quarry, CA1; Schiava-Masseria Montemaoro Quarry, SC2; Sarno-Tre Valloni, SA1; Sarno-Pian della Colla, SA3). c) Stratigraphic logs of the investigated pyroclastic units showing the distribution of the analysed samples and the type of the performed analysis.

101 2. Geological setting: The Neapolitan volcanoes

102 The Neapolitan volcanoes comprise Campi Flegrei, Ischia and Procida islands and Somma-Vesuvius (Fig.
103 1). The Campi Flegrei volcanic field was the site of the most intense activity among the four Neapolitan
104 volcanoes, as well as in the whole Mediterranean area. Three main eruptions occurred in this volcanic area,
105 i.e., the Campanian Ignimbrite (CI; 39.85 ± 0.14 ka; [Giaccio et al., 2017b](#)), the Masseria del Monte Tuff (MdMT;
106 29.3 ± 0.7 ka; [Albert et al., 2015, 2019](#)), and the Neapolitan Yellow Tuff (NYT; 14.5 ± 0.4 ka; [Deino et al., 2004](#);
107 [Galli et al., 2017](#)) caldera-forming eruptions. Overall, while there is quite satisfactory knowledge on the activity
108 occurred in-between and after these three main events, especially that following the NYT (e.g., [Smith et al.,](#)
109 [2011](#)), the eruptive history preceding the CI is still poorly resolved, being documented only by deposits
110 sporadically exposed outside the caldera and dated back to ~ 80 ka (e.g., [Pappalardo et al., 1999](#); [Scarpati et](#)
111 [al., 2013](#)). Far from the Campi Flegrei volcanic area, several pyroclastic units documenting explosive activity
112 in the Campania region can be dated as back as 290 ka ([De Vivo et al., 2001](#); [Rolandi et al., 2003](#)). This older
113 activity is however referred to the so-called Campanian Volcanic Zone ([Rolandi et al., 2003](#)), i.e., a
114 hypothesized diffuse, regional volcanism not related to the present Campi Flegrei source area.

115 Volcanic activity at Ischia Island, off the Naples gulf (Fig. 1b), is documented as back as 150 ka, which is the
116 age of the oldest exposed deposits, and up to historical times (e.g., [Poli et al., 1987](#)). The activity of Ischia is
117 subdivided in five stages (i.e., >150 -75 ka; 75-55 ka; 55-33 ka; 28-12 ka; 12 ka-1302 CE), characterised by
118 different eruptive styles and types of products (e.g., [Poli et al., 1987](#); [Brown et al., 2008](#)). The third stage of
119 activity (55-33 ka) included several explosive events, following the largest 55 ka Monte Epomeo Green Tuff
120 eruption (MEGT; [Poli et al., 1987](#)), recognized in the Mediterranean region as the Y-7 tephra marker horizon
121 (e.g., [Tomlinson et al., 2014](#)), although this attribution has been recently questioned ([D'Antonio et al., 2021](#)).

122 The Island of Procida, located between Ischia Island and Campi Flegrei (Fig. 1b), was active over a period of
123 ~ 60 kyr, between ~ 80 ka and $23,624 \pm 330$ cal yr BP (e.g., [De Astis et al., 2004](#); [Morabito et al., 2014](#)). Its
124 activity originated from five eruptive centres, i.e. Vivara, Terra Murata, Pozzo Vecchio, Fiumicello, and
125 Solchiaro ([Rosi et al., 1988a, 1988b](#)) and is documented by pyroclastic deposits and lava dome interbedded
126 with Campi Flegrei and Ischia units, which acts as stratigraphic, chronological markers (e.g., [Morabito et al.,](#)
127 [2014](#)).

128 The Somma-Vesuvius stratovolcano, east from the Naples metropolitan area (Fig. 1b), has completely grown
129 on the products of the CI eruption (e.g., [Santacroce and Sbrana, 2003](#)), and thus it is younger than 40 ka. Its
130 activity is subdivided in three main stages: (i) the pre-Mercato eruption stage (ca. 35-9 ka), (ii) the stage
131 between Mercato and the infamous AD 79 Pompeii eruption (ca. 9 ka-79 CE) and (iii) the stage following the

132 Pompeii eruption until present (i.e., last historical eruption of 1944 CE). These three stages differ from one
 133 another in terms of either the frequency of the related inter-Plinian eruptive episodes (e.g., [Andronico and](#)
 134 [Cioni, 2002](#)) or the silica undersaturation degree, both increasing over the time ([Santacroce et al., 2008](#)).

135

136 3. Methods

137 3.1. Sample selection

138 For the present study, we used samples collected from 4 eruptive units out of the 14 pre-CI eruption
 139 deposits recognised by [Di Vito et al. \(2008\)](#) in the Campanian Plain ([Fig. 1b](#)). They are, from bottom to top,
 140 SC2-a (hereafter Maddaloni), SC2-b (hereafter Montemaoro), CA1-a (hereafter Cancellò), and Santa Lucia
 141 ([Table 1; Fig. 1c](#)). However, new analysis for Montemaoro unit was not possible due to unavailability of the
 142 sample previously collected by [Di Vito et al. \(2008\)](#) and the inaccessibility of the outcrop during the new field
 143 investigations. The list of the investigated units is integrated with the fall deposit outcropping near the Triflisco
 144 village, at the edge of the Campanian Plain, here labelled Triflisco ([Fig. 1b-c](#)). Moreover, the isotopic
 145 characterisation has been performed also on samples CIL1 and CIL2 from the Cilento Coast being
 146 representative of the X5 and X6 stratigraphic markers ([Giaccio et al. 2012](#)).

147

148 **Table 1.** Location and data summary of the investigated units.

Units	Locality	Sample source	Coordinates	Sample/sub-units	Analysis			
					Major elements (EMPA)	Trace elements (LA-ICP-MS)	Sr-Nd isotopes	⁴⁰ Ar/ ³⁹ Ar age
Triflisco	Triflisco	This study	41°08'14" N 14°15'12" E	TRIF-Top	Y	Y	-	-
				TRIF-2/3	Y	Y	Y	-
				TRIF-1/3	Y	Y	Y	-
				TRIF-Base	Y	Y	-	Y
Santa Lucia (Santa Lucia)	Schiava, Masseria Montemaoro Quarry (SC2)	Di Vito et al. (2008)	40°56'39" N 14°33'56" E	ZS97-9	Y	Y	-	-
				ZS97-10	Y	Y	Y	Y
				ZS97-272	Y	Y	-	-
				ZS97-273	Y	Y	-	-
				ZS97-28	Y	Y	Y	-
Cancellò (CA1-a)	Sarno, Tre Valloni (SA1)	Di Vito et al. (2008)	40°59'11" N 14°29'27" E	ZS97-39	Y	Y	-	-
				ZS97-27	Y	-	-	-
Cancellò (CA1-a)	Schiava, Masseria Montemaoro Quarry (SC2)	Di Vito et al. (2008)	40°59'11" N 14°29'27" E	AS96-400	Y	Y	-	Y
				ZS97-8	Y	Y	-	-
Montemaoro (SC2-b)	Schiava, Masseria Montemaoro-Quarry (SC2)	Di Vito et al. (2008)	40°56'39" N 14°33'56" E	SC2-b	-	-	-	-
Maddaloni (SC2-a)	Santuario di San Salvatore	This study	41°03'11" N 14°23'47" E	Top	Y	-	-	-
				Middle	Y	-	-	-
				Base	Y	-	-	-
Maddaloni (SC2-a)	Schiava, Masseria Montemaoro-Quarry (SC2)	Di Vito et al. (2008)	40°56'39" N 14°33'56" E	ZS97-3	Y	Y	-	-
				Sarno, Pian della Colla (SA3)	40°48'44" N 14°39'31" E	ZS97-286	Y	Y
CIL1	Cilento Cost	Giaccio et al. (2012)	40°03'24" N 15°17'02" E	CIL1	Y ¹	-	Y	-
CIL2				CIL2	Y ¹	-	Y	-

149 "Y": type of analysis performed on the sample. "-": type analysis not performed on the sample. Literature data source: ¹ = [Giaccio et al.](#)
150 [\(2012\)](#).

151

152 3.2. Volcanic glass characterisation

153 3.2.1. Sample preparation

154 The samples selected for the major and trace glass composition ([Fig. 1c](#); [Table 1](#)) were wet sieved
155 with tap water through a series of sieves with decreasing mesh openings. All fractions were successively oven-
156 dried at 100°C until completely dry. For major element analysis, selected fractions of 60-250 µm were mounted
157 on 29 x 49 mm glass slides, embedded in epoxy resin, progressively ground to a thickness of 60-100 µm and
158 finally polished to be analysed with the electron microprobe. For trace element analysis, selected samples
159 were embedded in epoxy resin and successively polished.

160

161 3.2.2. Electron probe micro analyser (EPMA)

162 Glass shards and (micro-)pumice fragments were analysed by single-shard major element chemical
163 analysis using the electron probe micro analyser (EPMA). Analysis was first performed with a Jeol JXA-850F
164 equipped with five wave dispersive spectrometers (WDS), installed at the Institute of Petrology and Structural
165 Geology, Charles University of Prague (Prague, Czech Republic). The machine operated at 15 kV accelerating
166 voltage, 10 nA beam current and 10 µm defocused beam to limit alkali loss. Element counting times were of
167 20 s for all elements, except for Na, K, and S, for which counting times of 10 s (Na and K) and 30 s (S) were
168 employed respectively. For all measurements, the F content was always below the detection limit of the
169 machine. Standards for calibration were quartz (Si), corundum (Al), rutile (Ti), magnetite (Fe), periclase (Mg),
170 rhodonite (Mn), albite (Na), sanidine (K), diopside (Ca), apatite (P and F), tugtupite (Cl) and anhydrite (S). The
171 secondary standards GOR128-G ([Jochum et al., 2006](#)) and CFA47 ([Marianelli and Sbrana, 1998](#)) were
172 analysed at the beginning of each microprobe session for a total of one point each to evaluate analysis
173 accuracy.

174 Further WDS analyses were carried out at the Dipartimento di Scienze della Terra, Università degli Studi di
175 Firenze (Florence, Italy), with a Jeol Superprobe JXA-8230 equipped with five-WDS spectrometers. Operating
176 conditions were set to 15 kV accelerating voltage, 10 nA beam current and 10 µm defocused beam diameter
177 to limit Na mobilisation. Element counting times were 15 s for all elements except for Na (10s), F (20s), S
178 (30s), Mn, P and Cl (40s). Albite (Si and Na), ilmenite (Ti and Fe), plagioclase (Al), bustamite (Mn), olivine
179 (Mg), diopside (Ca), sanidine (K), apatite (P), fluorite (F), tugtupite (Cl) and celestine (S) were used as internal
180 standards. The accuracy of the measurements was assessed using the glass secondary standards GOR128-

181 G, ATHO-G and StHs6/80-G (Jochum et al., 2006), Lipari ID3506 (Kuehn et al., 2011), Scapolite NMNH, and
182 CFA47 (Marianelli and Sbrana, 1998).

183 For both analytical facilities, the ZAF method was used for matrix effect correction. We adopted 93 wt% as a
184 threshold for the measured totals. All compositional data are shown as oxide weight percentages (wt%) in the
185 TAS and bi-plots diagrams, with total iron measured as FeO, and normalised to 100% on a volatile-free basis
186 for correlation purposes. Collected data and secondary standards measurements are all reported in
187 Supplementary Materials-1.

188

189 3.2.3. *Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)*

190 Trace element analyses were conducted on volcanic glasses from the Triflisco, Santa Lucia, Canello,
191 and Maddaloni units. The analyses were performed using an Agilent 8900 triple quadrupole ICP-MS (ICP-
192 QQQ) coupled to a Resonetics 193nm ArF excimer laser-ablation device at the Department of Earth Sciences,
193 Royal Holloway, University of London. Full analytical procedures used for volcanic glass analysis follow those
194 reported in Tomlinson et al. (2010). Crater sizes of 20, 25 and 34 μm were used depending on the sample
195 vesicularity and/or size of glass surfaces available for analysis. The repetition rate was 5 Hz, with a count time
196 of 40 s on the sample, and 40 s on the gas blank to allow the subtraction of the background signal. Typically,
197 blocks of eight glass shards and one MPI-DING reference glass were bracketed by the NIST612 glass adopted
198 as the calibration standard. The internal standard applied was ^{29}Si (determined by EMP-WDS analysis). In
199 addition, MPI-DING reference glasses were used to monitor analytical accuracy (Jochum et al., 2006). LA-
200 ICP-MS data reduction was performed in Microsoft Excel, as outlined in Tomlinson et al. (2010). Accuracies
201 of LA-ICP-MS analyses of the MPI-DING reference glasses, ATHO-G and StHs6/80-G, were typically $\leq 5\%$
202 for the majority of elements measured. Tephra and standard measurements are all provided in Supplementary
203 Materials-1. Data averages reported in the text are accompanied by a ± 2 standard deviation (2 s.d.), whilst
204 error bars in the plots are typically smaller than the data symbols.

205

206 3.2.4. *Sr and Nd isotopes*

207 $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios have been determined on two samples from the Santa Lucia
208 and one from Maddaloni units (i.e., ZS97-10 and ZS97-28, and ZS97-286 respectively) previously investigated
209 by Di Vito et al. (2008), on two samples from the Triflisco unit (i.e., TRIF 1/3 and TRIF 2/3) and on the CIL1
210 and CIL2 units from the Cilento Coast (Giaccio et al. 2012; Fig. 1c; Table 1). Measurements have been
211 performed either on the glasses (pumices) and/or crystals (pyroxene or feldspar). $^{143}\text{Nd}/^{144}\text{Nd}$ measurement

212 were performed on the glass fraction of samples from Triflisco, Santa Lucia (ZS97-10) and Maddaloni (ZS97-
213 286) units. The different fractions were handpicked under a binocular microscope. Among all the available
214 glass shards/pumices the most homogeneous in colour, and visibly poorly affected by secondary alteration,
215 were selected for isotope analyses. Feldspar and pyroxene crystals were handpicked avoiding those
216 characterised by the presence of glass rinds attached on their surfaces.

217 Before chemical dissolution, glass shards/pumices were acid leached three to five times to reduce as much
218 as possible the alteration effects. The leaching procedure was prolonged until the acid solution became light-
219 yellow in colour. Leaching was carried out each time by placing the beakers containing samples and high purity
220 6N HCl on a hot plate for 10 min. During each leaching step and after the final leaching, samples were rinsed
221 with Milli-Q® H₂O. Feldspar and pyroxene were cleaned with Milli-Q® H₂O for 10 min. in an ultrasonic bath.
222 Dissolution was obtained with high-purity HF–HNO₃–HCl mixtures. Sr and Nd were separated from the matrix
223 through conventional ion-exchange procedures. Sr and Nd isotopic compositions were determined in a static
224 mode by thermal ionisation mass spectrometry (TIMS) using a Thermo Finnigan Triton TI® mass spectrometer
225 equipped with one fixed and six adjustable Faraday cups. Average 2σ mean, i.e., the standard error with N =
226 180, was better than ± 9x10⁻⁶ for Sr, and better than ± 7x10⁻⁶ for Nd measurements. The mean measured
227 values of ⁸⁷Sr/⁸⁶Sr for the NIST-SRM 987 standard and ¹⁴³Nd/¹⁴⁴Nd for the La Jolla standard were 0.710261 ±
228 0.000021 (2σ, N = 169) and 0.511845 ± 0.000010 (2σ, N = 55), respectively; external reproducibility (2σ)
229 during the period of measurements was calculated according to [Goldstein et al. \(2003\)](#). Measured ⁸⁷Sr/⁸⁶Sr
230 ratios were normalized for within-run isotopic fractionation to ⁸⁶Sr/⁸⁸Sr = 0.1194, and ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. The
231 final, measured isotope ratio values were normalized to the recommended values of the NIST SRM 987
232 (⁸⁷Sr/⁸⁶Sr = 0.71025) and La Jolla (¹⁴³Nd/¹⁴⁴Nd = 0.51185) standards, respectively. Chemistry processing and
233 isotope analyses were performed at the Radiogenic Isotope Laboratory (RIL) of the Istituto Nazionale di
234 Geofisica e Vulcanologia, Osservatorio Vesuviano, and the full analytical dataset is reported in Supplementary
235 Materials-2.

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237 3.2.5. ⁴⁰Ar/³⁹Ar dating

238 The ⁴⁰Ar/³⁹Ar ages were obtained at the Laboratoire des Sciences du Climat et de l'Environnement
239 (CEA, CNRS UMR 8212, Gif-sur-Yvette, France) dating facility. Fresh and transparent K-rich feldspars were
240 extracted from Triflisco, Santa Lucia, Canello and Maddaloni samples. After being washed in distilled water,
241 transparent K-feldspars (500-630 μm) without any visible inclusions were handpicked under a binocular and
242 used for dating these four pyroclastic units.

243 Between 20 and 30 crystals for each sample were irradiated in the Cd-lined, in core CLICIT facility of the
244 Oregon State University TRIGA reactor for 2 h (IRR. CO-007) for Triflisco and 1 h in the same reactor (IRR.
245 CO-009) for Santa Lucia, Canello, and Maddaloni. Interference corrections were based on the nucleogenic
246 production ratios given in [Balbas et al. \(2016\)](#). After irradiation, individual crystal for each tephra layers were
247 transferred into a copper 133 pits sample holder placed into a differential vacuum Teledyne Cetac window
248 connected to a home designed compact extraction line. Minerals were fused one by one using a 100W
249 Teledyne Cetac CO₂ laser during 15s at 2.5 W. Before fusion, each crystal underwent a 10s long sweeping at
250 0.3W to remove unwanted gas potentially trapped on the crystals surface and fractures. Extracted gases were
251 firstly purified by a SAES GP 50 cold getter for 90s and then for 230s by two hot SAES GP 50 getters. The
252 five Argon isotopes (i.e., ⁴⁰Ar, ³⁹Ar, ³⁸Ar, ³⁷Ar and ³⁶Ar) were measured using a multicollector NGX 600 mass
253 spectrometer equipped with 9 ATONA® amplifiers array and an electron multiplier. More technical
254 specifications regarding the NGX 600 ATONA detector array are presented in detail in [Cox et al. \(2020\)](#). ⁴⁰Ar,
255 ³⁹Ar, ³⁸Ar, and ³⁶Ar isotopes were collected simultaneously while the ³⁷Ar was measured in a second time. In
256 the first run, ⁴⁰Ar, ³⁹Ar and ³⁸Ar were measured simultaneously on 3 ATONA® amplifiers and ³⁶Ar on the
257 electron multiplier. Following this first run the ³⁷Ar was measured alone using the electron multiplier. Each
258 isotope measurement corresponds to 15 cycles of 20-seconds integration time. Peak intensity data were
259 reduced using ArArCALC V2.4 ([Koppers, 2002](#)). Neutron fluence J factor was calculated using co-irradiated
260 Alder Creek sanidine standard ACs-2 associated to an age of 1.1891 Ma ([Niespolo et al., 2017](#)) according to
261 the K total decay constant of [Renne et al. \(2011\)](#) ($\lambda_{e.c.} = (0.5757 \pm 0.016) \times 10^{-10} \text{ yr}^{-1}$ and $\lambda_{\beta^-} = (4.9548 \pm 0.013)$
262 $\times 10^{-10} \text{ yr}^{-1}$). To determine the neutron flux for each sample we used at least 6 flux monitor crystals coming
263 from pits framing the samples in each irradiation disk. J-values are of $0.00056080 \pm 0.00000062$ (Triflisco
264 [Base]); $0.00028350 \pm 0.00000023$ (Santa Lucia [ZS97-10]); $0.00028340 \pm 0.00000028$ (Canello [AS96-400]);
265 $0.00028340 \pm 0.00000020$ (Maddaloni [ZS97-286]). To verify the detectors linearity, mass discrimination was
266 monitored by analysis of at least 60 air shots of various beam sizes ranging from 5.0×10^{-3} up to 2.0×10^{-2} V (1
267 to 4 air shots). About 15 air shots analyses are performed every day. These measurements are done
268 automatically during the nights before and after the unknown measurements. Discrimination is calculated
269 according the ⁴⁰Ar/³⁶Ar ratio of 298.56 ([Lee et al., 2006](#)). Procedural blank measurements were achieved after
270 every two to three unknowns. For typical 5 min time blank backgrounds are between 2.5 and 4.0×10^{-4} V for ⁴⁰Ar
271 and 60 to 90 cps for ³⁶Ar (about 1.0 - 1.3×10^{-6} V equivalent). Full analytical data for each sample can be found
272 in Supplementary Materials-3.

273

274 4. Results

275 4.2. Stratigraphy

276 Most samples investigated in this study refer to the pyroclastic units already described in [Di Vito et al.](#)
277 [\(2008\)](#), to which the reader is referred for the lithostratigraphic details. They generally consist in dm-thick fallout
278 deposits made up of either pumice lapilli or coarse ash ([Fig. 1c](#)). At the site “Schiava” (SC2 in [Fig. 1b](#)) all the
279 four previously investigated units, i.e., Maddaloni, Montemaoro, Canello and Santa Lucia, occur as distinct
280 eruptive units separated by either paleosols, epiclastic deposits or unconformity bounding surfaces.

281 The newly recognised Triflisco unit ([Fig. 1b](#)), consists in an 80 cm-thick fallout deposit made up of moderately
282 sorted, white-pinkish and well-vesicular pumice lapilli (max Φ 3 cm) with intervening coarse ash layers.
283 Accidental lithics are scant ([Fig. 1c](#)). The Triflisco unit overlies a paleosol and at the top, in turn, it is capped
284 by a thick reddish paleosol on which lays a greyish pyroclastic flow deposit that we attribute to the CI ([Fig. 1c](#)).
285 Thus, our interpretation differs from previous ones that correlated the pumice fall at this locality to the CI Plinian
286 fall exposed elsewhere ([Civetta et al., 1997](#); [Fanara et al., 2015](#)).

287 The Maddaloni unit was also sampled in a new exposure at Santuario di San Salvatore ([Fig. 1b](#)), where it
288 consists in a 50 cm-thick fallout deposit made up of well sorted, white-greyish sandine-bearing and highly
289 vesicular pumiceous lapilli (max Φ 4-5 cm), with highly elongated bubbles, containing scant accidental lithics
290 ([Fig. 1c](#)). At this site, the Maddaloni unit overlies a paleosol, whereas its uppermost part is not exposed,
291 because of the vegetation cover.

292

293 4.3. Major and minor element volcanic glass chemistry

294 All samples analysed in this study have a dominant composition overlapping the boundary between
295 phonolite and trachyte fields ([Fig. 2a](#)) of the *Total alkali vs Silica* (TAS, [Le Maitre et al., 2002](#)) classification
296 diagram. Mean compositions are reported at 2σ (2 standard deviation) error.

297 **Triflisco unit.** It is made up by four sub-units ([Fig. 1c](#)) with a relatively homogeneous composition. The majority
298 of the data straddle the boundary between trachyte and phonolite fields (SiO_2 content of 59.5 ± 0.9 wt%, and
299 alkali sum of 12.8 ± 1.0 wt%), depicting a trend within the trachyte field with decreasing alkali negatively
300 correlated with a small increase in silica; [Fig. 2a-b](#)). The CaO/FeO values are < 1 (0.8 ± 0.1) and the Cl content
301 is 0.6 ± 0.1 wt% for all sub-units ([Fig. 2c](#)). Glasses display a High Alkali Ratio (HAR), with $\text{K}_2\text{O}/\text{Na}_2\text{O}$ generally
302 > 2 and up to 3.08 ([Fig. 2d](#)). There is no appreciable chemical variation from the lowermost (Triflisco Base) to
303 the uppermost (Triflisco Top) sub-units.

304 **Santa Lucia unit.** The glass of this unit, analysed in six samples (Fig. 1c; Table 1), is characterised by the
305 most heterogeneous composition among those analysed, although mainly phonolitic, with a mean SiO₂ content
306 of 59.0 ± 2 wt%, and an alkali sum of 12.8 ± 1 wt% (Fig. 2a-b). The CaO/FeO ratio is ≤ 1 (mean of 0.9 ± 0.1)
307 and the Cl content is medium-high (0.6 ± 0.1 wt%; Fig. 2c). Santa Lucia glasses display a HAR typically ≥ 2,
308 with a mean K₂O/Na₂O ratio of 2.1 ± 0.5 (Fig. 2d).

309 **Cancello unit.** Glasses from this unit are phonolitic-trachytic in composition, with a SiO₂ content of 60.9 ± 1.3
310 wt%, a mean alkali sum of 13.1 ± 0.9 wt% (Fig. 2a-b) and a HAR of 2.2 ± 0.6 (Fig. 2d). The CaO/FeO ratio
311 ranges between 0.7 and 1.0 and the Cl content between 0.5 and 0.7 wt% (Fig. 2c).

312 **Montemaoro unit.** As stated in the previous section, it was not possible to acquire new data for this unit. Thus,
313 for the purpose of this study, we rely on the available glass-EDS data from Di Vito et al. (2008). The
314 Montemaoro unit is mainly trachytic in composition with some points straddling the boundary with the phonolite
315 field, with silica and alkali sum content of c.a. 61 wt% and 13 wt%, respectively (Fig. 2a-b). The glasses display
316 a HAR, up to 2.5, with a CaO/FeO ratio of c.a. 0.7 (Fig. 2d), while Cl content was not determined.

317 **Maddaloni unit.** The glass of this unit, collected from the former SC2 and SA3 sections and the new Santuario
318 one (Fig. 1; Table 1), is characterised by a homogeneous SiO₂ content (mean 61.6 ± 0.8 wt%), with an alkali
319 sum of 13.8 ± 0.5 wt% (Fig. 2a-b). Respect to all the above-mentioned samples, Maddaloni glasses
320 predominantly display a Low Alkali Ratio (LAR), with K₂O/Na₂O typically ≤ 1.5 (1 ± 0.3; Fig. 2d), due to an
321 almost equal content of K₂O and Na₂O of ca. 7 wt%. In addition to a lower K₂O/Na₂O ratio, with respect to the
322 other analysed units, the glass of the Maddaloni pumices has noticeably lower CaO/FeO ratios (0.6 ± 0.1),
323 whilst the Cl content is appreciably higher, up to 1.1 wt% (Fig. 2c).

324

325 4.4. Trace element volcanic glass chemistry

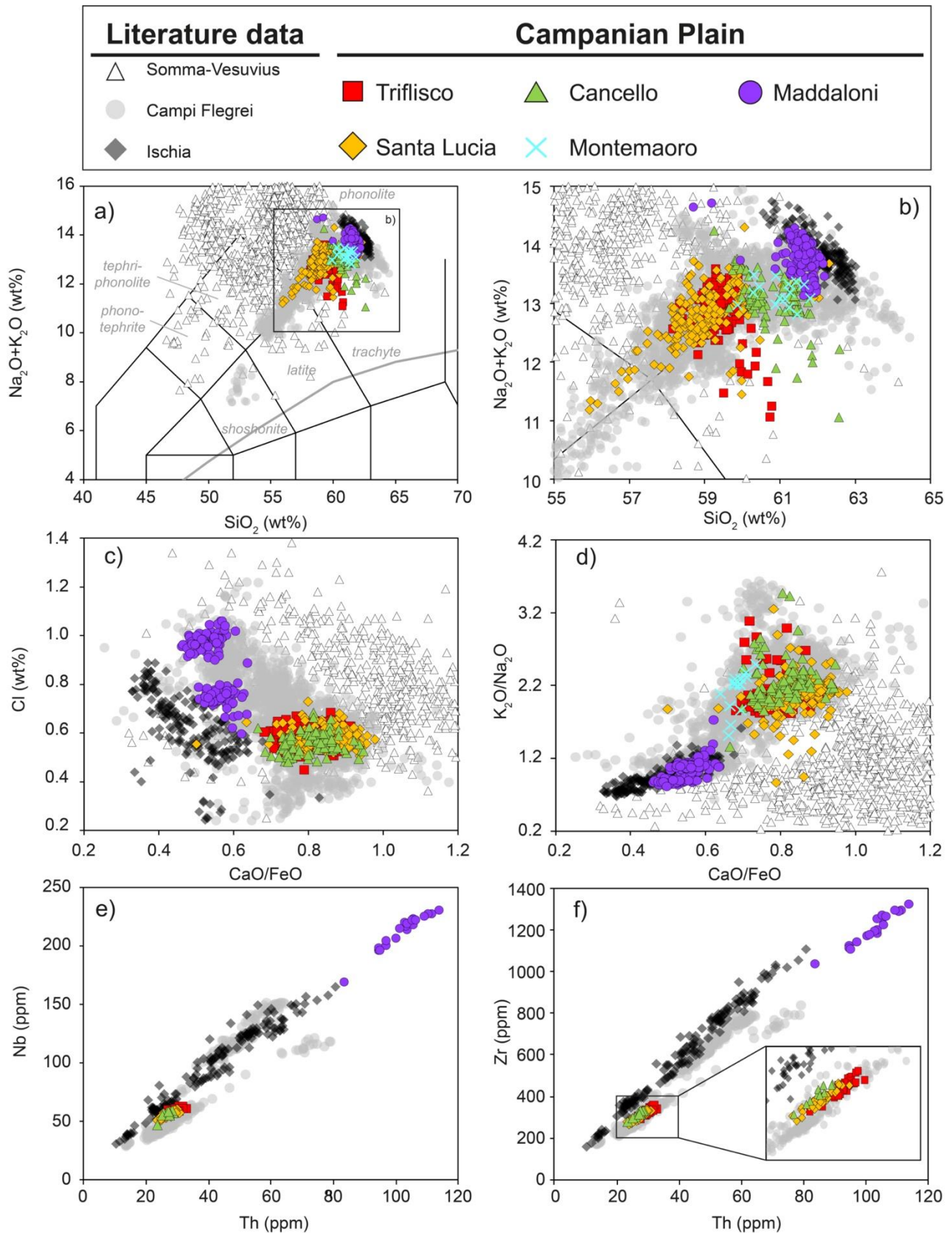
326 The Triflisco eruption unit contains HAR glasses that are fairly homogeneous in terms of their
327 incompatible trace element contents (e.g., Th = 29.9 ± 2.9 ppm [Fig. 2e-f]; Nb = 59.2 ± 4.0 ppm [Fig. 2e]; Zr =
328 327 ± 31 ppm [Fig. 2f]) and ratios of other High Field Strength elements (HFSE) to Th remaining constant (e.g.,
329 Nb/Th = 2.0 ± 0.1; Zr/Th = 10.9 ± 0.5). Light Rare Earth Elements (LREE) are enriched relatively to the Heavy
330 Rare Earth Elements (HREE) with La/Yb = 27.9 ± 3.7.

331 The HAR Santa Lucia eruption products in the SC2, CA1 and SA1 sections (see Table 1) are compositionally
332 consistent and fairly homogeneous (e.g., Th = 27.1 ± 3.1 ppm; Nb = 55.8 ± 4.5 ppm [Fig. 2e]; Zr = 306 ± 29
333 ppm [Fig. 2f]; Rb = 307 ± 25 ppm; La = 77.9 ± 6.0 ppm) with constant HFSE/Th ratios (Nb/Th = 2.1 ± 0.1; Zr/Th
334 = 11.3 ± 0.5) and displaying LREE enrichment relatively to HREE (La/Yb = 27.7 ± 3.1).

335 The Canello unit displays HAR glasses that are fairly homogeneous in composition (e.g., Th = 26.7 ± 3.0
336 ppm; Nb = 56.1 ± 7.0 ppm [Fig. 2e]; Zr = 316 ± 34 ppm [Fig. 2f]; La = 81.4 ± 8.3 ppm), with minor variation
337 relating to a single less enriched analysis. HFSE to Th ratios remain constant within the Canello glasses
338 (Nb/Th = 2.1 ± 0.2 ; Zr/Th = 11.8 ± 0.4), and LREE are enriched relative to the HREE where La/Yb = $27.6 \pm$
339 3.4.

340 The LAR Maddaloni tephra shows variable incompatible trace element glasses compositions (e.g., Th = 84-
341 114 ppm; Nb = 169-231 ppm [Fig. 2e]; Zr = 1037-1319 ppm [Fig. 2f]) and displays far greater levels of
342 enrichment relative to the above mentioned HAR units (i.e., Triflisco, Santa Lucia and Canello; Fig. 2e-f).
343 HFSE/Th values remain constant within these glasses (Nb/Th = 2.1 ± 0.1 ; Zr/Th = 11.8 ± 0.4) and are entirely
344 consistent with the HAR samples from Triflisco, Santa Lucia and Canello deposits (Fig. 2e-f).

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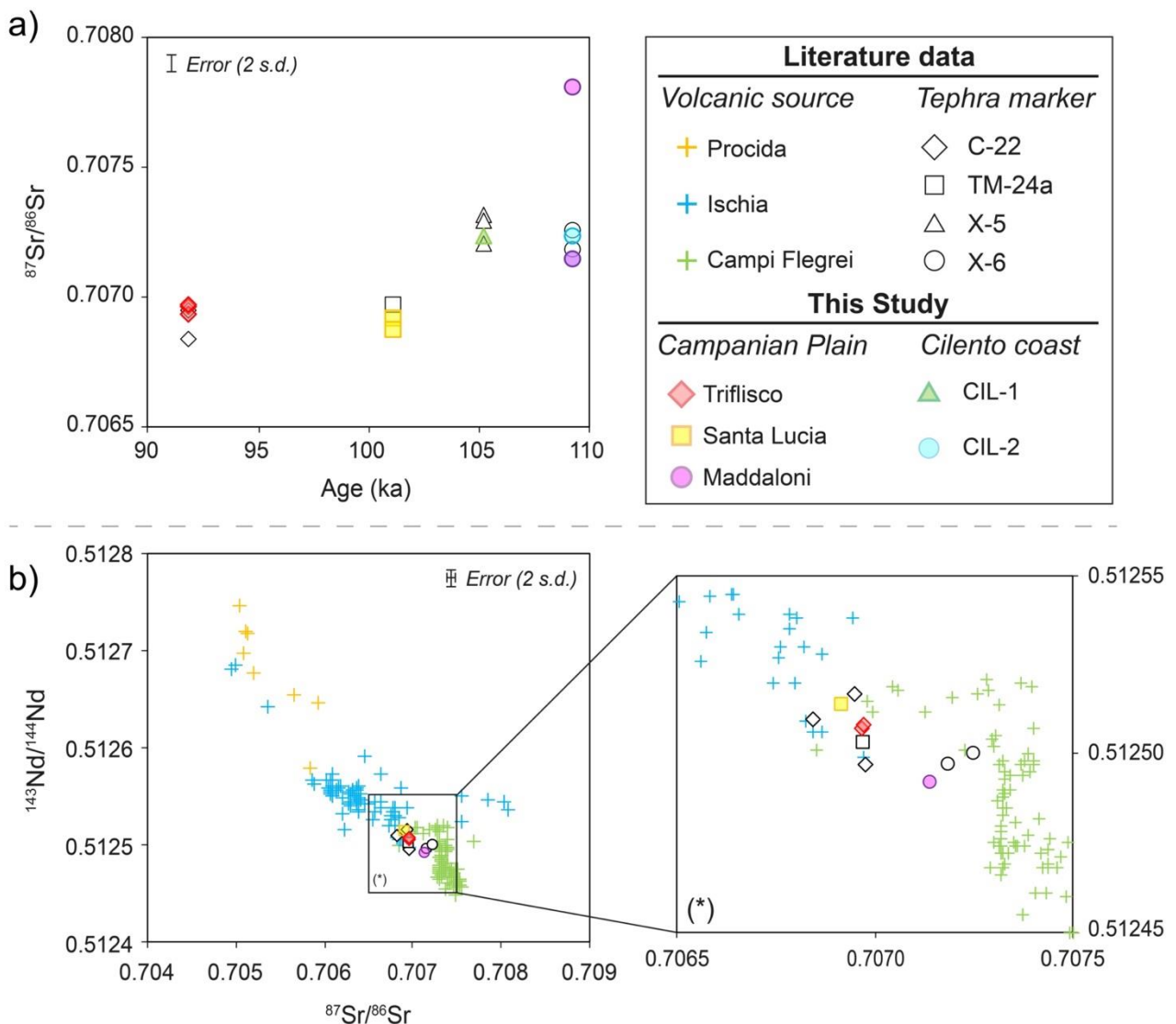


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 347
 348 **Figure 2.** Major and trace element compositions of the investigated medial Campanian Plain units in comparison with literature data of
 349 Ischia and Campi Flegrei volcanic systems. (a, b) *Total alkali vs silica* (TAS; [Le Maitre et al., 2002](#)), (c) *CaO/FeO vs Cl* classification
 350 diagram ([Giaccio et al., 2017a](#)), (d) *CaO/FeO vs K₂O/Na₂O*, (e) *Th vs Nb* (ppm) and (f) *Th vs Zr* (ppm). Glass-WDS data source: Triflisco,
 351 Santa Lucia, Canello and Maddaloni medial Campanian Plain units: this study; Somma-Vesuvius: [Santacroce et al. \(2008\)](#); Ischia:
 352 [Tomlinson et al. \(2014\)](#); Campi Flegrei: [Smith et al. \(2011, 2016\)](#), [Tomlinson et al. \(2012\)](#). Trace elements data source: Triflisco, Santa
 353 Lucia, Canello and Maddaloni medial Campanian Plain units: this study; Ischia: [Tomlinson et al. \(2014\)](#); Campi Flegrei ([Tomlinson et al.,](#)
 354 [2012](#)).

355 4.5. Sr and Nd isotopes

356 Whilst the $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios are homogeneous within the analytical error (c.a. 0.51250), the $^{87}\text{Sr}/^{86}\text{Sr}$
 357 ratios (Fig. 3a) range from 0.70687 and 0.70780 (glass from sample ZS97-286). The highest value is possibly
 358 due to post-depositional alteration of the glass as suggested by the Sr isotope composition of the embedded
 359 feldspar. Samples from Triflisco and Santa Lucia display similar and lower Sr isotope composition (c.a. 0.7069)
 360 with respect to sample from Maddaloni unit. CIL1 and CIL2 are characterized by Sr isotope ratios (from ca.
 361 0.7071 to 0.7072) similar to that of the Maddaloni feldspar (from c.a. 0.7071). Figure 3 displays the variations
 362 in terms of Sr-Nd isotope ratios compared with literature data.

363



364

365 **Figure 3.** Sr and Nd isotope ratios determined for the Triflisco, Santa Lucia and Maddaloni units from the Campanian Plain and CIL-1
 366 and CIL-2 tephra from the Cilento coast. In panel b the Sr isotope composition of the feldspar from the Maddaloni sample has been
 367 associated to the Nd isotope composition of its glass fraction, being the glass possibly affected by post depositional alteration. This latter
 368 did not modify the $^{143}\text{Nd}/^{144}\text{Nd}$, because the Nd is a less fluid mobile element. Tephra layers literature data source: **C-22**: POP-1 (Giaccio
 369 et al., 2012), TF-10 (Giaccio et al., 2017a), S14 (Petrosino et al., 2019); **TM-24a**: POP-2A (Giaccio et al., 2012); **X-5**: TF-12 (Giaccio et
 370 al., 2017a), S11 (Petrosino et al., 2019); **X-6** = TF-13 (Giaccio et al., 2017a), S10 (Petrosino et al., 2019). Literature data for Ischia, Procida
 371 and Campi Flegrei proximal deposits: Arienzo et al. (2009, 2010, 2015, 2016), Brown et al. (2014), Casalini et al. (2018), D'Antonio et al.
 372 (2007, 2013), Di Renzo et al. (2011), Pabst et al. (2008), Pelullo et al. (2020), Tonarini et al. (2009).

373

374 4.6. $^{40}\text{Ar}/^{39}\text{Ar}$ ages

375 All $^{40}\text{Ar}/^{39}\text{Ar}$ results for individual tephra layers are presented as probability diagrams (Fig. 4). Weighted
376 mean age uncertainties are all reported at 2σ , including J uncertainty and were calculated using Isoplot 4.0
377 (Ludwig, 2001). For each sample, inverse isochrones have an atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ initial intercept with
378 uncertainties suggesting that dated crystals are without detectable excess argon. Full inverse isochrones
379 dataset can be found in Supplementary Materials-3.

380 **Triflisco (TRIF-Base)** - 13 single crystals were individually dated. Eleven out of thirteen crystals analysed
381 gave a similar age within uncertainties (Fig. 4a). The two other older crystals, one sanidine and one plagioclase
382 according to their Ca/K ratio, are interpreted as xenocrysts. The main population of crystal interpreted as
383 juvenile allows to calculate a weighted mean age of 91.8 ± 1.2 ka (MSWD = 1.20, $p = 0.27$).

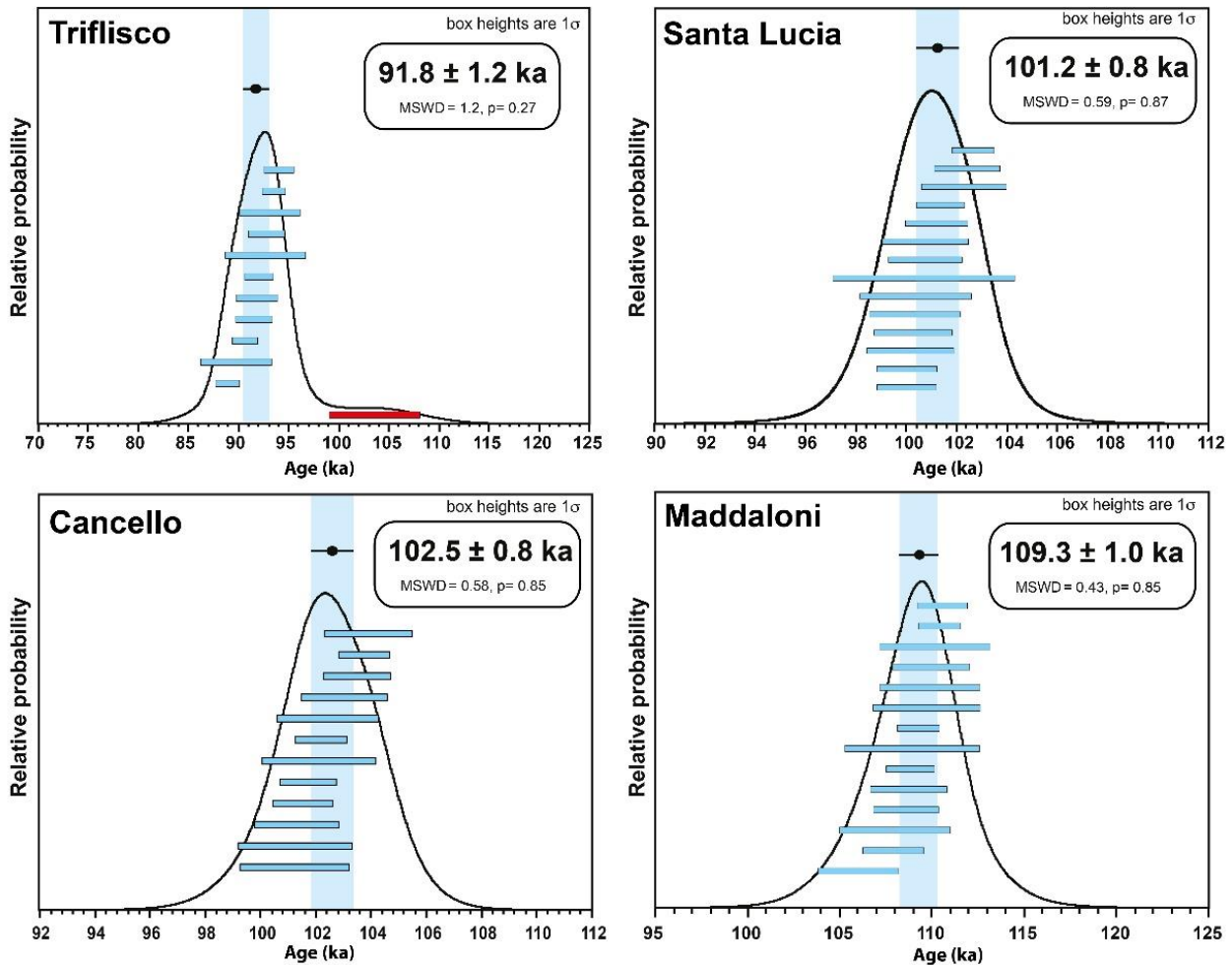
384 **Santa Lucia (ZS97-10)** - A total of 14 individual sanidine crystals were dated. The probability diagram is simple
385 (Fig. 4b) with one mode allowing to calculate a meaningful and precise weighted mean age of 101.2 ± 0.8 ka
386 (MSWD = 0.59, $p = 0.87$).

387 **Cancello (AS96-400)** - The probability diagram displays one single mode with no xenocrystal contamination
388 (Fig. 4c). These crystals are interpreted as juvenile ones (12 crystals), allowing to calculate a precise weighted
389 mean age of 102.5 ± 0.8 ka (MSWD = 0.58, $p = 0.85$).

390 **Maddaloni (ZS97-286)** - 14 crystals were dated individually. All gave within uncertainty the same age resulting
391 in a gaussian probability diagram (Fig. 4d). Using this very homogenous crystal population we calculated a
392 weighted mean age of 109.3 ± 1.0 ka (MSWD = 0.43, $p = 0.96$).

393 While for Maddaloni we obtained the $^{40}\text{Ar}/^{39}\text{Ar}$ age of 109.3 ± 1.0 ka, the overlying Montemaoro unit, which
394 was not resampled or re-analysed in this work, was not dated.

395



396

397

Figure 4. Age probability diagrams for the Triflisco, Santa Lucia, Canello and Maddaloni units.

398

399 5. Discussion

400 5.1. Volcanic source of the Campanian Plain Units

401 All the investigated pyroclastic fall units occur in a range of 30-35 km to 55-60 km in the eastern
 402 quadrants from the Neapolitan volcanoes, including Campi Flegrei, Ischia, Procida and Somma-Vesuvius (Fig.
 403 1b). Somma-Vesuvius can be reasonably excluded as a potential source since its oldest known activity is
 404 younger than Campanian Ignimbrite (i.e., < 40 ka; Santacrose et al., 2008) and thus incompatible with the 109-
 405 92 ka chronology obtained here for the Campanian Plain units. Also, in terms of glass chemical composition,
 406 the Somma-Vesuvius products appear incompatible due to the higher alkali sum at similar SiO₂ content (Fig.
 407 2a-b), and the significantly higher CaO/FeO at same Cl content and alkali ratio (Fig. 2c-d). Procida island can
 408 also be excluded based on the Sr-Nd isotope compositions, which are clearly different from those of the
 409 Campanian Plain units (Fig. 3a-b). Among the two remaining potential sources for the investigated units (i.e.,
 410 Campi Flegrei and Ischia), based on the lithostratigraphic and geochemical characteristics, as already argued
 411 by Di Vito et al. (2008), the Campi Flegrei volcanic area is the most probable. In terms of major element glass

412 composition, although Campi Flegrei and Ischia products partially overlap, each of the two volcanic sources
413 show distinctive features in terms of oxide concentrations and ratios (Fig. 2a-d). This applies to four out of the
414 five investigated units (i.e., Triflisco, Santa Lucia, Canello, and Montemaoro), which unambiguously plot in
415 the compositional field of the Campi Flegrei glass because of the higher K_2O/Na_2O and CaO/FeO values with
416 respect to the Ischia products (Fig. 2b-c). Trace elements glass compositions also support the attribution of
417 the Triflisco, Santa Lucia and Canello units to the Campi Flegrei, for instance all these units show enrichment
418 in Zr that is diagnostic of the Campi Flegrei products and is slightly lower than that of the products typically
419 erupted at Ischia (Fig. 2f).

420 Owing to its distinctive K_2O/Na_2O and CaO/FeO values, which are lower than those of the most common
421 Campi Flegrei products (Fig. 2c-d), the source attribution of the Maddaloni unit is not so straightforward.
422 Indeed, CaO/FeO and K_2O/Na_2O ratios of Maddaloni unit partly overlap with those of Ischia (Fig. 2b-c).
423 However, using the CaO/FeO vs. Cl diagram, the glass composition of Maddaloni unit falls out of the Ischia
424 field and within the Campi Flegrei one, though, sporadically, the Campi Flegrei compositions can overrun the
425 typical Ischia one (Fig. 2c). Indeed, such chemical characteristics, i.e., LAR trachyte-phonolite with relatively
426 low CaO/FeO ratio, are also found in Campi Flegrei products (e.g., Tomlinson et al., 2012), notably in the Cl
427 (Smith et al., 2016) and some minor Campi Flegrei eruptions following the NYT caldera-forming eruption (e.g.,
428 Averno 2, Fondi di Baia, Monte Nuovo; Smith et al., 2011). Likewise, the Maddaloni unit can be attributed to
429 the Campi Flegrei and ascribed to this less common, LHR trachyte-phonolite compositional group of this
430 volcanic area. Incompatible trace element enrichment of the Maddaloni glasses exceeds that currently
431 recognised in the known products of Campi Flegrei and Ischia (Fig. 2e-f) making their use again less
432 conclusive. However, the lower Zr/Th ratios observed in the Maddaloni glasses are seemingly more akin to
433 those of Campi Flegrei, rather than to the higher values typically observed in the eruptive products of Ischia
434 spanning a period of intense explosive volcanism at ~40-80 ka (Tomlinson et al., 2014). More convincing, and
435 seemingly definitive, evidence to confirm Campi Flegrei as the source for the Maddaloni unit, is provided by
436 isotope data. Indeed, the Sr- and Nd-isotope compositions for the Maddaloni samples are positioned well
437 within the field of the Campi Flegrei (Fig. 3a-b).

438 In summary, the volcanological and sedimentological constraints, the acquired major and trace elements glass
439 composition, the geochronological and Sr- and Nd-isotope data consistently indicate that Campi Flegrei is the
440 most probable source for all the five investigated Campanian Plain units. This significantly extends back in
441 time the known explosive activity of this volcanic field, previously documented only up to ca. 80 ka (Scarpati
442 et al., 2013), or as far back as 290 ka (CVZ; De Vivo et al., 2001; Rolandi et al., 2003). Regardless the precise

443 vent location, our data point to a frequent activity that took place within the Campi Flegrei volcanic area.
444 Specifically, we recognised five eruptions that, based on their lithological features in medial settings, can be
445 likely considered of Plinian intensity and magnitude. These occurred across approximately a 17 kyr time-
446 window, with recurrence times of a few thousands of years and in one case are barely more than 1 kyr (e.g.,
447 time elapsed between the 102.5 ± 0.8 ka Cancellò and the 101.2 ± 0.8 ka Santa Lucia eruptions).
448 Consequently, the period of 109-92 ka was characterized by a high frequency of moderate to large explosive
449 eruptions, i.e., an eruptive behaviour that has not been recognised within the more recent (i.e., post-CI) activity
450 of the Campi Flegrei volcano.

451

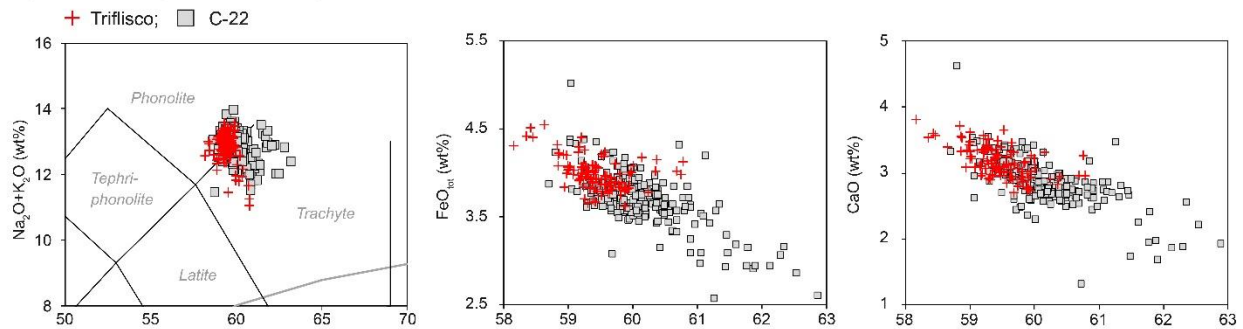
452 5.2. *Tephra correlations*

453 To correlate the investigated units of the Campanian Plain with MIS 5 Mediterranean tephra markers, we
454 refer to the Central Mediterranean tephrostratigraphic successions spanning this interval that (i) record in
455 stratigraphic order most MIS 5 tephra markers, (ii) have a good geochemical characterization of all tephra, (iii)
456 have a good radioisotopic or stratigraphic chronology, and (iv) have a good expression of the MIS 5 climate
457 variability, which enable a reliable assessment of the tephra climato-stratigraphic position.

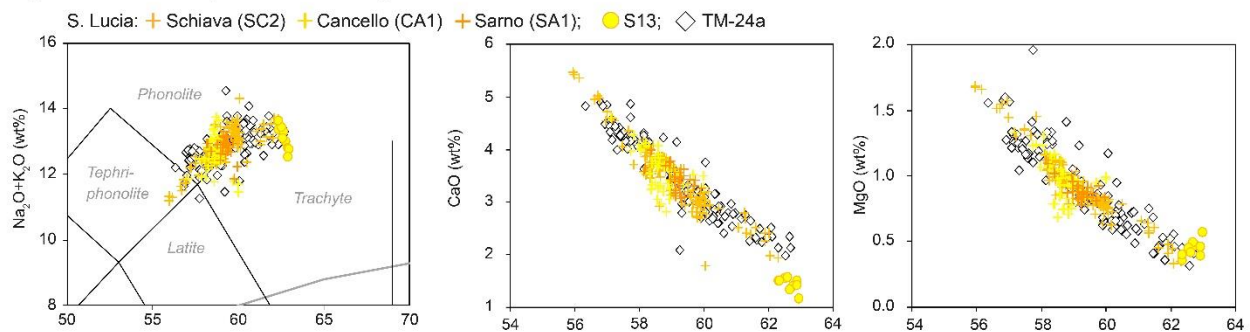
458 These requisites are fully or partially met by (i) the rich tephrostratigraphic record of the Lago Grande di
459 Monticchio, southern Italy (Fig. 1a), located ca. 120 km east of the Neapolitan volcanoes – thus in an ideal
460 position for recording their explosive activity (Wulf et al., 2004, 2012) – and (ii) the Popoli MIS 5 succession,
461 in Sulmona Basin (Fig. 1a), where MIS 5 tephra were dated by $^{40}\text{Ar}/^{39}\text{Ar}$ method (Giaccio et al., 2012; Regattieri
462 et al., 2017), allowing a direct, unambiguous comparison with the $^{40}\text{Ar}/^{39}\text{Ar}$ chronology here obtained for the
463 investigated Campanian Plain units.

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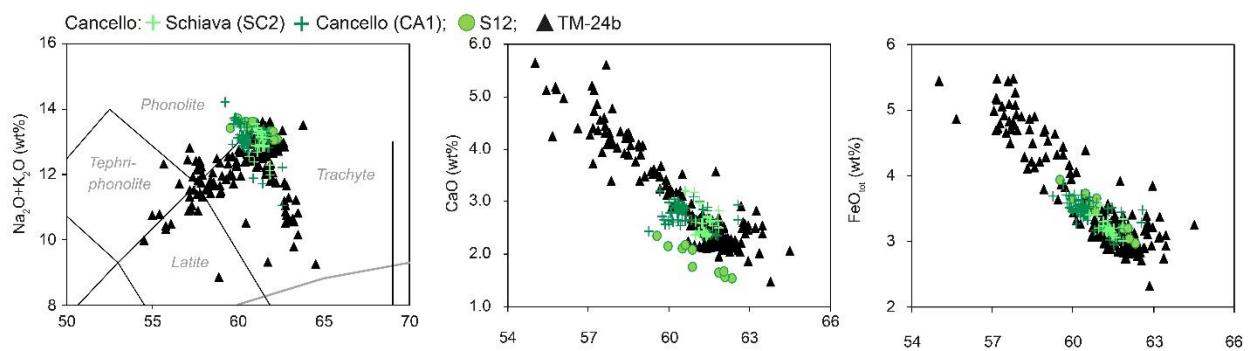
a) Triflisco (91.8 ± 1.2 ka) vs C-22



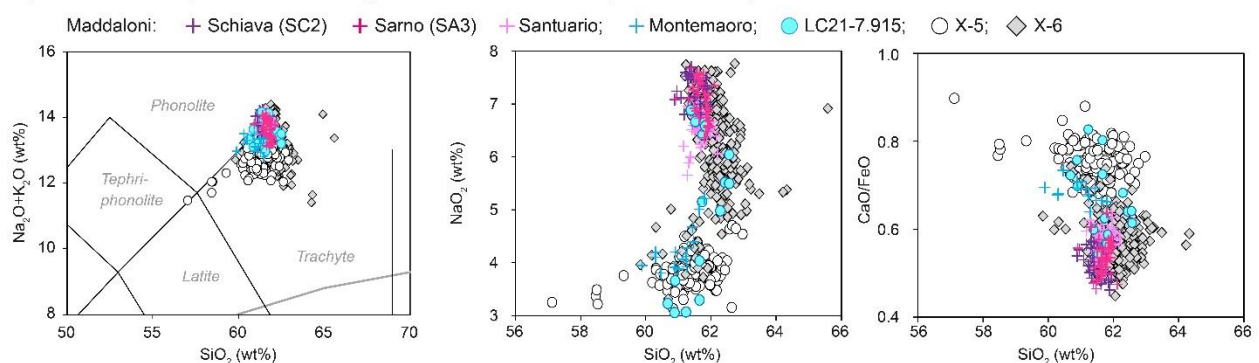
b) Santa Lucia (101.2 ± 0.8 ka) vs TM-24a



c) Canello (102.5 ± 0.8 ka) vs TM-24b



d) Maddaloni (109.3 ± 1.0 ka) and Montemaoro (109-103 ka) vs X-6 and X-5



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Figure 5. Major element bi-plots and ratios of Triflisco, Santa Lucia, Canello, Montemaoro and Maddaloni units from the Campanian Plain in comparison with literature data. Literature EDS data source: SC2-b (Di Vito et al., 2008), S13, S12 (Munno and Petrosino, 2007). Literature glass-WDS data source: C-22 marker = TM-23-11 (Wulf et al., 2004), POP-1 (Giaccio et al., 2012), PRAD-2525 (Bourne et al., 2015), TF-10 (Giaccio et al., 2017a), TP05-25.195 (Wulf et al., 2018); TM-24a marker = TM-24a (Wulf et al., 2012), POP-2 (Regattieri et al., 2015); TM-24b marker = TM-24b (Wulf et al., 2012), POP-2A (Giaccio et al., 2012), OH-DP-0404 (Leicher et al., 2016), TF-11 (Giaccio et al., 2017a); X-5 marker = TM-25 (Wulf et al., 2012), POP-3, CIL-1 (Giaccio et al., 2012), LeS1 (Donato et al., 2016), TF-12 (Giaccio et al., 2017a), LC21-7.915 (Satow et al., 2015); X-6 marker = TM-27 (Wulf et al., 2012, 2018), CIL-2 (Giaccio et al., 2012), I-9 (Insinga et al., 2014), POP-4 (Regattieri et al., 2015), PRAD-2812 (Bourne et al., 2015), OH-DP-0435 (Leicher et al., 2016), Tarsia, LeS2 (Donato et al., 2016), TF-13 (Giaccio et al., 2017a), TP05-27.915 (Wulf et al., 2018), Cavallo-G (Zanchetta et al., 2018).

476 **Triflisco** - Both $^{40}\text{Ar}/^{39}\text{Ar}$ chronology and major elements (Fig. 5a) glass composition of Triflisco unit ($91.8 \pm$
477 1.4 ka) are fully consistent with those of the Sulmona tephra POP1 (92.1 ± 4.6 ka; Giaccio et al., 2012) that,
478 in turn, was correlated to the Monticchio tephra TM-23-11 (Giaccio et al., 2012; Fig. 5a), dated at 95.18 ± 4.76
479 ka (Wulf et al., 2012). POP1/TM-23-11 was also correlated to the widespread C-22 tephra marker (Giaccio et
480 al., 2012) of the Tyrrhenian Sea tephra series (Paterne et al., 1986, 1988). The correlation of Triflisco with
481 POP1/TM-23-11/C-22 is supported also by incompatible trace element contents plotted against Th (Fig. 6a).
482 Furthermore, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of Triflisco perfectly match literature values for the POP1/TM-23-11/C-22
483 tephra layers/markers (Fig. 3a), strengthening this correlation.

484 The POP1/TM-23-11/C-22 was also identified in Fucino succession, as layer TF-10 (Giaccio et al., 2017a),
485 and in San Gregorio Magno basin, as layer S14, (Munno and Petrosino, 2007; Petrosino et al. 2019; Fig. 1a).
486 The C-22 was also correlated to the 11 cm- thick tephra layer CET1-10/14 in the Tyrrhenian core CET-1
487 (Petrosino et al., 2016). This marker was also identified in the marine core PRAD 1-2, in the Adriatic Sea, as
488 layer PRAD-2517 (Giaccio et al., 2012; Bourne et al., 2015). Finally, in the peatland succession of Tenaghi
489 Philippon, in Greece (Figs. 1a, 7), recent cryptotephra investigations by Wulf et al. (2018) allowed the
490 correlation of the C-22 marker with tephra layer TP05-25.195 (Fig. 5a).

491 **Santa Lucia** – Both major (Fig. 5b) and trace (Fig. 6a) element compositions, as well as the chronology of
492 Santa Lucia unit are compatible with TM-24a tephra of Monticchio, to which the Sulmona tephra POP2 was
493 also correlated (Giaccio et al., 2012; Fig. 7). The Monticchio varve-supported age for TM-24a is 102.0 ± 5.7
494 ka (Wulf et al., 2012; Monticchio chronology MON-2014, Sabine Wulf, personal communication 2017), whereas
495 the modelled age of POP2 is 102.0 ± 2.4 ka (Regattieri et al., 2015). In Sulmona paleo-hydrological record,
496 POP2 falls in the early stage of a period of increasing precipitation correlated to the Greenland Interstadial 23,
497 which in reference records (e.g., Corchia Cave, North Greenland Ice Core Project members et al., 2004;
498 Drysdale et al., 2007) starts about 102-103 ka, thus in agreement with the estimated age of POP2/TM-24a.
499 Here Santa Lucia unit is precisely $^{40}\text{Ar}/^{39}\text{Ar}$ dated at 101.2 ± 0.8 ka (Fig. 4b), supporting this correlation.

500 $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios determined on Santa Lucia samples show values similar to those obtained for
501 Triflisco/C-22 tephra layer/marker (Fig. 3a), but they can be discriminated based on the higher HFSE (e.g., Th,
502 U) contents of the Triflisco/C-22 glasses than the Santa Lucia ones, thus preventing erroneous correlations
503 (Fig. 6a).

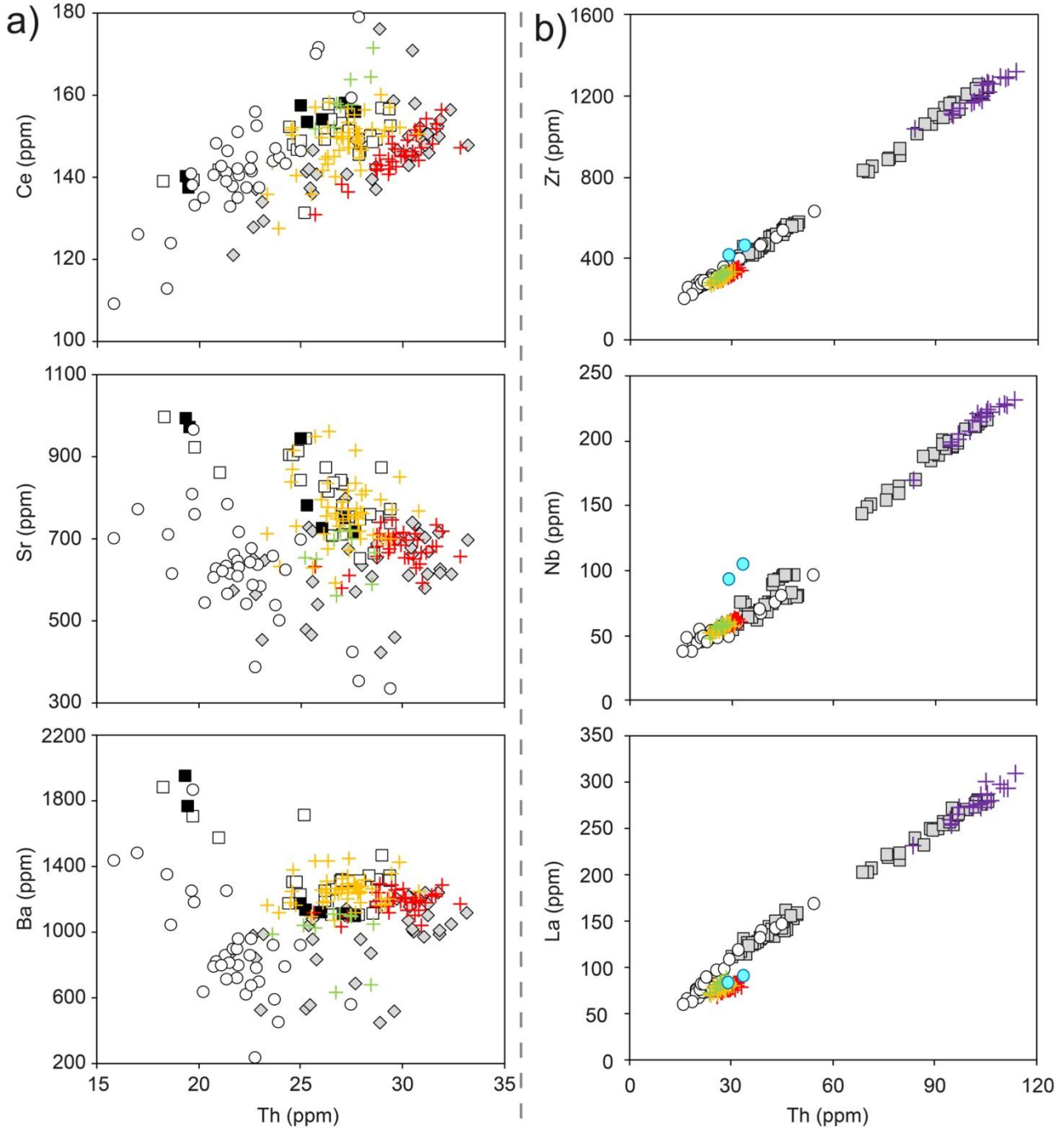
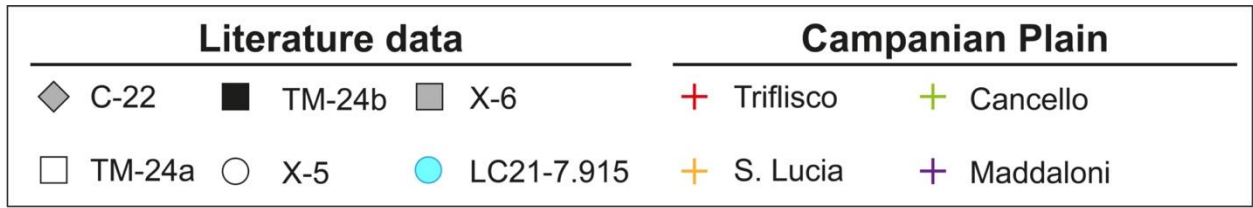
504 At Fucino Basin (Figs. 1a, 7), tephra layer TF-11, located immediately below tephra layer TF-10/C-22, was
505 correlated by Giaccio et al. (2017a) to the Monticchio tephra POP2/TM-24a (Fig. 7). The same marker horizon
506 was also recognized in Lake Ohrid (North Macedonia-Albania; Figs. 1a, 7) as layer OH-DP-0404 (Leicher et

507 al., 2016). The crypto-tephra CET1 12-13-14 in the Tyrrhenian core CET1 (Fig. 1a) also has major element
508 composition compatible with TM-24a/POP2 (Petrosino et al., 2016), thus representing the unique so far known
509 occurrence of Santa Lucia unit in the marine realm. Finally, at San Gregorio Magno (Munno and Petrosino,
510 2007; Petrosino et al., 2019), tephra layer S13, underlying tephra layer S14/C-22, would be stratigraphically
511 well suited to be a potential candidate for the TM-24a/Santa Lucia unit (Fig. 7). However, EDS-glass chemical
512 composition supports only partially this correlation (Fig. 5b), and WDS-glass composition should be acquired
513 on purpose.

514 **Cancello** – The Cancello pumice fall occurs below Santa Lucia unit=TM-24a/POP2 (Di Vito et al., 2008; Fig.
515 1b), thus indicating POP2a (Giaccio et al., 2012) and TM-24b (Wulf et al., 2012), which respectively underlay
516 POP2 and TM-24a, as the best candidates for correlation to this unit (Fig. 7). Major element biplots confirm
517 this correlation (Fig. 5c), also supported by trace element comparison (Fig. 6a). In particular, with respect to
518 the Santa Lucia unit, the Cancello unit appears to extend to lower Th contents (Figs. 2f, 6a), which allows
519 discriminating these two tephra markers. At Monticchio, TM-24b is varve-dated at 103.1 ± 5.7 ka (Wulf et al.,
520 2012; MON-2014), while in Sulmona Basin a modelled age of 103.3 ± 1.4 ka was obtained for POP2a
521 (Regattieri et al., 2015), in agreement with the more precise age of 102.5 ± 0.8 ka here measured for the
522 Cancello unit (Fig. 4c). In summary, the correlation of Cancello unit to POP2a/TM-24b is fully supported by all
523 the geochemical and geochronological data.

524 At San Gregorio Magno (Munno and Petrosino, 2007; Petrosino et al., 2019), the tephra layer S12 is
525 stratigraphically well suited for being a good correlation candidate for POP2a/TM-24b (Fig. 7). The
526 geochemical correlation of S12 with Cancello unit, based on the available EDS-glass composition, is quite
527 convincing (Fig. 5c), but more compelling WDS data would be required. Finally, the crypto-tephra CET1-15 in
528 the Tyrrhenian core CET1 (Fig. 1a) is stratigraphically (Fig. 7) and compositionally consistent with TM-
529 24b/POP2b (Petrosino et al., 2016).

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533 **Figure 6.** Incompatible trace element patterns against Th for the Triflisco, Santa Lucia, Canello and Maddaloni units in comparison with
 534 literature data. Literature data source: C-22 = TM-23-11, PRAD 2525 (Bourne et al., 2015), S14 (Petrosino et al., 2019); TM-24a = TM-
 535 24a (Wulf et al., 2012); TM-24b = TM-24b (Wulf et al., 2012); X-5 = TM-25 (Wulf et al., 2012), POP-3 (Giaccio et al., 2012), LC21-7.915
 536 (Satow et al., 2015), LeS1 (Donato et al., 2016), TF-12 (Giaccio et al., 2017a), S11 (Petrosino et al., 2019); X-6 = TM-27, PRAD 2812
 537 (Bourne et al., 2015), LeS2 (Donato et al., 2016), TF-13 (Giaccio et al., 2017a), S10 (Petrosino et al., 2019).

538 **Maddaloni and Montemaoro** – At Masseria Montemaoro quarry (Fig. 1a), these two, stratigraphically

539 superimposed units underlie the Canello unit (Fig. 1c). The $^{40}\text{Ar}/^{39}\text{Ar}$ age of 109.3 ± 1.0 ka determined for

540 Maddaloni unit is virtually indistinguishable from that of 109.1 ± 0.8 ka, obtained for the Sulmona tephra layer
541 POP4 (Regattieri et al., 2017), which was correlated to the X-6 tephra marker (Regattieri et al., 2015),
542 corresponding to the Monticchio TM-27 (Wulf et al., 2012). Consistent with this chronological information, the
543 major (Fig. 5d) and trace (Fig. 6b) elements composition of the Maddaloni unit well match the most evolved
544 term of POP4/TM-27 tephra layer/marker and those of the other X-6 equivalent layers in distal archives through
545 the central Mediterranean area (Fig. 1a). Sr-Nd isotope values obtained from the Maddaloni unit are consistent
546 with those of CIL-2/X-6 tephra layer/marker from the Cilento coast and other X-6 occurrences (Fig. 3a-b), thus
547 further supporting its correlation with the X-6 marker. Moreover, major and trace elements glass compositions
548 are extremely distinctive (e.g., different alkali ratio and Cl content, incompatible trace element patterns), and
549 we thus highly recommend the employment of these geochemical tracers as a correlation tool for the X-6
550 tephra (Figs. 5d, 6b; Supplementary Materials-1). All geochemical and chronological data thus corroborate
551 Maddaloni as the most proximal equivalent of the X-6 tephra marker.

552 The Ionian X-6 tephra marker (Keller et al., 1978), and its other marine and terrestrial equivalents, is the most
553 widespread MIS 5 Campi Flegrei tephra (Figs. 1a, 7), while considering the whole Campi Flegrei record, in
554 terms of dispersal area it is second only to the CI (e.g., Costa et al., 2012). It has been recognised in a series
555 of sedimentary successions in the central Mediterranean area (Figs. 1a, 7), including the Ionian Sea (I-9,
556 Insinga et al., 2014), Tyrrhenian Sea (C-31, Paterne et al., 2008), Adriatic Sea (PRAD-2812, Bourne et al.
557 2015), Fucino Basin (TF-13, Giaccio et al., 2017a), Cilento Coast (Giaccio et al., 2012; Donato et al., 2016),
558 San Gregorio Magno Basin (S10, Petrosino et al., 2019), Valle del Crati (Tarsia, Donato et al., 2016), Grotta
559 del Cavallo Palaeolithic site (Unit G, Zanchetta et al., 2018), Lake Ohrid (OH-DP-0435, Leicher et al., 2016),
560 and Tenaghi Philippon (TP05-27.915, Wulf et al., 2018).

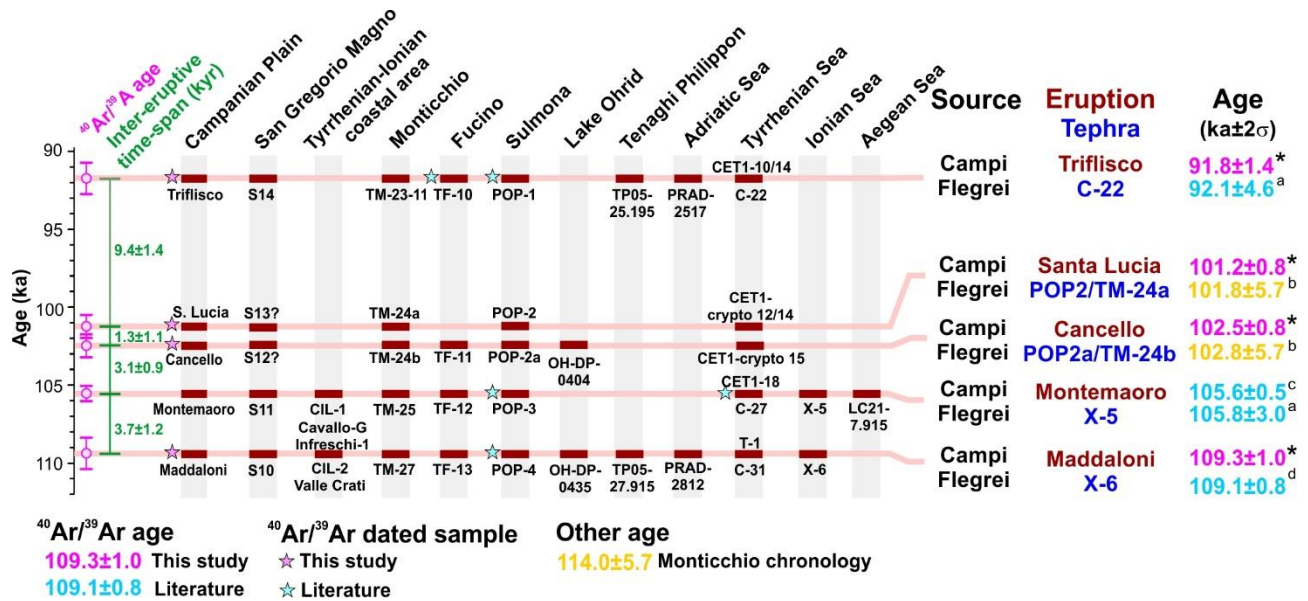
561 Regarding Montemaoro unit, its stratigraphic position between Maddaloni/X-6 and Canello/TM-24b, which
562 chronologically constrains it between ~ 109 ka and ~ 103 ka, makes it the best candidate for the terrestrial
563 counterpart of the Ionian Sea marker X-5, which lays immediately above the X-6 (Keller et al., 1978). The X-5
564 is equivalent to tephra layer TM-25 in the Lago Grande di Monticchio succession, dated at 105.6 ± 0.5 ka
565 (recalculated with ACs at 1.1891 Ma; Tyrrhenian Sea; Petrosino et al., 2015), or POP3 $^{40}\text{Ar}/^{39}\text{Ar}$ dated at 105.8
566 ± 1.3 ka (Sulmona Basin, Giaccio et al., 2012). Although it was not possible to acquire new major (glass-WDS)
567 and/or trace element data, the available glass-EDS composition for the Montemaoro unit supports this
568 correlation (Fig. 5d). Consequently, we suggest that the Montemaoro unit is the most likely proximal
569 counterpart of the X-5, based on the chronological and stratigraphical constraints provided in this study and

570 the existing chemical data. Future discovery of a new field exposure of Montemaoro would allow further
571 verification of this correlation.

572 Although less dispersed, the X-5 marker, like the X-6, was reported in several stratigraphic successions (Figs.
573 1a, 7), including the Fucino Basin (TF-12, [Giaccio et al., 2017a](#)), Cilento Coast (CIL1, [Giaccio et al., 2012](#);
574 LeS1, [Donato et al., 2016](#)), San Gregorio Magno Basin (S11, [Petrosino et al., 2019](#)), and as the lowermost
575 tephra layer in CET1 core (i.e., CET1-18, [Petrosino et al., 2015](#)), $^{40}\text{Ar}/^{39}\text{Ar}$ dated at 105.18 ± 0.5 ka (2σ
576 analytical uncertainty).

577 A potential correlative for either the X-6 or X-5 marker was also recognised at the remote site of marine core
578 LC21 ([Satow et al., 2015](#)), in the Aegean Sea (Fig. 1a). Specifically, the crypto-tephra LC21-7.915, whose
579 base was dated at 104.1 ± 2.2 ka, according to the LC21 age model ([Satow et al., 2015](#)), presents two
580 geochemical compositions indicating both Santorini and Campanian sources. The Campanian component is
581 in turn represented by two glass HAR and LAR trachyte-phonolite populations, which are compatible with X-5
582 and X-6 compositions, respectively (Fig. 5d). Moreover, in terms of trace element composition, the few
583 available data appear quite consistent with both markers (Fig. 6b). However, both the age and
584 climatostratigraphic position of the crypto-tephra LC21-7.915 make the X-5 the most probable correlative.
585 Indeed, LC21-7.915 precisely marks the onset of the sapropel S4 deposition, at the base of which in the
586 Tyrrhenian Sea records the tephra X-5/C-27 is also found (Fig. 8; [Paterne et al., 2008](#); [Regattieri et al., 2015](#)).
587 Therefore, we are inclined to consider the X-5 as the most likely correlative for the HAR component of the
588 Campanian portion of LC21-7.915 crypto-tephra, though the co-presence of the LAR component would require
589 a plausible explanation.

590 Overall, the correlations of the investigated Campanian Plain units with the five distal tephra markers are well
591 supported by several line of consistent, independent evidence, including their stratigraphic order,
592 geochronology, and geochemistry (major and trace elements, and the Sr-Nd isotopes). However, in some
593 cases, the geochemical variability of the investigated Campanian Plain units is less wide than the
594 corresponding distal tephra. This is especially true for Canello and Maddaloni units, the composition of which
595 covers only a part of the wider variability observed in distal settings (Figs. 5c-d and 6b). This is not surprising,
596 as the occurrence of the analysed medial units is relatively scant with respect to the distal ones, and thus could
597 be not representative of the complete eruptive sequence and geochemical variability. This would suggest that
598 not all the eruptive phases or sub-units, e.g., pyroclastic flow or fall, of Canello and Maddaloni units reached
599 the distance of 30-40 km, at which the investigated sections are located (Fig. 1b) or had dispersal axes not
600 compatible with pumice deposition in these localities.



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Figure 7. Age and occurrences of the C-22, POP2/TM-24a, POP2a/TM-24b, X-5, and X-6 tephra markers in terrestrial and marine sedimentary environments through the Mediterranean region. $^{40}\text{Ar}/^{39}\text{Ar}$ ages are according to ACs at 1.1891 Ma and FCs at 28.294 Ma. * This study, ^a Giaccio et al. (2012); ^b Wulf et al. (2012); ^c Petrosino et al. (2016); ^d Regattieri et al. (2015).

5.3. Implications for the chronology of the millennial-scale climatic oscillations of the MIS 5c-d

The great relevance of some of the investigated tephra layers as fundamental chronological and stratigraphic markers for the Mediterranean MIS 5c-d high frequency climatic variability was widely acknowledged and discussed in previous papers (e.g., Giaccio et al., 2012; Regattieri et al., 2015). However, the acquisition of new high-precision $^{40}\text{Ar}/^{39}\text{Ar}$ ages for two previously undated tephra (Cancello/TM-24b and Santa Lucia/TM-24a tephra layers/markers), the substantial improvement in accuracy of the Triflisco/C-22 unit, as well as the acquisition of new high-resolution records containing these tephra markers (e.g., Tenaghi Philippon; Wulf et al., 2018), give us the opportunity to discuss the implications of these new data from a palaeoclimatological perspective, in particular on the timing and spatial synchronicity of MIS 5c-d climatic variability.

For this purpose, we consider the records endowed with suitable resolution and good expression of the millennial scale climate oscillations of the MIS 5d-c, which can be reasonably correlated to the succession of stadial and interstadial events documented in the reference record of the Greenland ice (e.g., North Greenland Ice Core Project members et al., 2004). These are (i) the Lago Grande di Monticchio pollen profile, Southern Italy (e.g., Brauer et al., 2007; Wulf et al., 2012), (ii) the isotope series of Sulmona Basin, Central Italy (Regattieri et al., 2015, 2017), (iii) the Tenaghi Philippon pollen record, in Greece (Milner et al., 2012, 2013, 2016), and (iv) the pollen record of Lake Ohrid, North Macedonia-Albania (Sinopoli et al., 2018; Figs. 1a, 8). For the sapropel stratigraphy, we also consider the Tyrrhenian Sea record of the core KET 8004 (Paterne et

625 al, 2008), which contains three out of the five markers (Fig. 8), and the Aegean Sea core LC21, likely containing
626 the X-5 layer (Satow et al., 2015; Fig. 8).

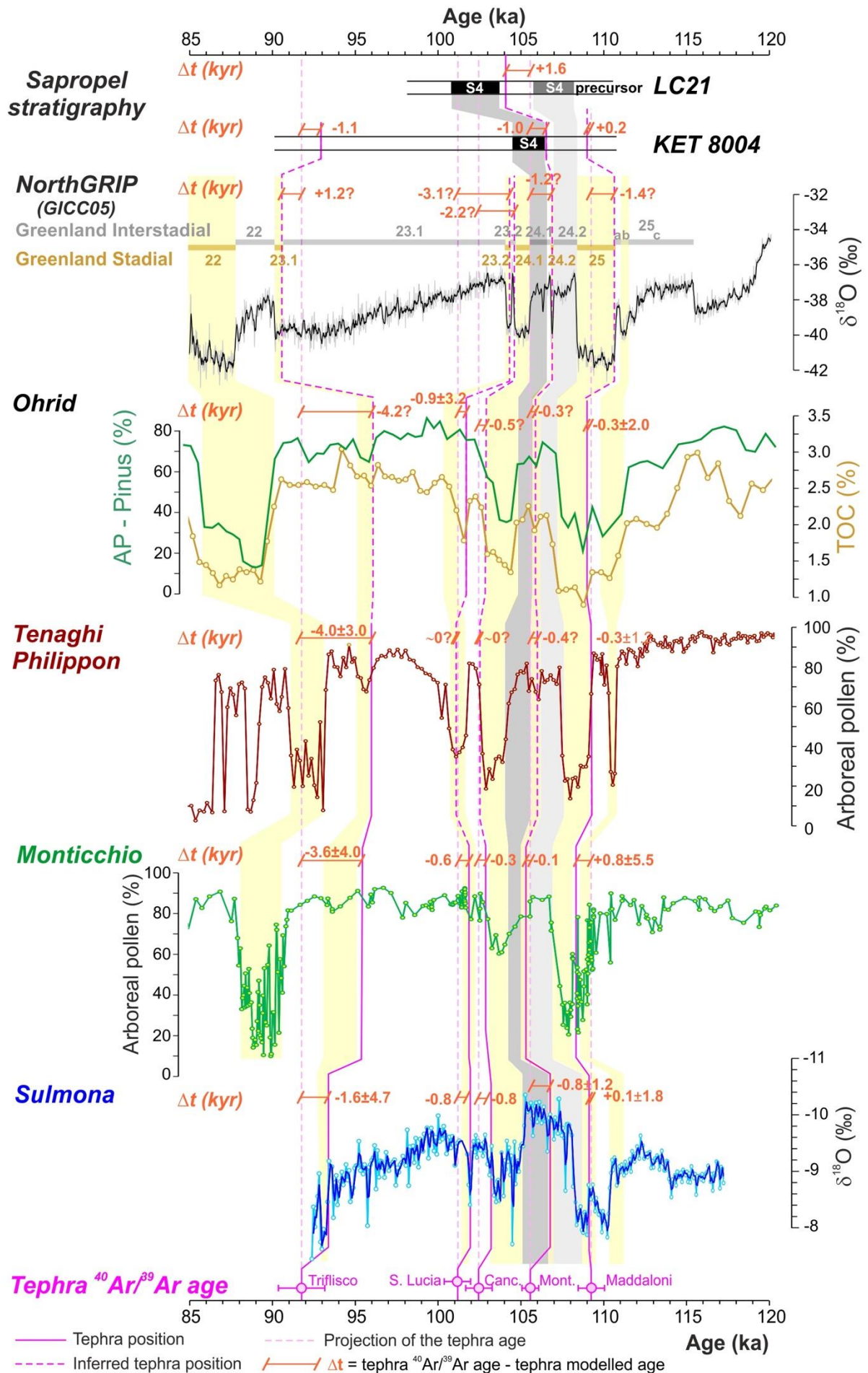
627 So far, Monticchio and Sulmona are the only Mediterranean records containing all the five MIS 5d-c tephra
628 from Campi Flegrei (Fig. 8), whereas Tenaghi Philippon and Ohrid contain only two markers, i.e., Maddaloni/X-
629 6 and Triflisco/C-22, and Maddaloni/X-6 and Santa Lucia/TM-24a, respectively (Fig. 8; Table 2).

630 The Maddaloni/X-6 unit, the most common tephra in the considered records (Fig. 7), occurs at the very end of
631 a short interstadial pulsation, likely corresponding to Greenland Interstadial (GI) 25_a. It precedes the onset of
632 the first marked stadial oscillation of the MIS 5 period, the Greenland Stadial (GS) 25_a, corresponding to the
633 North Atlantic cold event C24 (e.g., Shackleton et al., 2004; Fig. 8). The temporal offset, i.e., the difference
634 between the radioisotopic ⁴⁰Ar/³⁹Ar age of Maddaloni/X-6 tephra and the age reported in the various
635 paleoclimatic records (Δt in Fig. 8), is small, reaching the maximum value of ca. 1 kyr in the Monticchio record
636 (Fig. 8; Table 2). However, assuming that the inferred position of Maddaloni/X-6 tephra layer/marker in the
637 Greenland isotope record is correct, then, the age of the end of the GI-25_a, 110.6 ka, according to GICC05
638 (Rasmussen et al., 2014), should be approximately 1.3 kyr younger (Fig. 8). On the contrary, Sardinian
639 stalagmite evidence suggests instead that the GI-25_b ended at 110.5 ka (Columbu et al., 2017), which is fully
640 consistent with the GICC05 chronology.

641 The Montemaoro/X-5 tephra occurs in the medial of an interstadial oscillation correlated to the GI-24 (e.g.,
642 Regattieri et al., 2015). More precisely, Montemaoro/X-5 tephra occurs close to a very brief stadial pulsation
643 within the GI-24 that is quite evident in all the considered records and that likely corresponds to the short GS-
644 24.2 (Fig. 8). The Δt , relative to the Montemaoro/X-5 tephra, is of ca. 1 kyr in all records, except Monticchio, in
645 which it is negligible (Fig. 8; Table 2). In the Tyrrhenian Sea, and likely in the Aegean Sea, the Montemaoro/X-
646 5 also represents an excellent marker for the Sapropel S4, which is in turn correlated to the GI-24.1 (Regattieri
647 et al., 2015; Fig. 8).

648 The Canello and Santa Lucia tephra layers form an interesting couplet of temporally closely related tephra,
649 which mark the onset of an interstadial and the ensuing stadial phase, likely corresponding to the GI-23.2 and
650 the GS-23.2, respectively (Fig. 8). In all the considered records, the negligible Δt relative to this couplet of
651 tephra evidences a good agreement between the ⁴⁰Ar/³⁹Ar chronology and the age models of the records (Fig.
652 8).

653



655 **Figure 8.** Chronological offset between $^{40}\text{Ar}/^{39}\text{Ar}$ and modelled tephra age in selected high-resolution Mediterranean records containing
 656 the here investigated tephra and showing the millennial-scale climatic oscillations of the MIS 5d-c, compared to Greenland ice succession
 657 of stadial-interstadial events (Rasmussen et al., 2014). The Mediterranean sapropel stratigraphy from the Tyrrhenian Sea core KET 8004
 658 (Paterne et al., 2008) and Aegean Sea core LC21 (Satow et al., 2015), is also shown. The sapropel nomenclature is according to Ziegler
 659 et al. (2010). Data source: Lake Ohrid Arboreal pollen minus *Pinus* (AP – Pinus) and total organic carbon (TOC): Sinopoli et al. (2018),
 660 Wagner et al., (2017, 2019); Tenaghi Philippon pollen record: Milner et al. (2012, 2013, 2016); Monticchio pollen record; Brauer et al.
 661 (2007); Sulmona isotope record, Regattieri et al (2015).
 662

663 Finally, the Triflisco/C-22 tephra occurs at the beginning of a stadial event that interrupts a relatively long
 664 interstadial period, likely corresponding to the GS-23.1, which occurs at the end of the long-term cooling period
 665 featuring the GI-23.1 (Fig. 8). Noteworthy, the Δt relative to this tephra is quite long for the Monticchio and
 666 Tenaghi Philippon pollen records, reaching the considerable value of ca. 4 kyr (Fig. 8). The Δt is instead quite
 667 negligible for the NorthGRIP record (~1.2 kyr), provided that the inferred climatostratigraphic position of
 668 Triflisco/C-22 in the Greenland record is correct.

669 In summary, the Δt is relatively little for most of the climatic events, for which the Campi Flegrei MIS 5 tephra
 670 act as fundamental markers, and generally do not exceed the uncertainty associated to both $^{40}\text{Ar}/^{39}\text{Ar}$ ages
 671 and the age models of the respective paleoclimatic records (Table 2). However, the event associated with the
 672 Triflisco/C-22 represents a notable exception, for which the Δt can exceed the uncertainty associated to the
 673 $^{40}\text{Ar}/^{39}\text{Ar}$ dating of Triflisco/C-22 and of the paleoclimatic record age models (Figs. 7, 8; Table 2). With this
 674 regard, we emphasize that such wide Δt cannot be explained invoking an uncertainty of the tephra position
 675 within the records, as, at least for Monticchio and Tenaghi Philippon), where the Δt is -3.6 ± 4.0 kyr and $-4.0 \pm$
 676 3.0 kyr (Table 2), it is not relayed on an inference, this being based on undisputable stratigraphic evidence
 677 (Fig. 8).

678 Overall, the investigated tephra can be considered good stratigraphic markers of some of the stadial-
 679 interstadial events, as well as of the very short sub-stadial and sub-interstadial oscillations that punctuated the
 680 MIS 5c-d climatic variability (Table 2), whose chronology can greatly benefit from the high precision $^{40}\text{Ar}/^{39}\text{Ar}$
 681 dating of the Campi Flegrei eruption products.
 682

683 **Table 2.** Detailed climatostratigraphic position of the Campi Flegrei units with respect to the millennial to sub-millennial scale MIS 5
 684 paleoclimatic events as recorded in reference archives of the central Mediterranean area (Figs. 1, 7 and 8). The temporal offset, i.e., the
 685 difference between the radioisotopic $^{40}\text{Ar}/^{39}\text{Ar}$ age of Campi Flegrei tephra and the age of the corresponding distal tephra, as reported in
 686 the various paleoclimatic records, is also shown. Data source: Sulmona: Regattieri et al. (2015, 2017); Monticchio: Wulf et al. (2012),
 687 Regattieri et al. (2015); Ohrid: Leicher et al. (2021); Tenaghi-Philippon: Wulf et al. (2018); LC21: Satow et al. (2015).

Campanian Plain	Sulmona	Monticchio	Ohrid	Tenaghi-Philippon	LC21	Correlated event
Tephra $^{40}\text{Ar}/^{39}\text{Ar}$ age (ka \pm 2 σ)	Tephra Age \pm 2 σ ka $\Delta t \pm 2\sigma$ kyr	Tephra Age \pm 2 σ ka $\Delta t \pm 2\sigma$ kyr	Tephra Age \pm 2 σ ka $\Delta t \pm 2\sigma$ kyr	Tephra Age \pm 2 σ ka $\Delta t \pm 2\sigma$ kyr	Tephra Age \pm 2 σ ka $\Delta t \pm 2\sigma$ kyr	
Triflisco 91.8 \pm 1.4	POP1 93.4 \pm 4.5	TM-23-11 95.4 \pm 3.8		TP05- 25.195		Onset of the GS-23.1

	-1.6±4.7	-3.6±4.0		95.8±2.6 -4.0±3.0		
Santa Lucia 101.2±0.8	POP2 102.0±2.4 -0.8±2.5	TM-24a 101.8±5.0 -0.6±5.1	OH-DP- 0404 102.1±3.1 -0.9±3.2			Middle part of the GS-23.2
Cancello 102.5±0.8	POP2a 103.3±1.4 -0.8±1.6	TM-24b 102.8±5.1 -0.3±5.2				Onset of the GI-23.2
Montemaoro 105.6±0.5	POP3 106.4±1.1 -0.8±1.2	TM-25 105.5±5.3 0.1±5.3			LC21- 7.915 104.0±2.0 1.6±.1	End of the GS-24.2 - base of the sapropel S4
Maddaloni 109.1±0.8	POP4 109.0±1.5 0.1±1.8	TM-27 108.3±5.4 0.8±5.5	OH-DP- 0435 109.4±1.8 -0.3±2.0	TP05- 27.915 109.4±0.9 -0.3±1.2		Onset of the GS-25 - End GI-25a

688

689 6. Conclusions

690 In this study, we presented a wide dataset (i.e., stratigraphy, major, minor, and trace elements, Sr-Nd
691 isotopic composition and $^{40}\text{Ar}/^{39}\text{Ar}$ ages) required for a full characterization of four pumice fall deposits, named
692 Triflisco, Santa Lucia, Cancello, and Maddaloni, occurring in the Campanian Plain, 30 to 60 km east of the
693 Campi Flegrei volcanic field, and stratigraphically laying below the CI (~40 ka). Based on these data, these
694 units are here attributed to a previously unknown 109-92 ka explosive activity at Campi Flegrei volcano and
695 correlated with the widespread C-22, TM-24a/POP-2, TM-24b/POP-2a and X-6 tephra markers, respectively.
696 Furthermore, the chronological and stratigraphic constraints provided in this study, and a review of previous
697 EDS data, allow us also to propose the correlation of a fifth unit (i.e., Montemaoro) with the X-5 marine tephra
698 marker as well.

699 Our data confidently allow us to trace the volcanic source of these fundamental Mediterranean marker
700 horizons, so far only hypothesized. This extends the activity history of the Campi Flegrei volcano back ~110
701 ka at least, setting the groundwork for a reassessment of the volcanic history, and related hazards, and
702 confirming the Campi Flegrei volcano as one of the Europe's most productive sources of widespread and
703 disruptive ash fall events. The Maddaloni/X-6, given its wide dispersal area, clearly arises from one of the
704 largest explosive events through the whole Campi Flegrei eruptive history and demands further volcanological
705 investigations.

706 The new high-precision $^{40}\text{Ar}/^{39}\text{Ar}$ dating of the investigated units provide new fundamental temporal constraints
707 for refining and consolidating the chronology of MIS 5d-c period, characterised by a marked millennial- to sub-
708 millennial scale climatic variability, well documented in Mediterranean archives. Specifically, the ages obtained
709 for the Cancello and Santa Lucia tephra markers provide two new chronological constraints for the climatic
710 oscillations likely corresponding to the Greenland interstadial GI-23.2 and Greenland stadial GS-23.2.
711 Furthermore, the improved precision of the age for Triflisco would imply a substantial extension of the duration

712 of the interstadial period corresponding to the GI-23.1 up to 92 ka, i.e., ~4 kyr later than the ~96 ka age reported
713 for the GI-23.1 in several reference Mediterranean records. (Fig. 8). A reappraisal of the related chronologies
714 is thus required.

715 Future research development on the eruptive history and long-term hazard assessment at Campi Flegrei, as
716 well as paleoclimatic and archaeological investigations in central Mediterranean, will greatly benefit from the
717 geochemical and geochronological dataset provided in this contribution. Given the strong geochemical
718 similarities of the HAR Triflisco/C-22, Santa Lucia/TM-24a, and Canello/TM-24b units, we encourage caution
719 to avoid potentially misleading correlations based solely on major elements. Therefore, especially when a
720 specific tephra layer occurrence lacks bracketing tephra units, we recommend integrating major element data
721 with trace element and Sr-Nd isotope analysis, as they proved to be the best discriminating tool for these
722 tephra deposits.

723
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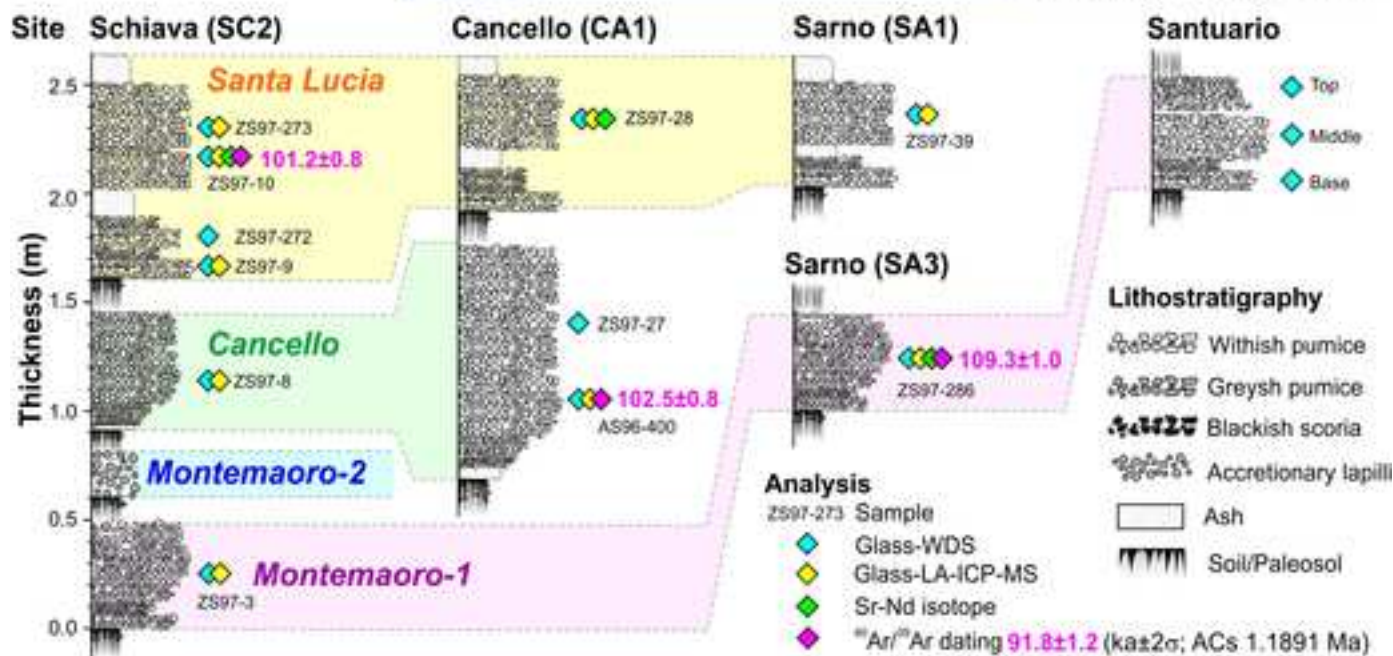
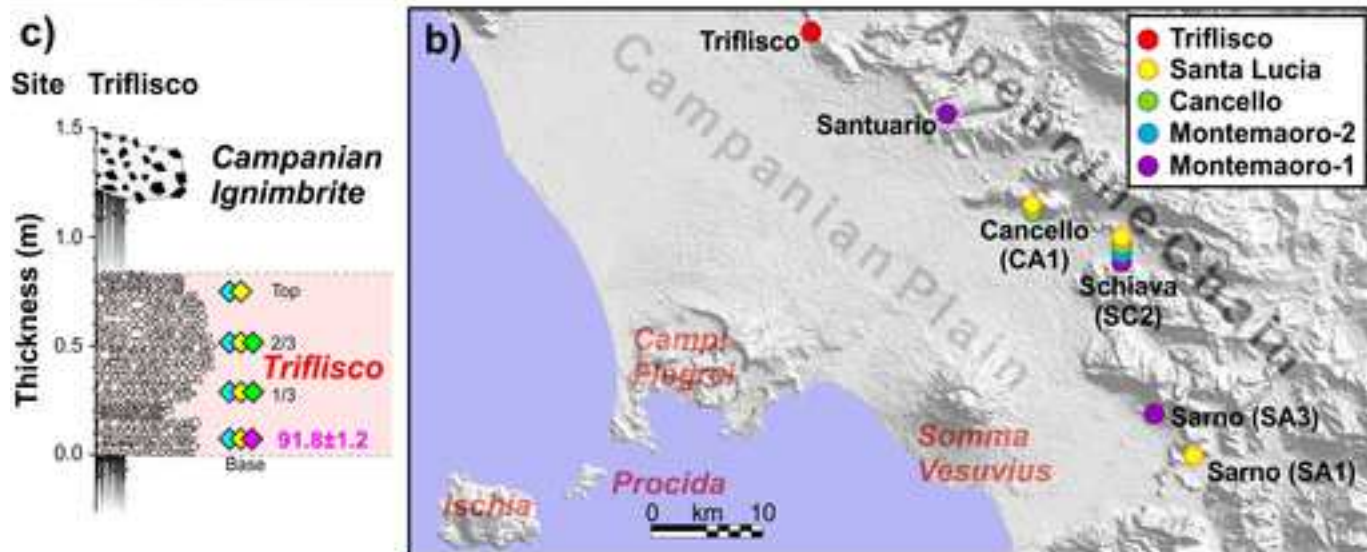
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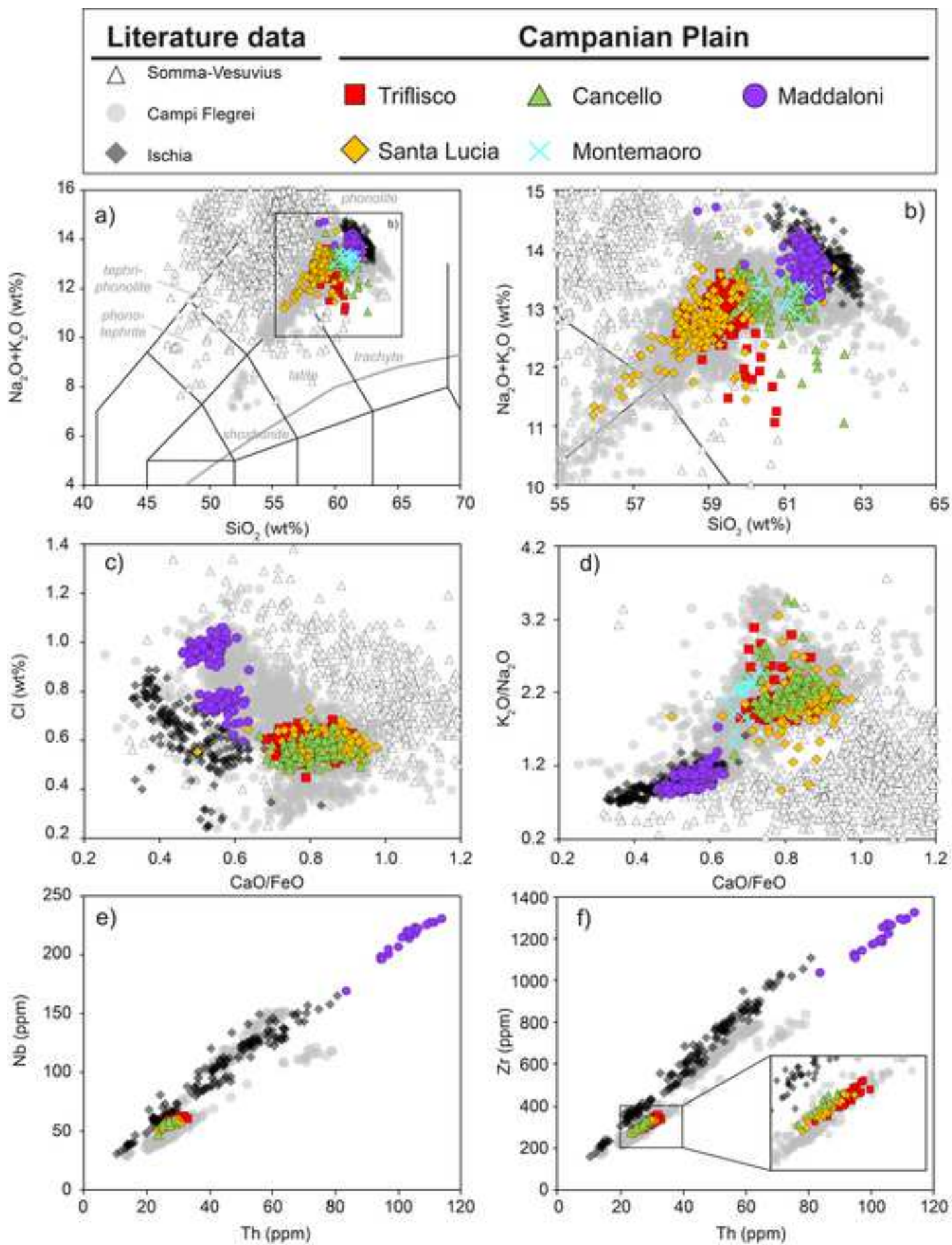
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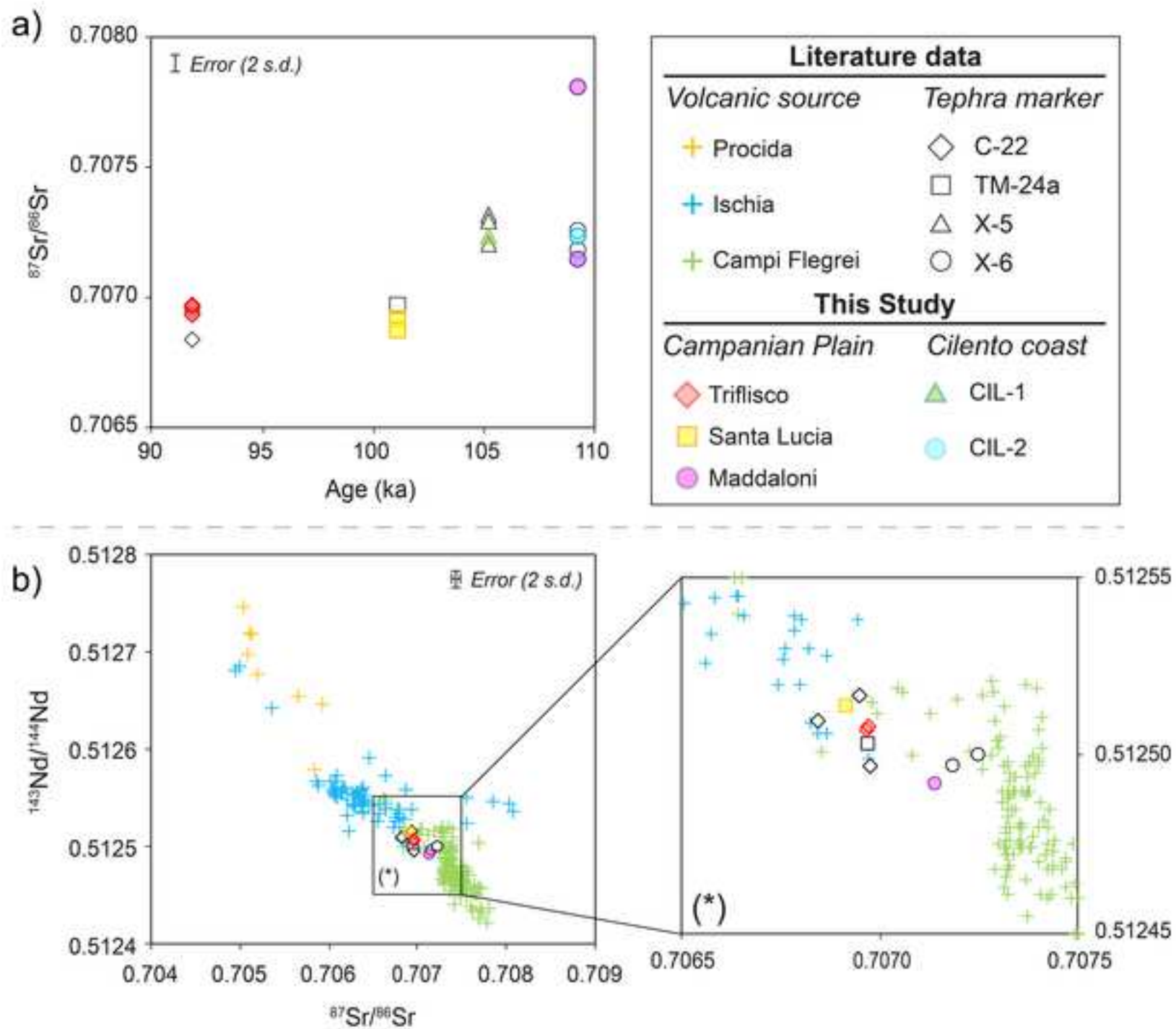
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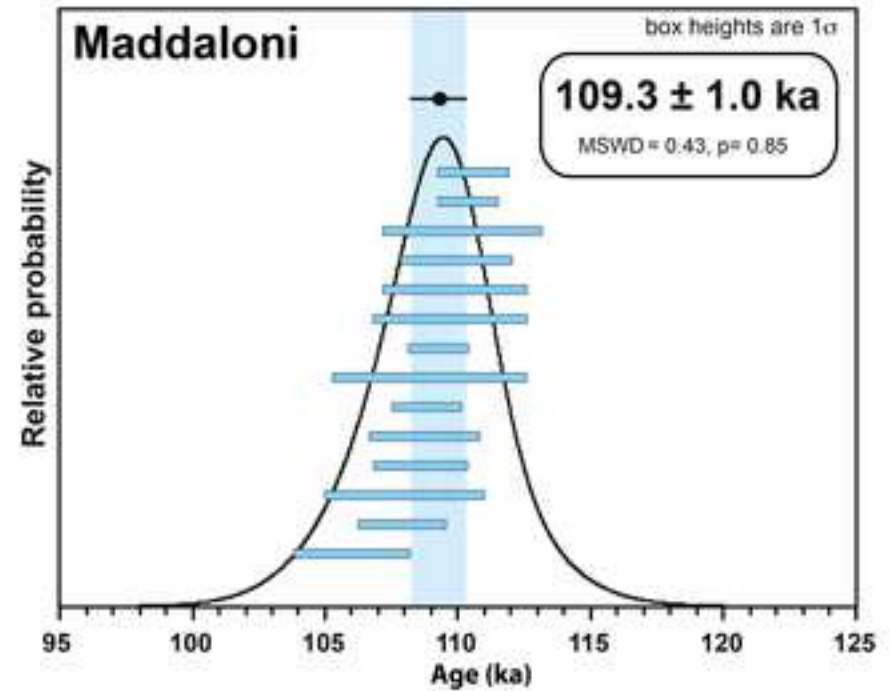
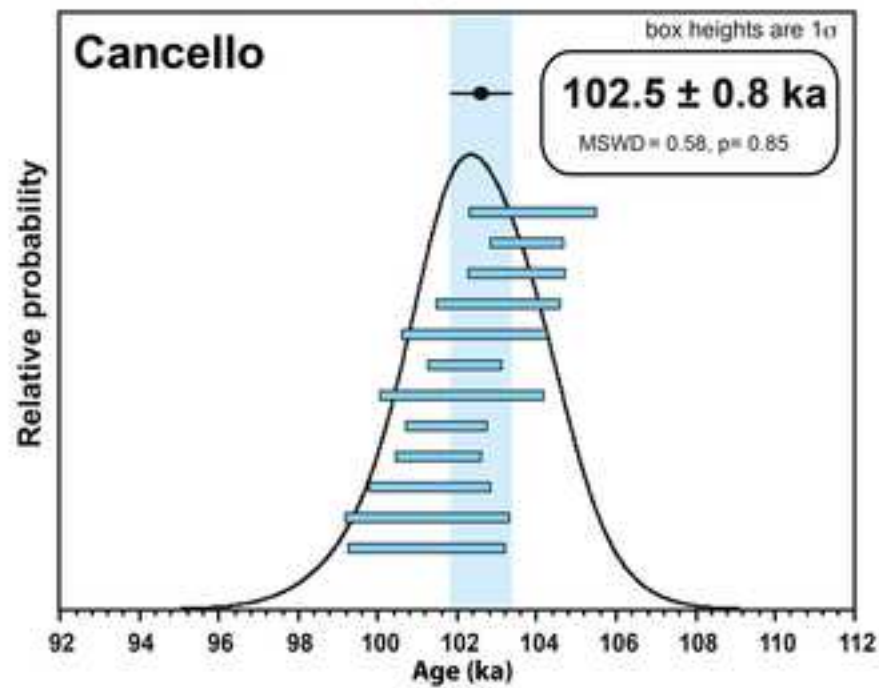
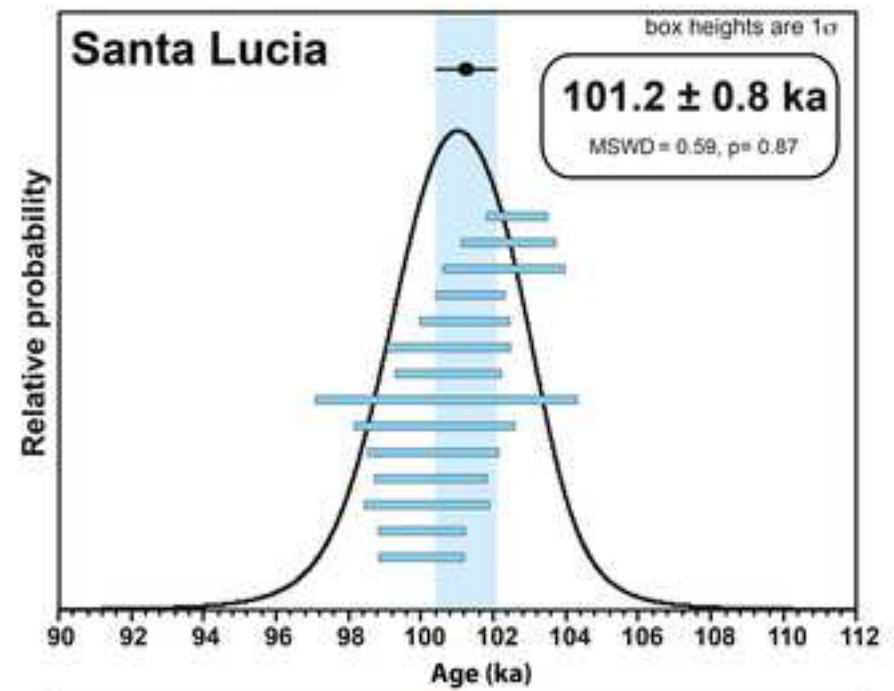
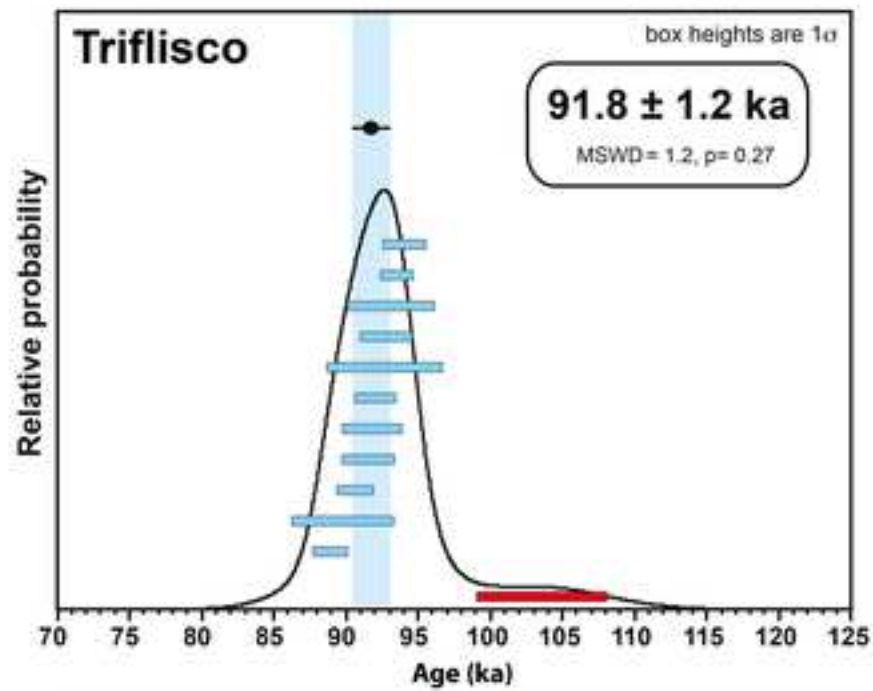
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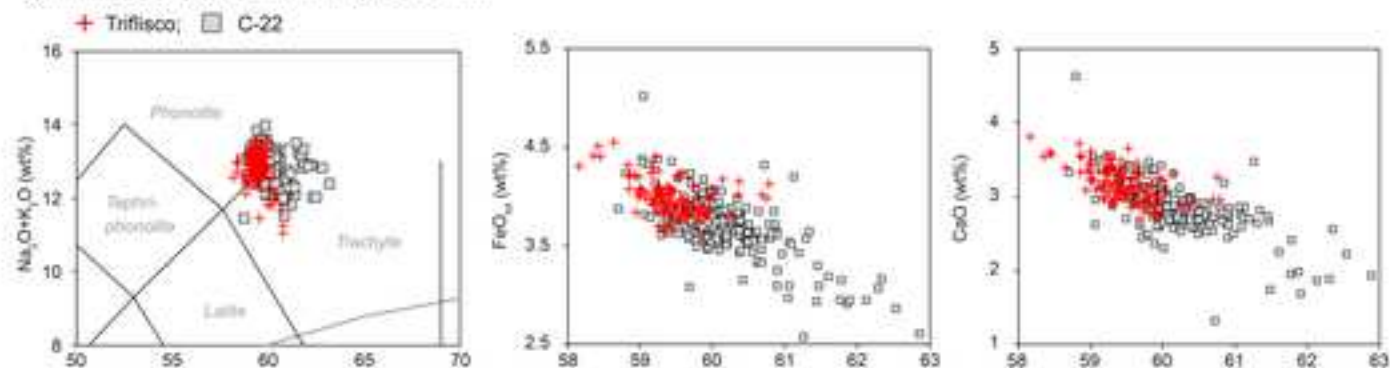
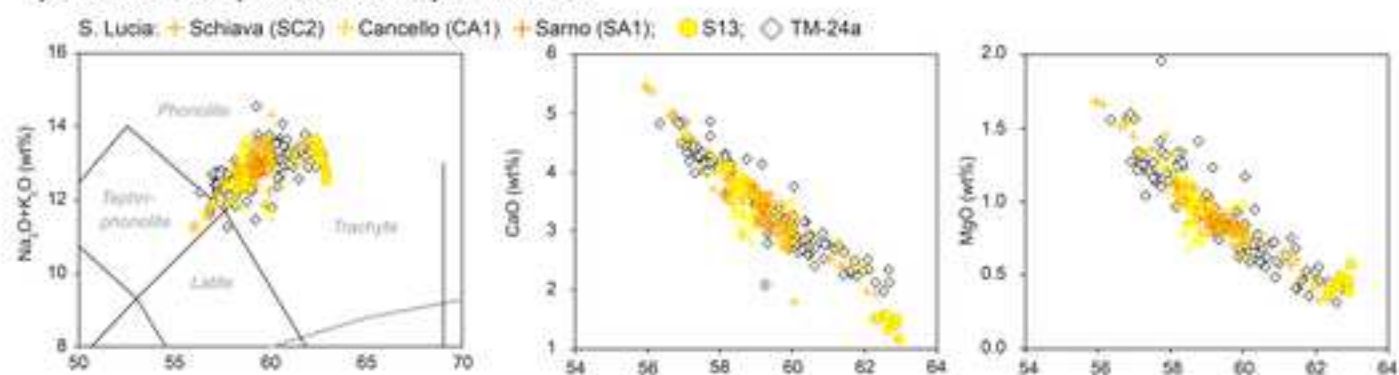
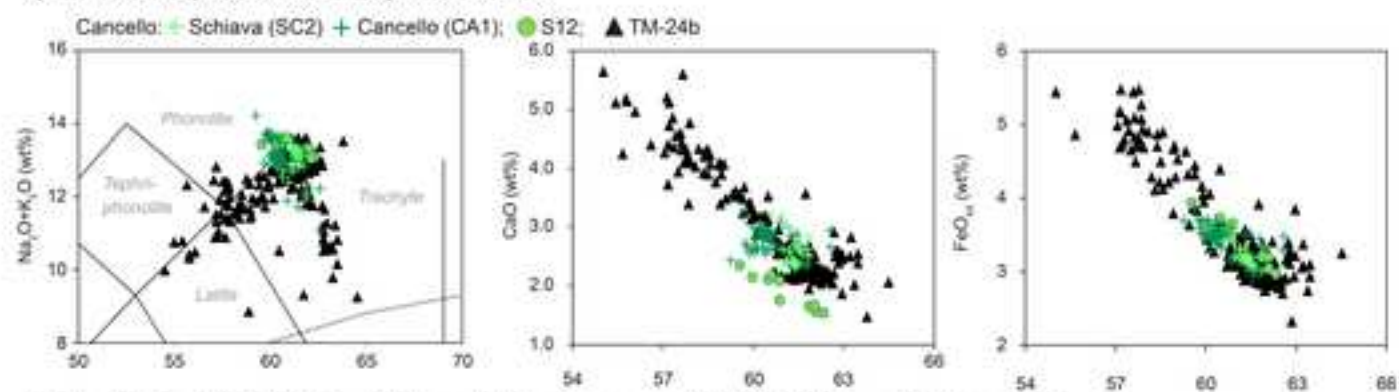
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a) Triflisco (91.8 ± 1.2 ka) vs C-22**b) Santa Lucia (101.2 ± 0.8 ka) vs TM-24a****c) Canello (102.5 ± 0.8 ka) vs TM-24b****d) Maddaloni (109.3 ± 1.0 ka) and Montemauro (109-103 ka) vs X-6 and X-5**