Unravelling the Ancient (> 46 ka) Volcanostratigraphy of Pantelleria Island (Sicily Strait, Italy) by Single-Grain $^{40}Ar/^{39}Ar$ Dating

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INTRODUCTION

Peralkaline magmatism is frequently associated with highly explosive activity (*e.g.*, Parker & White, 2008; Claessens et al., 2016; Wallace et al., 2025), making the precise reconstruction of eruptive cycles essential for volcanic hazard assessment, particularly in densely populated magmatic districts such as Pantelleria Island.

Located within the Sicily Strait Rift Zone (Italy), Pantelleria represents the subaerial portion of a large, active, composite Quaternary volcanic complex, distinguished as the type locality for pantellerite, an iron-rich, peralkaline (Na+K/Al > 1; Macdonald, 1974) rhyolite. Peralkaline magmatism has primarily driven the subaerial eruptive history of the island, accounting for ~ 95% of the exposed lithology (Fig. 1), emplaced as ignimbrites, fallout deposits, and lava flows. Basaltic lava flows and cinder cones constitute only ~ 5% of the total volcanic products, and together they represent the typical bimodal alkaline rock suite (the 'Daly Gap') characteristic of certain intraplate settings (*e.g.*, Scaillet & Macdonald, 2001; White et al., 2009; Romengo et al., 2012; Macdonald et al., 2022).

Pantelleria boasts a subaerial eruptive history spanning over 320 kyr (Mahood & Hildreth, 1986), characterised by the emplacement of nine recognised ignimbrite deposits (ignimbrite periods), linked to at least two caldera collapse events (*e.g.*, Mahood & Hildreth, 1986; Rotolo et al., 2013; Scaillet et al., 2013; Jordan et al., 2018). While the last seven ignimbrites have been geochronologically well-constrained by the $^{40}Ar/^{39}Ar$ method within the range of 187-46 ka (Rotolo et al., 2013; Scaillet et al., 2013; Jordan et al., 2018), the earliest two have remained poorly constrained or undated. Specifically, the Zinedi Fm. was dated by the K/Ar method at ~ 189 ka (Mahood & Hildreth, 1986) but with large analytical errors (± 6 ka; 1σ) and poor internal systematics, whereas the Pozzolana Fm. was broadly constrained between 189 and 128 ka based on field

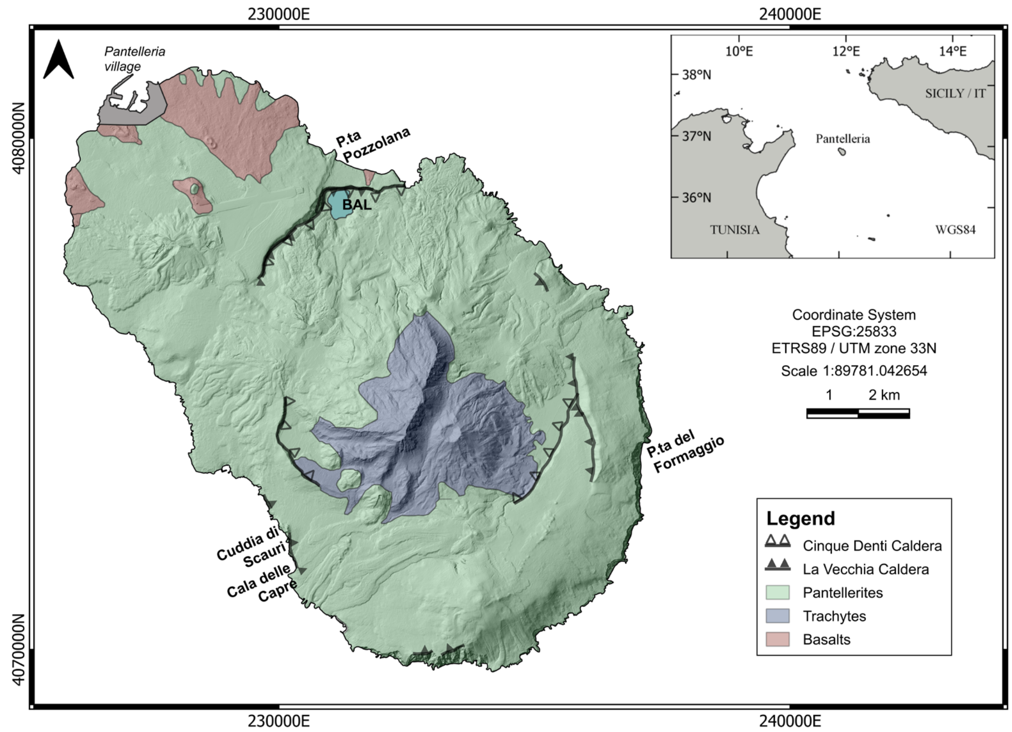

Figure 1 *Digital Elevation Model (DEM) of Pantelleria Island with a simplified geological extent. The location of Pantelleria within the Sicily Strait (Italy) is indicated in the top right box. BAL = Bagno dell'Acqua Lake.*

relationships (Mahood & Hildreth, 1986; Jordan et al., 2018).

The ignimbrite-forming eruptions were interspersed with several less explosive to effusive activity (inter-ignimbrite periods) from minor, locally distributed eruptive centres (*e.g.*, Civetta et al., 1984, 1988; Mahood & Hildreth, 1986; Rotolo et al., 2007; Scaillet et al., 2011; Romano et al., 2022). The more recent eruptive history, following the emplacement of the last ignimbrite deposit, the Green Tuff Formation (GT Fm.) (~ 46 ka; Scaillet et al., 2013), has been widely investigated by the scientific community (*e.g.*, Civetta et al., 1984, 1988; Mahood & Hildreth, 1986; Rotolo et al., 2007; Scaillet et al., 2011; Romano et al., 2022). In contrast, the older (pre-GT) eruptive cycles had remained poorly constrained. The existing geochronological framework for the pre-GT deposits had mostly relied on 24 K/Ar ages, all dating back to the 1980s (Civetta et al., 1984; Mahood & Hildreth, 1986), affected by large analytical uncertainties (up to ± 72 ka; 1σ), with some representing duplicate dates from the same eruptive centres.

This study focused on $^{40}Ar/^{39}Ar$ geochronology as a tool to refine the island's stratigraphy by dating previously unknown rock formations and enabling reliable field correlations. We conducted radiometric analyses on single anorthoclase crystals, a ubiquitous phase within the peralkaline eruptive units (*e.g.*, Scaillet & Macdonald, 2001; White et al., 2009; Scaillet et al., 2011, 2013). We targeted the earliest recognised ignimbrite units and associated lava and breccia deposits to establish the stratigraphic sequence of the major eruptions. Additionally, we dated some of the earliest eruptive units, mostly located in a few discontinuous, southern coastal sections, in order to assess the subaerial eruptive onset and early eruptive cyclicity. This approach has provided improved constraints on the subaerial eruptive history of Pantelleria, enabling the evaluation of eruptive timescales and associated volcanic hazards.

SAMPLE PREPARATION AND ANALYTICAL TECHNIQUES

Samples for $^{40}Ar/^{39}Ar$ dating were collected based on their freshness on site and further examined under a petrographic microscope. After dry-crushing and sieving into 0.5-1 mm and 1-2 mm, feldspar phenocrysts were separated using an isodynamic magnetic separator and etched with 5 mol% HF for ~ 5 min in an ultrasonic bath to remove adhering glass (if any). Feldspars were then carefully hand-picked under a binocular microscope for final concentrations, discarding crystals with incipient alteration or hosting inclusions.

Samples were wrapped in Al foils and stacked in a cylindrical sample holder (10 mm diameter) with 7 grains of a known age fluence monitor (Fish Canyon Tuff, 28.305 ± 0.036 Ma; Renne et al., 2010, 2011) interspersed every five sample packets, and sent for neutron irradiation into the Cadmium-Lined in-Core position CLICIT of Corvallis Nuclear Reactor (Oregon State University, United States).

$^{40}Ar/^{39}Ar$ analyses were conducted at the Institut des Sciences de la Terre d'Orléans (CNRS-ISTO) using a Thermo Fisher Helix mass spectrometer. After loading, samples were baked at ~ 200°C for approximately 48 hours. A minimum of 27 single-grain analyses were carried out for each sample using one-step laser ablation at high temperature with a CO_2 laser operated at 20% full power for about 40 seconds and equipped with a focusing lens.

Ages are reported as Weighted Mean Age (WMA), determined on the analyses sorted by increasing age, as long as the Mean Square Weighted Deviates (MSWD) remained within the fiducial interval (review in Schaen et al., 2021). Age calculations used an initial atmospheric $^{40}Ar/^{36}Ar$ ratio of 295.5 (Nier, 1950) and a total decay constant for ^{40}K of 5.543×10^{-10} y^{-1} (Steiger & Jäger, 1977). Ages are reported with uncertainties of 1σ.

DISCUSSION

A total of 25 new eruptive ages are provided, covering 2 ignimbrites, 12 lava flows, 8 fallout deposits, 1 dyke, and 1 welded breccia, resulting in a substantial revision of the previously accepted stratigraphy (Fig. 2). These new eruptive ages have enabled more robust stratigraphic correlations between isolated volcanic units, refining the temporal and stratigraphic framework of Pantelleria Island. In particular, the revised chronology allows for a clearer temporal ordering of eruptive cycles, improves the identification of stratigraphic gaps, and facilitates more accurate correlation of dispersed outcrops across the island.

Refinement of the Ignimbrite Stratigraphy

Previously considered the oldest ignimbrite units of Pantelleria, the Zinedi and Pozzolana Fms. yielded WMAs of 178.1 ± 0.8 ka (1σ) and 156.5 ± 1.1 ka (1σ), respectively. These new data have led to a revised stratigraphy of the island's highly explosive volcanic events, significantly modifying the previously accepted chronological framework (Fig. 3). The oldest ignimbrite deposit is now recognised as the Polacca Fm. (~ 187 ka; Jordan et al., 2018), slightly younger than or subcoeval with the lava flow (Punta Pozzolana lava; Fig. 1) set at the base of the stratigraphic sequence (beneath the Zinedi Fm.) in the northeast sector, which yielded a WMA of 188.9 ± 1.6 ka (1σ). This raises the possibility that the Polacca Fm. may extend below the present-day sea level, as it is improbable that it is exposed only in the southern sector of the island, despite being the most voluminous ignimbrite (DRE of ~ 0.64 km^3; Jordan et al., 2018).

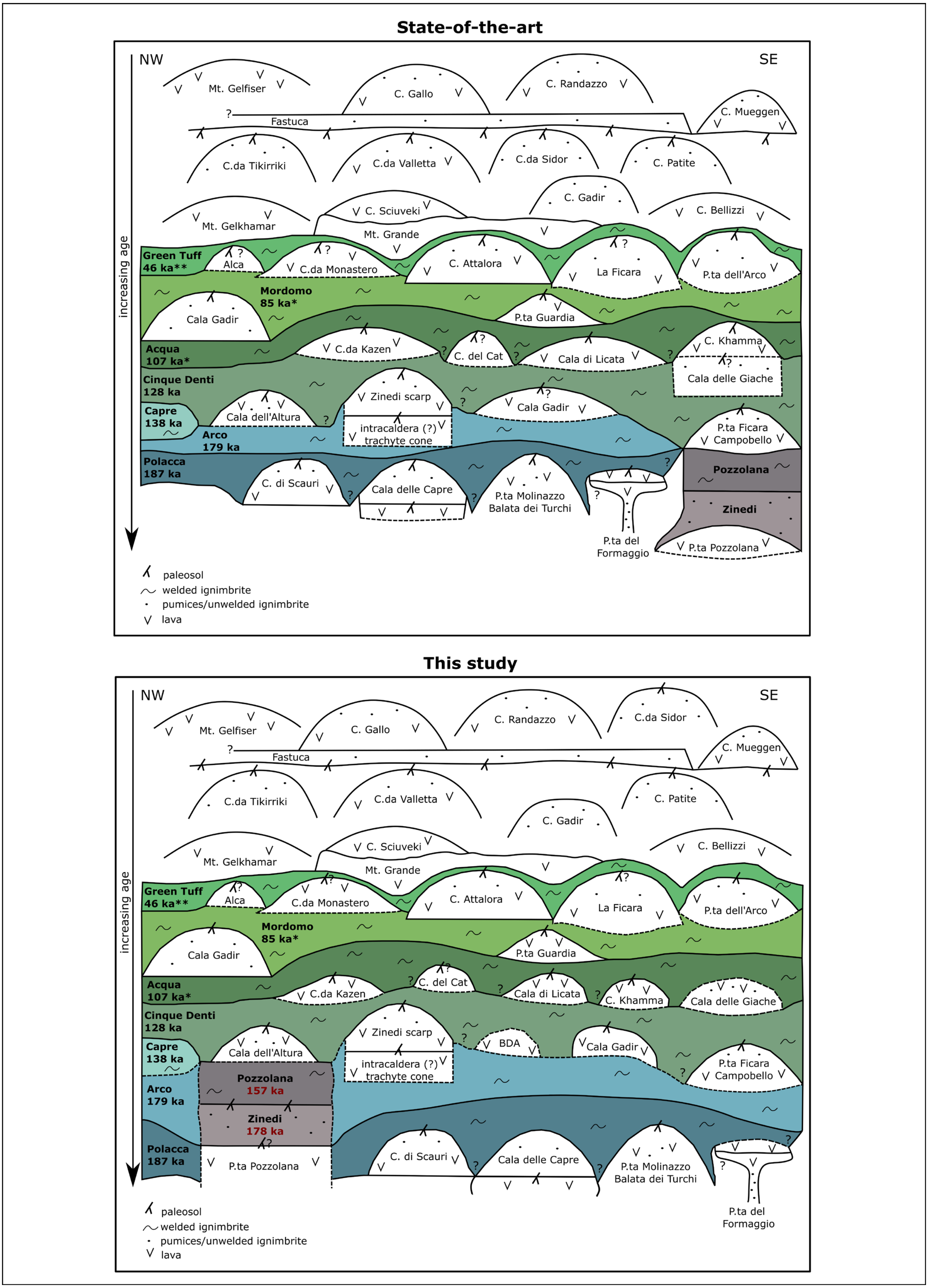

*Figure 2 Schematic stratigraphic schemes of Pantelleria (modified after Rotolo et al., 2021), according to the state-of-the-art (above) and after this study (below). Coloured levels represent ignimbrite deposits, with eruptive ages from Jordan et al. (2018), except for: *ages from Rotolo et al. (2013); **age from Scaillet et al. (2013). New eruptive ages from this study are in red.*

Earlier (> 46 ka) eruptive cycles

The earliest deposit has been recorded in the southwestern sector of the island, at Cala delle Capre (Fig. 1), where the lava flow at the base of the stratigraphic sequence provided a WMA of 326.5 ± 0.9 ka (1σ). The volcanic activity then migrated less than 1 km to the northwest, at Cuddia di Scauri (Fig. 1), where the dating of a fallout deposit provided a WMA of 323.1 ± 1.6 ka (1σ), suggesting the early development of a complex eruptive system along a narrow coastal corridor. Subsequently, volcanism progressed to the southeast up to Punta del Formaggio (≤ 200 ka; Fig. 1), likely being active simultaneously with the previously mentioned Pozzolana centre to the northeast, as no older deposits have been recorded to the north. Evolved, peralkaline magmas primarily drove the emplacement of multiple lava flows and fallout deposits from localised, short-lived eruptive centres, which preceded the earliest Polacca ignimbrite (~ 187 ka; Jordan et al., 2018). After this initial stage and the emplacement of the nine known ignimbrite deposits, the intervening (inter-ignimbrite) periods were dominated by effusive to mildly explosive eruptions, more widely distributed across the island. We particularly constrained fallout deposits in the range of 154-60 ka, and lava flows between 151 and 47 ka, sometimes considerably refining previous K/Ar ages affected by large analytical uncertainties (up to ± 72 ka; 1σ).

CONCLUSIONS

Pantelleria Island has been characterised by vigorous volcanic activity, punctuated by several explosive to effusive eruptions mainly fed by peralkaline magmas. The subaerial activity preceding the emplacement of the earliest ignimbrite-forming eruption, currently set as the Polacca Fm. (~ 187 ka; Jordan et al., 2018), is now accurately assessed at ~ 327 ka in the southwestern coastal section. The Polacca Fm. predates the Zinedi (~ 178 ka) and Pozzolana (~ 157 ka) Fms., which had previously been considered the earliest major explosive events. An average ignimbrite eruption frequency of ~ 0.064 events/kyr (one ignimbrite every ~ 15.7 ka) was calculated between 186.9 and 45.7 ka (Rotolo et al., 2013; Scaillet et al., 2013; Jordan et al., 2018; this study). However, significant temporal variability is observed, including the earliest three ignimbrite events within ~ 9 kyr and a prolonged quiescence of ~ 39 kyr prior to the latest GT eruption.

The inter-ignimbrite periods were characterised by the emplacement of several lava flows and fallout deposits, which occurred simultaneously along the entire volcanic history of the island, as several local eruptive centres produced both explosive and effusive activities. The eruptive activity involved various sectors of the island from north to south, potentially influenced

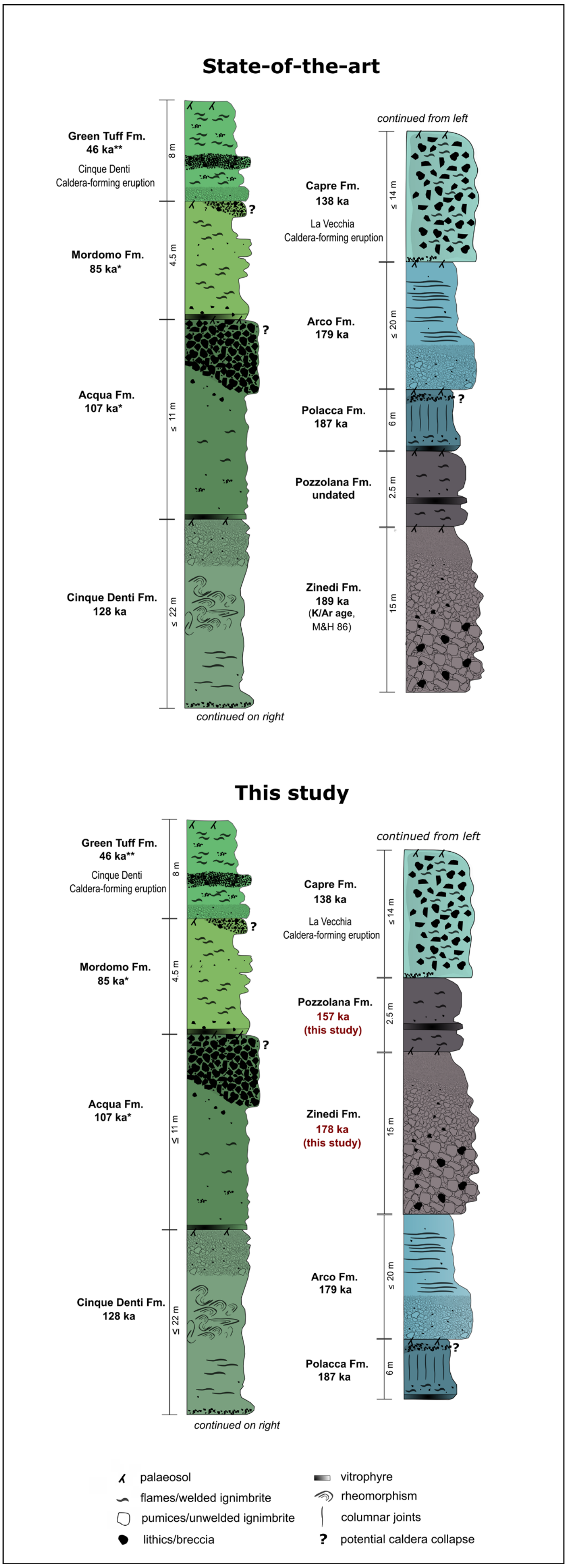

Figure 3 Synthetic logs of the ignimbrite stratigraphy of Pantelleria (modified after Jordan et al., 2018), according to the state-of-the-art (above) and after this study (below). $^{40}Ar/^{39}Ar$ ages are from Jordan et al. (2018), except for: *ages from Rotolo et al. (2013); **age from Scaillet et al. (2013). New eruptive ages from this study in red. M&H 86 refers to Mahood & Hildreth (1986). Question marks indicate welded breccias associated with potential caldera collapses.

by the emplacement of ignimbrite-forming eruptions and associated caldera collapses, which repeatedly modified the geological and structural setting of the island. The post-GT eruptive activity appears to have migrated from the south to the north, with the last inland eruption occurring ~ 7 ka (Scaillet et al., 2011) and the 1891 submarine eruption (Foerstner volcano) ~ 4 km northwest of Pantelleria (Kelly et al., 2014), consistent with the tectonic alignment of the Sicily Strait (*e.g.*, Civile et al., 2010).

The obtained results have several scientific implications and will offer valuable insights for ongoing and future research. Defining the entire subaerial eruptive history of the island and integrating it with the geochemical and geophysical data acquired by the active monitoring networks will permit us to define the true state of activity of the volcanic system. In this way, it may be possible to investigate any long and short-term volcanic cyclicity, with implications for possible volcanic unrest. It is important to consider that the diffusive volcanism that followed the latest GT ignimbrite (~ 46 ka; Scaillet et al., 2013), with a multitude of volcanic centres up to the latest inland eruption (~ 7 ka; Scaillet et al., 2011), may itself represent an inter-ignimbrite period. The age data, coupled with macro- and micro-scale petrological observations and whole-rock analyses, will enable the evaluation of the degree of magma evolution over time. This will lead to a deeper understanding of the plumbing system dynamics, particularly the productivity of pantellerite magmas, given its propensity to originate highly explosive eruptions on the island. Moreover, a refined stratigraphy will allow correlations with distal tephra deposits, enabling the assessment of the true dispersal of major eruption deposits and the quantitative determination of their magnitude. The obtained ages will also serve as a valuable constraint for the ongoing compilation of the geological map "Torretta Granitola – Pantelleria" at the scale 1:50.000 by the Geological Survey of Italy-ISPRA (CARG-Project). Finally, a comparison with Linosa Island, for which $^{40}Ar/^{39}Ar$ dating is still in progress, will provide deeper insights into the volcanic and magmatic dynamics of the Sicily Strait district, which can then be applied to similar highly productive Quaternary volcanic centres worldwide, particularly in terms of volcanic hazard assessment.

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