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### *Sciences de la Planète*

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Perspectives on alkaline magmas / *Perspectives sur les magmas alcalins*

# Evolution of the magma system of Pantelleria (Italy) from 190 ka to present

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**Abstract.** The eruptive history of Pantelleria has been marked by the eruption of nine peralkaline ignimbrites, with inter-ignimbrite episodes from small, local volcanic centres. New whole-rock geochemical data are presented for seven ignimbrites and used with published data for younger units to track compositional changes with time. From ~190 ka, silicic magmatism was dominated by comenditic trachyte to comendite compositions, evolving along generally similar liquid lines of descent (LLOD). The final ignimbrite, the Green Tuff (~46 ka), was tapped from a compositionally zoned pantelleritic upper reservoir to a trachytic mush zone. Younger (20–7 ka) silicic magmatism has been relatively small scale, with compositions similar to the earliest pre-Green Tuff pantelleritic ignimbrite (Zinedi). These data suggest that the comenditic reservoirs may have been emplaced at deeper levels than the pantelleritic reservoirs. While both types of series evolved along similar LLOD dominated by fractionation of alkali feldspar, it is the fractionation of iron that determines whether comendite or pantellerite is produced. The deeper reservoirs were more oxidizing and wetter, thus leading to the crystallization of magnetite and therefore the fractionation of iron.

**Keywords.** Pantelleria, Ignimbrite, Magma reservoirs, Compositional changes with time, Comendite, Pantellerite.

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## 1. Introduction

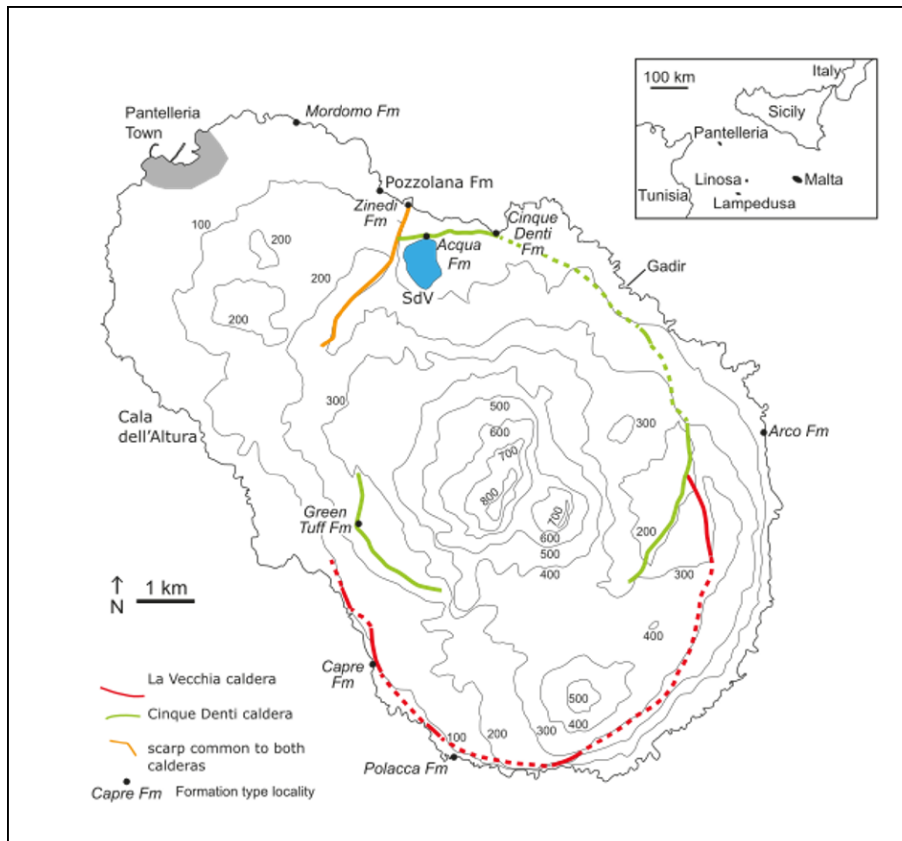
The volcanic island of Pantelleria (adj. Pantescan) has, for the past 40 years or so, been an important focus of petrological and volcanological studies of peralkaline silicic magmatism. It is a small island (83 km<sup>2</sup>; Figure 1), for the most part very accessible and with excellent coastal exposures. It consists of a wide range of rock types (basalt, trachyte, comendite, pantellerite), erupted by a variety of mechanisms (lava flows and dome building, pyroclastic falls and flows), and in the pyroclastic units showing very complex lateral and vertical facies changes. Researchers from many institutions internationally have contributed to studies of Pantescan geology. Foremost among the reasons for this interest are the unusual geochemistry (Pantelleria is the type locality for *pantellerite*, a strongly peralkaline, iron-rich rhyolite) and the extremely complex evolutionary history, despite the volcano's youthfulness (~400 ka of subaerial activity). Attempts to evaluate the nature of, and processes within, the plumbing system have been made *via* geophysics [Gianelli and Grassi, 2001, Mattia *et al.*, 2007], geochemical, and thermodynamic modelling [Avanzinelli *et al.*, 2004, Bagiński *et al.*, 2018, Civetta *et al.*, 1984, 1988, 1998, Giuffrida *et al.*, 2020, Liszewska *et al.*, 2018, Neave *et al.*, 2012, Neave, 2020, Romano *et al.*, 2019, White *et al.*, 2005, 2009, 2020], and high P–T experiments [Di Carlo *et al.*, 2010, Romano *et al.*, 2018, 2020]. There is a broad consensus on the presence of an active geothermal system and shallow magma reservoir (at ~4 km depth) which is currently deflating and cooling [Mattia *et al.*, 2007, Civile *et al.*, 2008]. The majority of studies have been made on the Green Tuff ignimbrite (a major marker unit dated at  $45.7 \pm 1.0$  ka; Scaillet *et al.*, 2013), and younger rocks, such that much less is known of earlier units. In this report, we use the Jordan *et al.* [2018] revision of the pre-Green Tuff stratigraphy and new whole-rock compositional data to examine how the Pantescan magma system may have changed over the period ~190 ka to the present. Detailed petrological studies of the earlier units will be presented elsewhere. A review of the volcanological evolution of Pantelleria is discussed in Rotolo *et al.* [2021]. We fully appreciate that a critical part of any magmatic system is the input from mafic magmas. Basaltic magmas have always been an important part of Pantescan magmatism and are almost

certainly the heat engine that has kept the system active. Here, however, we have concentrated on the silicic magmatism; White *et al.* [2020] provide an account of the distribution, compositions, and mantle sources of the basalts.

## 2. Geological setting

The island of Pantelleria lies in the Strait of Sicily, a submerged continental rift between Sicily and Tunisia (Figure 1). Most exposed rocks are felsic, ranging from metaluminous trachyte to peralkaline rhyolite, but mafic magmatism has occurred at several stages in the island's history including the most recent, offshore, eruption in 1891. The oldest documented radiometric date for felsic magmatism is  $517 \pm 19$  ka (<sup>40</sup>Ar/<sup>39</sup>Ar), from a pantelleritic microgranite inclusion in an ignimbrite [Rotolo and Villa, 2001]. Rotolo *et al.* [2013] divided the geologic history of the island into three phases. The first phase (~324–190 ka; Mahood and Hildreth, 1986) consists of effusive and explosive activity extensively buried by younger deposits and exposed exclusively along the remote south coast; there are extremely few geochronological or geochemical data available for rocks from this phase. The second phase (~190–46 ka) includes the eruption of eight ignimbrites, ranging in composition from trachyte to comendite/pantellerite, with >20 effusive to strombolian eruptions of pantelleritic magma from small, local centres occurring between the ignimbrite events [Jordan *et al.*, 2018]. The older “La Vecchia” caldera structure on the island formed during this second phase, has been variously dated at 114 ka [Mahood and Hildreth, 1986], between 175 and 133 ka [Speranza *et al.*, 2012], and between 140 and 146 ka [Rotolo *et al.*, 2013]. The third phase began with the  $45.7 \pm 1.0$  ka eruption of the Green Tuff [Scaillet *et al.*, 2013], the caldera-forming ignimbrite of the Cinque Denti caldera, and was followed by a prolonged period of effusive and mildly explosive activity (to ~7 ka; Scaillet *et al.*, 2011).

Jordan *et al.* [2018] applied formal stratigraphic guidelines, along with detailed field studies, palaeomagnetic data, and <sup>40</sup>Ar/<sup>39</sup>Ar ages, to compile a new eruptive history back to the first major ignimbrite eruption, at ~190 ka, the first of eight pre-Green Tuff peralkaline ignimbrites. Ages and descriptions of the eruption units, designated as Formations,

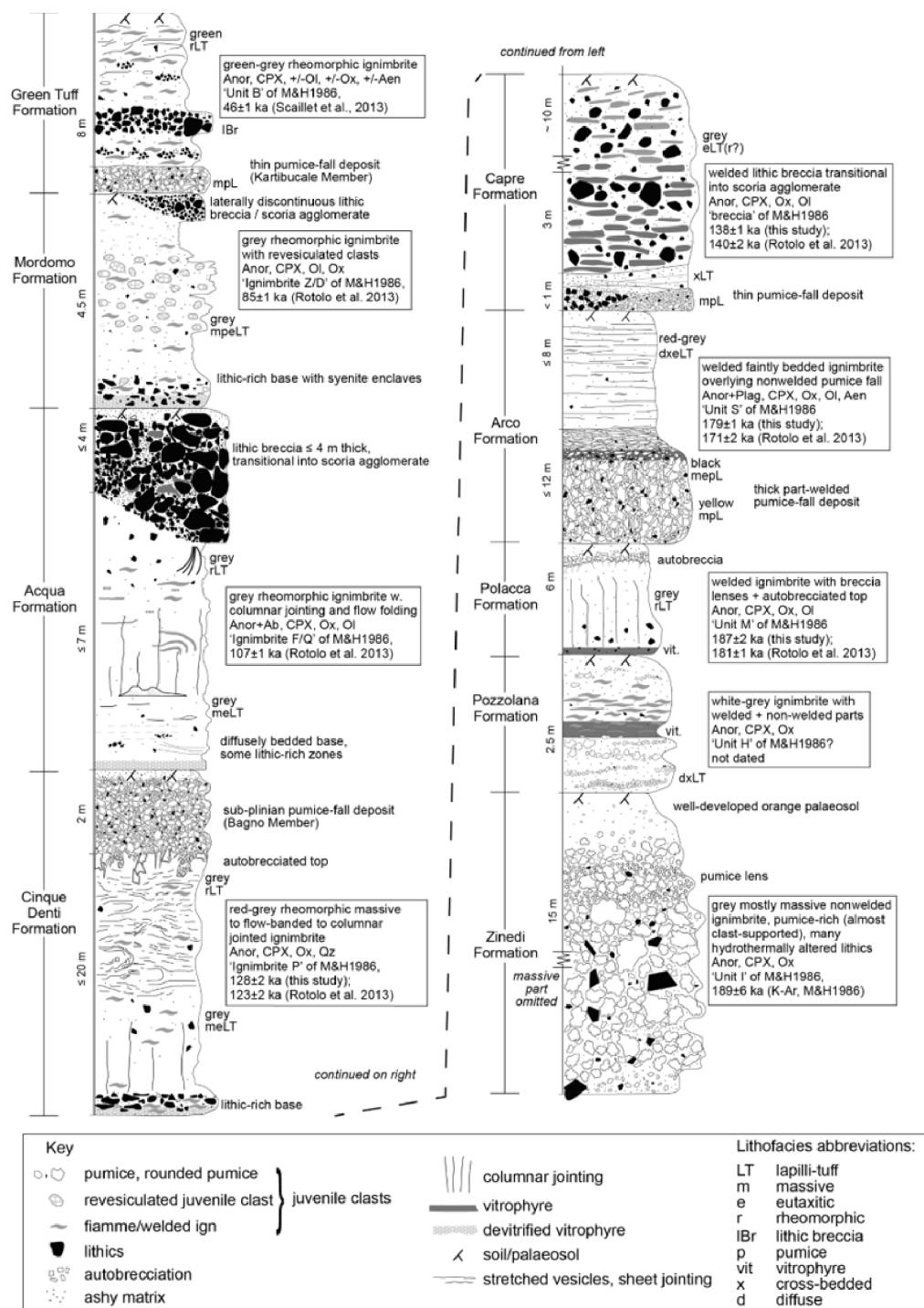


**Figure 1.** Map of Pantelleria showing topography (CI = 100 m), proposed calderas (after Mahood and Hildreth, 1986), post-caldera faults, type localities of the ignimbrite formations (after Jordan *et al.*, 2018), and selected locations (SdV: Lago Specchio di Venere).

are presented in Table 1 and Figure 2. An important conclusion of their study was that there were at least two and as many as five caldera collapse events associated with the ignimbrite eruptions. The ignimbrites are typically welded and variably rheomorphic and are commonly associated with pumice deposits and lithic breccias, which are interpreted as markers of caldera collapse possibly from reactivated structures [Jordan *et al.*, 2018, Rotolo *et al.*, 2013, 2021]. The onset of eruptions was normally marked by pumiceous air-fall tephra followed by ignimbrite emplacement, which in many cases blanketed the whole island; in one case, the Cinque Denti Formation, pumice fallout followed the ignimbrite emplacement [Jordan *et al.*, 2018]. Jordan *et al.* [2018] estimated the total onshore volume of all nine ignimbrites, including the Green Tuff, to be 2.32 km<sup>3</sup> DRE, with individual volumes ranging from 0.003

to 0.64 km<sup>3</sup> DRE. They stressed that these are on-shore values only because little is known about the amounts deposited at sea. A noteworthy observation is that eruption sizes decreased from 187 to 85 ka, with an increase in the 45.7 ka Green Tuff (Table 1; Figure 3). Inter-ignimbrite periods were characterized by effusive and explosive eruptions from small pumice cones. They are not considered here but it is acknowledged that they could add some complicating details to the evolutionary history of the magma reservoir.

As noted above, Jordan *et al.* [2018] recognized lithic breccias in several formations as markers of caldera collapse, indicating that they are located close to the inferred source caldera. They also suggested that some collapse events reshaped existing caldera scarps. If calderas can be taken to lie more or less directly above their plumbing systems,

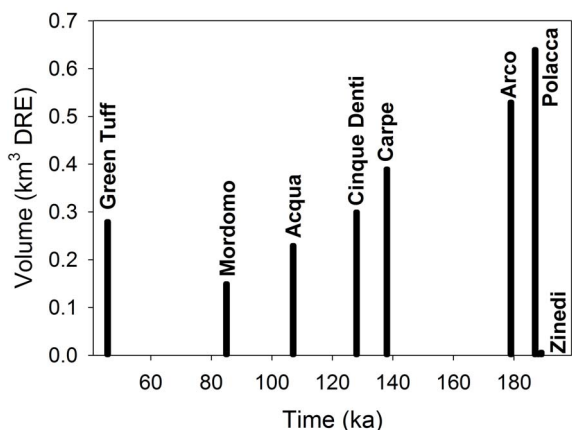


**Figure 2.** General vertical stratigraphy of ignimbrite-producing eruptions on Pantelleria (not to scale) from Jordan *et al.* [2018]. Logs are from the type localities of each unit. Abbreviations: M&H86, Mahood and Hildreth [1986]; Anor, anorthoclase; Cpx, clinopyroxene; Ol, olivine; Ox, Fe-Ti oxides; Aen, aenigmatite; Ab, albite; Qz, quartz; Plag, plagioclase.

**Table 1.** Summary of ignimbrite formations, ages, and geochemistry

Formation	Lat (N)	Long (E)	Age (ka)	Source	<i>n</i>	wt% SiO <sub>2</sub>	wt% TA	PI.	wt% FeO <sup>T</sup>	wt% Q*	ppm Zr	Zr/Nb	Ce/Y
Green Tuff	36.7750	11.9745	45.7	(1)	36	63.9–71.3	9.8–11.9	1.0–1.8	4.9–8.3	1.3–39.0	291–2061	5.1 ± 0.5	2.6 ± 0.5
Mordomo	36.8375	11.9631	85	(2)	29	65.5–70.3	10.2–11.6	1.0–1.3	4.6–5.8	5.0–22.2	658–1415	5.0 ± 0.5	2.9 ± 0.9
Acqua	36.8191	11.9872	107	(2)	25	64.5–70.8	10.3–12.1	1.1–1.4	4.3–5.7	1.5–24.9	450–1668	5.0 ± 0.3	2.4 ± 0.4
Cinque Denti	36.8200	12.0005	128	(3)	22	65.1–69.4	10.0–13.2	0.9–1.5	3.8–5.7	6.1–19.3	533–1172	5.0 ± 0.1	2.4 ± 0.3
Carpe	36.7533	11.9790	138	(3)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Arco	36.7890	12.0530	179	(3)	8	64.1–72.8	9.8–12.5	1.0–1.4	4.6–6.3	0.4–36.5	481–2173	5.0 ± 0.5	2.6 ± 0.3
Polacca	36.7382	11.9932	187	(3)	8	65.0–66.7	11.5–12.2	1.1–1.2	5.0–5.6	4.1–10.3	397–835	4.9 ± 0.4	2.6 ± 0.2
Pozzolana	36.8265	11.9790	n.a.	n.a.	5	69.7–70.0	10.5–11.8	1.2–1.4	4.8–5.1	22.3–24.9	1616–1783	5.4 ± 0.1	2.5 ± 0.1
Zinedi	36.8242	11.9844	189	(4)	5	66.8–68.0	10.6–11.7	1.1–1.3	6.8–7.9	16.1–21.6	869–1188	4.9 ± 0.1	2.3 ± 0.2

Formation names from Jordan *et al.* [2018]. Green Tuff data are from Williams *et al.* [2014] and Liszewska *et al.* [2018]. Geographic coordinates are for type sections (see Figure 1), datum WGS84. *n* = Number of samples analysed and used in this report. Sources for ages are: (1) Scaillet *et al.* [2013] <sup>40</sup>Ar/<sup>39</sup>Ar; (2) Rotolo *et al.* [2013] <sup>40</sup>Ar/<sup>39</sup>Ar; (3) Jordan *et al.* [2018] <sup>40</sup>Ar/<sup>39</sup>Ar; (4) Mahood and Hildreth [1986] K–Ar. wt% TA = Na<sub>2</sub>O + K<sub>2</sub>O; PI. = peralkalinity index (mol Na + K/Al); FeO<sup>T</sup>, total iron as FeO; wt% Q\* = normative Q renormalized to Q + Or + Ab = 100, calculated following Kelsey [1965] with iron oxides calculated following Le Maitre [1976]. n.a., not analysed/not applicable; n.d., no data.



**Figure 3.** Onshore volumes plotted against eruption ages for the ignimbrite formation (see Table 2; adapted from Jordan *et al.*, 2018).

it seems that the reservoir has been located close to the present reservoir, which geophysical models place at ~4 km below sea level [Mattia *et al.*, 2007]. We assume, therefore, that the magmatic evolution of the island since ~190 ka has been related to one plumbing system, where that system may have varied in its structure and degree of complexity with time.

### 3. Analytical methods

One hundred and two samples of pre-Green Tuff ignimbrite were collected from Pantelleria during

fieldwork from 2009–2012. Representative whole-rock compositional data are presented in Table 2; the full data set is in Supplementary Table 1. Samples were dried at 100 °C overnight, crushed on a flypress to ~2 mm and then milled on an agate planetary mill to a fine powder. For whole-rock samples of ignimbrite, lithic fragments were removed as much as possible during the crushing. Loss on ignition (LOI) was determined in two steps to avoid sample fusion, which renders the powders unusable for bead making. Fusion beads (for major elements) were made from 0.6 g of powder dried following the first step mixed with a flux consisting of 0.6 g lithium tetraborate and 2.4 g lithium metaborate and melted at 1200 °C for 5–10 min. Powder pellets (for trace elements) were made from 6 g of dried powder and 1.5 g of a paraffin wax binding agent at approximately 138 MPa for 30 s. Fused beads and powder pellets were analysed on a Philips PW4400 Axios WD-XRF with a 4 kW rhodium tube at the University of Leicester. The detection limit for major elements is <0.02 wt% and in most cases ~0.003 wt%. For trace elements, detection limits range between 0.1 and 8.2 ppm. Precision, expressed as relative standard deviation across multiple analyses of any given reference material, is typically ~1–3% for major elements (except P<sub>2</sub>O<sub>5</sub> and SO<sub>3</sub>) and <10% for trace elements (Supplementary Table 2). In terms of accuracy, data obtained at Leicester tend to be slightly higher than the values accepted on the GeoREM database [Jochum *et al.*, 2007].

**Table 2.** Representative whole-rock analyses

Formation:	Green Tuff	Green Tuff	Mordomo	Mordomo	Acqua	Acqua	Cigñue Denti	Cinque Denti	Arco	Arco	Polacca	Polacca	Pozzolana	Pozzolana	Zinedi	Zinedi
Sample ID:	150522	160542	300512-4	090612-1	100612-3d	191010-1	BDA1b	250511-2	060612-1	140612-1	310511-1	250912-1a	ukn100d	190610-1	051109-2a	061109-2a
Class:	CT	P	CT	CT	CT	C	MT	CT	CT	P	CT	CT	C	C	PT	PT
SiO <sub>2</sub> , wt%	64.68	69.33	65.38	67.74	63.24	69.56	62.62	66.99	61.59	67.66	64.20	66.04	68.52	68.63	63.97	66.03
TiO <sub>2</sub>	0.69	0.50	0.66	0.52	0.68	0.44	0.79	0.60	0.74	0.35	0.73	0.63	0.44	0.43	0.64	0.58
Al <sub>2</sub> O <sub>3</sub>	15.21	9.05	15.30	12.80	15.49	12.33	15.21	13.08	15.47	9.04	15.26	14.40	12.11	11.71	12.33	11.43
Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup>	5.88	8.59	5.31	5.71	5.34	5.32	5.60	6.04	4.96	6.55	5.42	5.55	5.27	5.49	7.16	8.50
MnO	0.21	0.29	0.20	0.24	0.22	0.21	0.19	0.24	0.20	0.24	0.21	0.23	0.22	0.24	0.27	0.32
MgO	0.47	0.11	0.43	0.27	0.44	0.31	0.52	0.55	1.01	0.34	0.37	0.38	0.17	0.22	0.53	0.25
CaO	1.23	0.39	0.85	0.52	1.17	0.47	1.77	0.96	1.43	0.29	0.96	0.83	0.41	0.34	0.71	0.67
Na <sub>2</sub> O	6.31	6.51	6.92	6.41	6.97	5.43	6.17	5.91	7.05	4.60	6.77	6.87	7.11	5.67	5.47	5.93
K <sub>2</sub> O	4.57	4.62	4.58	4.54	4.54	4.72	3.83	4.40	4.00	4.50	4.99	4.55	4.53	5.01	4.57	4.44
P <sub>2</sub> O <sub>5</sub>	0.15	0.03	0.05	0.05	0.12	0.02	0.08	0.08	0.18	0.02	0.14	0.09	0.04	0.03	0.05	0.04
SO <sub>3</sub>	n.a.	n.a.	0.03	0.05	0.31	bdl	0.02	0.01	0.13	0.09	0.03	0.06	0.13	0.04	0.03	0.03
Cl	n.a.	n.a.	0.57	0.59	0.72	0.41	bdl	0.66	1.14	1.23	0.14	bdl	bdl	bdl	0.22	bdl
LOI	0.20	0.10	0.57	1.27	1.73	0.92	1.38	0.82	2.97	5.94	0.33	0.74	1.93	2.90	4.57	1.75
Sum	99.60	99.52	100.86	100.71	100.95	100.14	98.17	100.33	100.88	100.87	99.55	100.37	100.89	100.71	100.53	99.98
O=Cl	n.a.	n.a.	0.13	0.13	0.16	0.09	0.00	0.15	0.26	0.28	0.03	0.00	0.00	0.00	0.05	0.00
Total	99.60	99.52	100.73	100.58	100.79	100.04	98.17	100.18	100.62	100.59	99.51	100.37	100.89	100.71	100.47	99.98
PI.	1.01	1.74	1.07	1.21	1.06	1.14	0.94	1.11	1.03	1.38	1.08	1.13	1.37	1.26	1.13	1.27
Q*	5.82	34.54	6.25	18.88	2.80	23.40	7.28	16.54	0.40	36.50	5.01	10.25	22.34	24.87	16.09	21.08
Sc, ppm	10.0	3.0	6.5	4.9	9.2	3.4	7.5	4.7	5.5	4.8	7.1	2.6	2.4	4.0	3.7	4.6
V	10.0	13.0	2.3	bdl	bdl	1.6	9.1	7.2	3.4	bdl	2.4	3.0	1.9	1.1	2.0	bdl
Co	1.7	0.2	3.6	3.1	2.4	4.2	5.8	3.0	bdl	2.7	3.2	3.5	2.9	2.9	3.8	3.4
Ni	bdl	bdl	bdl	bdl	bdl	bdl	bdl	4.1	bdl	1.6	bdl	bdl	2.6	2.2	0.7	bdl
Cu	n.a.	n.a.	56.7	58.8	57.7	bdl	0.3	bdl	57.0	61.6	bdl	bdl	3.9	3.6	2.4	bdl
Zn	n.a.	n.a.	146.6	227.4	140.2	222.8	127.9	163.0	131.3	353.7	115.4	171.9	263.7	284.1	208.0	286.1
Ga	31.3	34.7	32.4	34.3	30.8	34.7	28.2	34.2	28.6	33.9	30.9	34.6	35.4	34.9	37.7	40.6
As	n.a.	n.a.	2.5	11.3	1.4	5.4	bdl	2.8	bdl	10.3	bdl	2.4	bdl	bdl	4.8	bdl
Rb	66.0	170.7	77.5	135.4	59.8	144.5	60.8	109.7	57.0	212.3	53.6	83.5	133.5	144.5	96.2	107.6
Sr	65.4	2.8	21.3	13.2	64.3	11.9	240.1	50.0	158.1	11.1	20.1	35.1	12.6	6.8	10.8	19.7
Y	50.5	146.9	44.3	106.6	59.2	95.6	52.5	95.0	51.7	178.7	43.8	77.7	132.8	141.2	92.0	141.3
Zr	552.5	1725.2	658.4	1412.9	449.9	1668.0	533.2	1172.4	523.9	2173.0	396.9	835.1	1616.3	1783.0	868.7	1188.4
Nb	112.1	315.1	146.2	273.0	100.1	325.3	108.6	230.0	110.4	400.1	90.4	172.2	300.8	329.5	180.7	242.1
Mo	n.a.	n.a.	5.6	13.2	6.0	10.7	5.8	5.3	5.6	17.0	5.1	8.9	12.4	19.4	9.4	9.7
Sn	n.a.	n.a.	3.7	9.1	2.5	10.6	bdl	4.3	3.6	16.3	bdl	4.7	bdl	bdl	6.0	bdl
Sb	n.a.	n.a.	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	1.2	bdl	bdl	bdl	bdl
Cs	0.2	1.8	bdl	7.8	bdl	6.7	bdl	4.3	bdl	16.3	bdl	3.6	10.2	12.5	7.1	8.7
Ba	1893.0	52.0	668.0	142.4	812.8	50.7	1584.2	410.9	1545.6	25.6	903.0	736.6	161.6	119.1	49.0	25.0
La	84.0	212.2	49.8	137.4	68.3	141.8	66.2	134.1	68.0	229.3	53.3	103.3	164.7	181.4	117.9	142.8
Ce	152.4	394.8	96.6	281.4	134.6	301.5	135.7	257.3	135.7	455.8	113.2	210.2	320.3	369.3	223.3	275.5
Nd	67.3	153.7	44.6	108.3	62.4	107.6	53.8	115.4	58.1	175.6	48.8	86.3	125.4	138.1	99.8	119.2
W	n.a.	n.a.	2.4	3.5	1.5	bdl	bdl	2.3	bdl	9.4	1.4	1.6	bdl	bdl	bdl	bdl
Pb	n.a.	n.a.	6.6	10.3	4.9	10.0	6.2	5.7	5.6	15.0	4.1	7.6	10.6	12.9	7.4	8.5
Th	10.8	32.3	9.6	24.1	6.5	28.6	8.1	19.8	9.0	37.5	6.3	13.7	28.2	31.6	14.7	19.7
U	1.3	10.2	2.4	6.2	2.2	6.2	2.8	2.5	2.6	10.8	2.6	3.8	8.4	8.6	4.5	5.1

Full results for pre-Green Tuff Formations are in Supplementary Table 1. Representative Green Tuff samples are from Liszewska *et al.* [2018]. Class (following Le Maitre 2002; Macdonald 1974): MT, Metaluminous Trachyte; CT, Comenditic Trachyte; C, Comendite; PT, Pantelleritic Trachyte; P, Pantellerite. Fe<sub>2</sub>O<sub>3</sub><sup>T</sup>, total iron as Fe<sub>2</sub>O<sub>3</sub>. LOI, Loss on Ignition. PI., peralkalinity index (= mol [Na + K]/Al). Q\* = normative quartz renormalized to Q + Or + Ab = 100, calculated following Kelsey [1965] with iron oxides adjusted following Le Maitre [1976]. n.a., not analysed; bdl, below detection limit. Sample BDA1b collected by Rebecca Williams.

#### 4. Significance of the Green Tuff

The Green Tuff is a very remarkable deposit; along with the post-caldera trachytes, it has provided our

most complete insight into processes in the Pantescan plumbing system. The eruption had the largest drawdown, penetrating a feldspar-rich crystal mush, subsequently erupted as the post-caldera trachytes

[White *et al.*, 2009]. It contains a complete spectrum of compositions from metaluminous trachytes to the most-evolved (pantellerite) melts yet recorded on the island ( $\sim 10$  wt%  $\text{FeO}^{\text{T}}$ , 5–3 wt%  $\text{Al}_2\text{O}_3$ , P.I. [peralkalinity index;  $\text{mol}(\text{Na} + \text{K})/\text{Al}] = 2.61$ ; Liszewska *et al.*, 2018). The trachytes show strong textural disequilibrium, perhaps related to thermal and compositional inputs from more mafic magmas [Ferla and Meli, 2006, Liszewska *et al.*, 2018]. Direct evidence of magma mixing processes occurs in a small lava flow of benmoreite capping the post-caldera trachytes on Montagna Grande [Romengo *et al.*, 2012]. Using olivine compositions, Romengo *et al.* [2012] raised the possibility that the trachytes may have evolved along with more than one liquid line of descent (LLOD). A suite of syenodioritic xenoliths in the trachytes also point to the presence in the system of melts of intermediate composition [Ferla and Meli, 2006]. In an innovative approach to eruptive dynamics, Williams *et al.* [2014] used Zr contents as stratigraphic markers to show that the pyroclastic flow member was deposited from a complex diachronic distribution of density currents. High-resolution analysis of the architecture of the deposit provided new insights into how the flow dynamics evolved. During eruption, mingling between layers, especially in the pantellerites, was ubiquitous, at scales down to the micrometer level, a process revealed only by detailed analysis of within-sample glasses, the first record of such intimate mixing in a peralkaline system [Liszewska *et al.*, 2018].

Thermodynamic modelling and experimental studies have provided precise estimates of conditions within the reservoir. From the bottom to the top of the magma reservoir, temperatures decreased from 900 to 700 °C, oxygen fugacity ( $f\text{O}_2$ ) increased from  $\Delta\text{FMQ}-1.5$  to  $\Delta\text{FMQ}-0.5$ , and silica activity relative to quartz saturation ( $a\text{SiO}_2[\text{Qtz}]$ ) increased from 0.74 to 1.00 [Di Carlo *et al.*, 2010, Liszewska *et al.*, 2018, Romano *et al.*, 2018, 2020, White *et al.*, 2005, 2009]. The change in oxygen fugacity has been interpreted by these authors as reflecting a roofward increase in water content in the magma. However, evidence from melt inclusions revealed nearly identical concentrations of  $\sim 4$  wt%  $\text{H}_2\text{O}$  from the middle and base of the Green Tuff section, but with much lower concentrations ( $\sim 1.2$  wt%  $\text{H}_2\text{O}$ ) in the comenditic trachyte top of the section [Lanzo *et al.*, 2013, Romano *et al.*, 2019] and may also reflect an increase

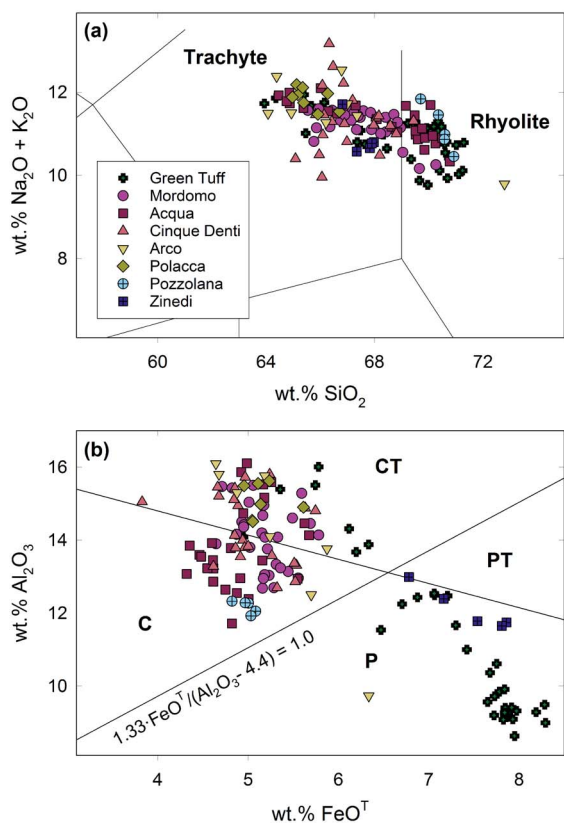
of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  due to increasing peralkalinity [Stabile *et al.*, 2017]. Finally, using data from olivine zoning in basalts, Giuffrida *et al.* [2020] suggested that eruption of the Green Tuff and collapse of the Cinque Denti caldera had a profound influence on the internal structure of Pantelleria. For example, the supply of magma from deep crustal storage zones decreased after the eruption, while the dynamics of magma transfer in the upper parts of the plumbing system were enhanced.

## 5. Geochemistry of the pre-Green Tuff Formations

The rocks of the pre-Green Tuff Formations range from metaluminous (P.I. = 0.94–0.99) to peralkaline (P.I. > 1.0). All units plot together on the total-alkalis silica (TAS) diagram (Figure 4a; Le Maitre, 2002), with trachyte being the dominant rock type. In contrast with the Green Tuff, most of the pre-Green Tuff peralkaline types lie in a cluster straddling the comenditic trachyte–comendite boundary on the  $\text{FeO}^{\text{T}}-\text{Al}_2\text{O}_3$  classification diagram (Figure 4b; Macdonald, 1974). Some analyses from the Zinedi and Arco Formations plot just within the pantellerite field. Harker diagrams (Figure 5) show that comenditic trachytes ( $\sim 64$  wt%  $\text{SiO}_2$ ) from each suite are broadly similar with respect to major element compositions ( $\sim 0.7$  wt%  $\text{TiO}_2$ ,  $\sim 15.3$  wt%  $\text{Al}_2\text{O}_3$ ,  $\sim 5.4$  wt%  $\text{FeO}^{\text{T}}$ ,  $\sim 6.7$  wt%  $\text{Na}_2\text{O}$ ). With increasing  $\text{SiO}_2$  contents, there are decreases in  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{Na}_2\text{O}$  for all suites, with  $\text{Al}_2\text{O}_3$  decreasing more rapidly in the Green Tuff and Zinedi formations.  $\text{K}_2\text{O}$  shows approximately unchanging behaviour in all formations. For nearly all of the pre-Green Tuff Formations,  $\text{FeO}^{\text{T}}$  also demonstrates little variability, decreasing slightly at higher  $\text{SiO}_2$  in contrast to the Green Tuff and Zinedi Formations, which show iron-enrichment trends.

$\text{SiO}_2$  is plotted against three other compositional parameters in Figure 6. In all formations, peralkalinity increases with increasing  $\text{SiO}_2$ , with the more rapid decrease of  $\text{Al}_2\text{O}_3$  in the Green Tuff resulting in overall higher peralkalinity. Figure 6b plots  $\text{SiO}_2$  versus  $1.33 \cdot \text{FeO}^{\text{T}}/(\text{Al}_2\text{O}_3-4.4)$  [hereafter labelled  $\text{Fe}^{\text{T}}/\text{Al}$ ], which has a value of 1.0 along the pantelleritic–comenditic boundary seen in Figure 4b; the trachyte–rhyolite boundary occurs at 69 wt%  $\text{SiO}_2$  (Figure 4a). This figure more clearly shows the variation in  $\text{FeO}^{\text{T}}$  relative to  $\text{Al}_2\text{O}_3$  with increasing  $\text{SiO}_2$



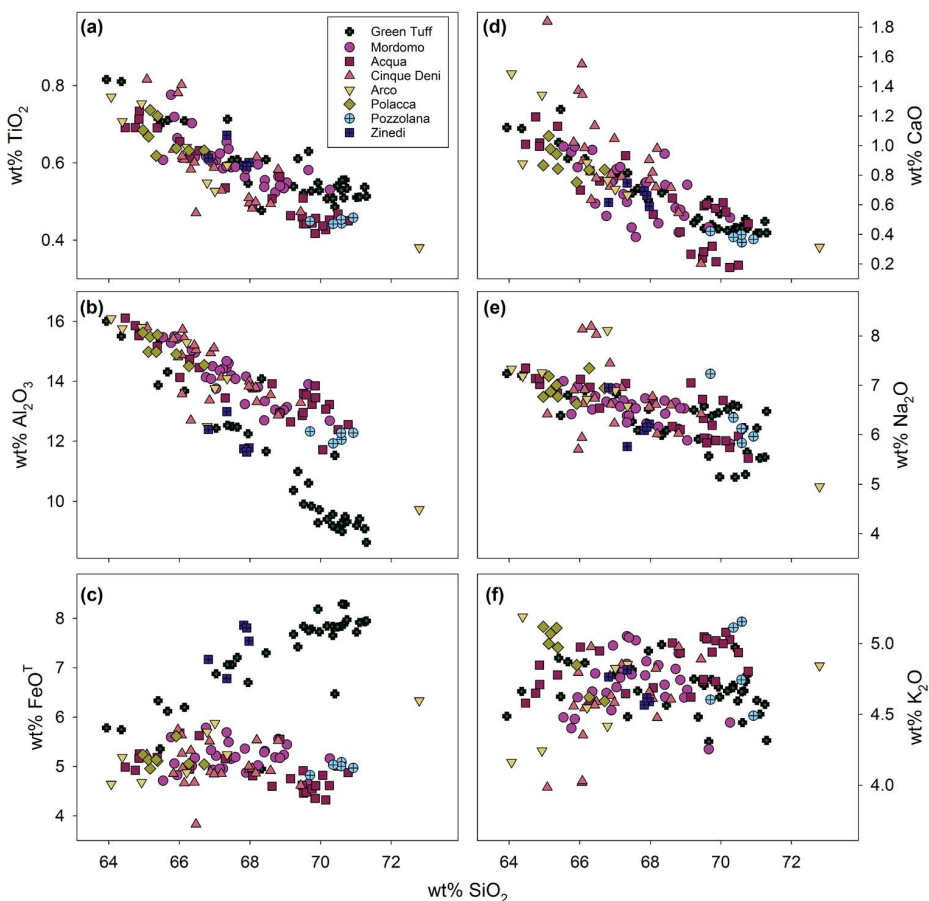


**Figure 4.** Geochemical classification of the ignimbrites on the (a) total-alkali silica (TAS; Le Maitre, 2002) diagram and on the (b) Macdonald [1974] classification scheme for peralkaline silicic rocks. Green Tuff whole-rock data are from Liszewska *et al.* [2018] and Williams *et al.* [2014]. Pre-Green Tuff data are presented in Supplementary Table 1.

and provides a comprehensive classification scheme consistent with Le Maitre [2002] which we adopt for use in Table 2 and Supplementary Table 1. This plot also shows that, unlike the Green Tuff and Zinedi Formations that have relatively rare comenditic trachyte compositions, comenditic trachyte is the dominant rock type in the pre-Green Tuff Formations, and it evolves towards comendite with only a slight increase in  $\text{Fe}^T/\text{Al}$ . In all formations, there is a generally strong positive correlation and range of values between  $\text{SiO}_2$  and Zr (Figure 6c). Normative quartz ( $Q^*$ ) renormalized to quartz (Q) + orthoclase (Or) + albite (Ab) = 100 is presented in Figure 6d. This parameter is used to quantify silica-oversaturation as the LLOD moves

from the feldspar join ( $Q^* = 0$ ) in the system Q–Or–Ab to a minimum composition on the feldspar–quartz cotectic. To determine these values, iron oxides were adjusted following Le Maitre [1976] and CIPW norms for whole-rock analyses were calculated using the method of Kelsey [1965]. This plot clearly shows that although least-evolved (~64 wt%  $\text{SiO}_2$ ) comenditic trachyte in all formations is close to quartz saturation,  $Q^*$  in the pre-Green Tuff formations (except Zinedi and Arco) is significantly lower with increasing  $\text{SiO}_2$ . Because there is an inverse relationship between silica activity and pressure [Nicholls *et al.*, 1971], this may reflect deeper-seated magma chambers for the comenditic trachyte–comendite formations and shallower magma chambers for the comenditic trachyte–pantellerite formations. This is supported by the experimental work of Tuttle and Bowen [1958], Johannes and Holtz [1996], Wilke *et al.* [2017], and others who document a strong negative correlation between the maximum value of  $Q^*$  on the feldspar–quartz cotectic and pressure.

Incompatible trace element ratios are remarkably similar for all units (Figure 7 and Table 1), which suggests that throughout the 190 ka history discussed here the felsic magmas evolved from a similar type of basalt. A common basaltic origin for these rocks is also supported by similar patterns observed in multi-element variation diagrams (Figure 8, normalized to depleted MORB mantle [DMM]; Salters and Stracke, 2004), which are nearly identical in shape to each other and to a representative sample of the low Ti–P, pre-Green Tuff basalt shown in Figure 8a (sample 130911; White *et al.*, 2020) with the exception of the compatible trace elements Ba, Sr, P, and Ti, which may reflect fractionation of feldspar, apatite, and Fe–Ti oxides [cf. Civetta *et al.*, 1998, Neave *et al.*, 2012, White *et al.*, 2009]. For a given concentration of Zr, Sr and Ba are higher in the Mordomo, Cinque Denti, and Arco Formations than the others although they all converge to similar levels at >1500 ppm Zr. The elevated Sr and Ba concentrations in these rocks may suggest a significant role for accumulation of alkali feldspar in these rocks. From basalt to comenditic trachyte, all trace elements in Figure 8 show a similar magnitude of increase, with the exception of P, Sr, and Ti, suggesting these trachytes were derived from basalt via fractionation of plagioclase, Fe–Ti oxides, and apatite. From comenditic trachyte to pantellerite, most elements continue to increase

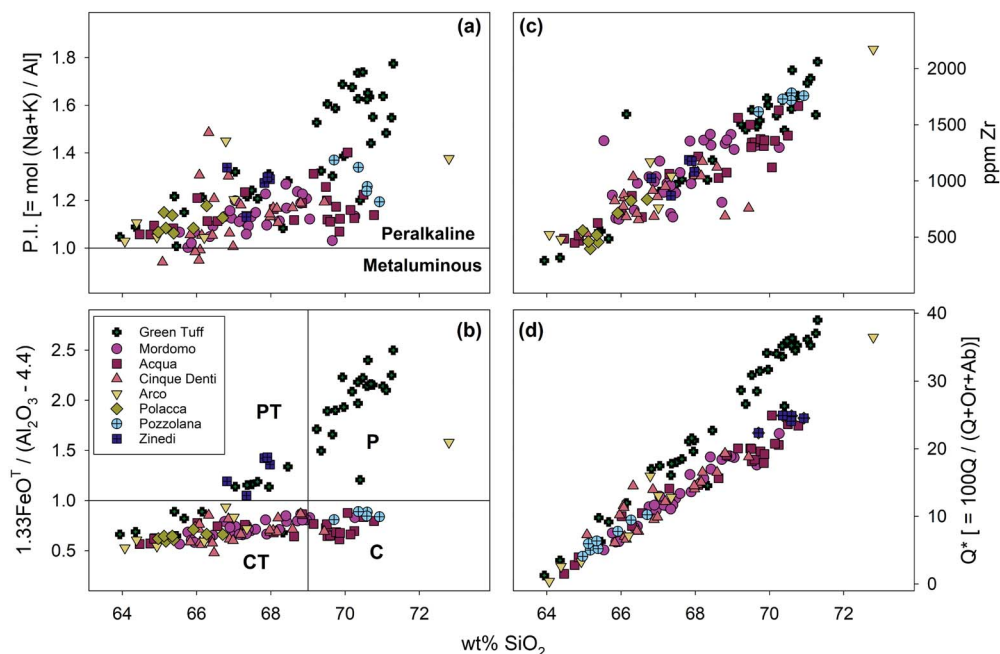


**Figure 5.** Major element variation diagrams for whole-rock data from the ignimbrites (see Supplementary Table 1). Green Tuff whole-rock data are from Liszewska *et al.* [2018] and Williams *et al.* [2014].

with the exception of K, which shows nearly constant behaviour (cf. Figure 5f), Ti (which decreases slightly), P (apatite fractionation) and Sr and Ba, reflecting a dominant role of alkali feldspar fractionation in the formation of both comendite and pantellerite from comenditic trachyte. The trends are similar to those reported in previous studies of Pantescan suites [Civetta *et al.*, 1998, Liszewska *et al.*, 2018, Neave *et al.*, 2012, White *et al.*, 2009]. The petrology of individual ignimbrite formations is the subject of ongoing investigations.

Coexisting basalt–comendite and basalt–pantellerite series have been documented in other intraplate settings, such as the Boseti volcanic complex, Ethiopia [Ronga *et al.*, 2009], Changbaishan, China–North Korean [Andreeva *et al.*, 2019], and Terceira, Azores [Mungall and Martin, 1995]. At Ter-

ceira, Mungall and Martin [1995] observed that magnetite is the dominant Fe–Ti oxide (>2.5 vol%) in the basalt–comendite series, whereas ilmenite (s.s. with low haematite component) is the dominant oxide (0.4 to 0.6 vol%) in the basalt–pantellerite series. The same seems to be true at Pantelleria: although ilmenite is the dominant or sole oxide phase in the pantellerites [White *et al.*, 2005, 2009], magnetite (s.s. with high ulvöspinel component) is the dominant or sole oxide phase in the comendites [Jordan, 2014]. Experimental studies have shown that  $fO_2$  exerts a strong control on oxide crystallization, with more reducing conditions favouring ilmenite and more oxidizing conditions favouring magnetite [Ishihara, 1977, Toplis and Carroll, 1995], and also favouring fayalitic olivine over clinopyroxene [Romano *et al.*, 2018]. At Terceira, Mungall and Mar-



**Figure 6.** Variation of  $\text{SiO}_2$  with (a) the peralkalinity index [P.I.]; (b) relative variability of  $\text{FeO}^T$  and  $\text{Al}_2\text{O}_3$  (adapted from Macdonald, 1974); (c) concentration of Zr; and (d) silica-oversaturation, as  $Q^* = 100 \cdot Q / (Q + \text{Or} + \text{Ab})$  for the ignimbrites. Green Tuff whole-rock data are from Liszewska *et al.* [2018] and Williams *et al.* [2014].

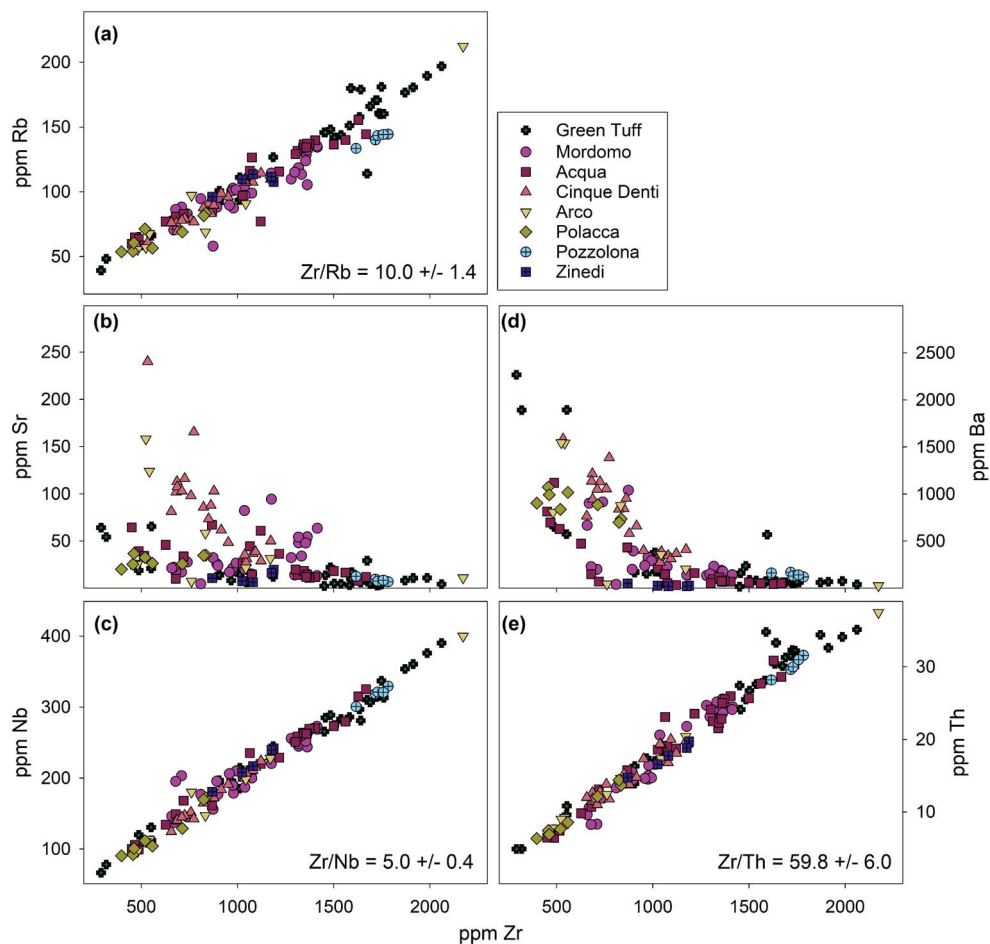
tin [1995] proposed that the differences between the two series were therefore primarily the result of higher  $f_{\text{O}_2}$  in the basalt–comendite series most likely due to higher water content, and a similar process was proposed at Changbaishan [Andreeva *et al.*, 2019]. We propose that the same may also be true at Pantelleria.

## 6. Post-Green Tuff trachyte and pantellerite

Eruption of caldera-filling metaluminous trachyte lavas that comprise the Monte Gibeles–Montagna Grande shield volcano followed the eruption of the Green Tuff ignimbrite and collapse of the Cinque Denti caldera (K/Ar  $44 \pm 8$  to  $28 \pm 16$  ka; Cornette *et al.*, 1983, Mahood and Hildreth, 1986). The creation of this intracaldera shield volcano was followed by eruption of pantelleritic trachyte to pantellerite lavas and tuffs, which formed a series of at least 24 coalescing domes, cones, and shields mostly along the rim of, or within, the moat of the caldera from 30–7 ka [Cornette *et al.*, 1983, Mahood and Hildreth,

1986, Scaillet *et al.*, 2011]. The pantellerites are generally similar to those formed during the late stages of formation of the post-caldera trachytes. Some, at least, were compositionally zoned, for example, the Khaggiar lava flow and Randazzo pumices, which can be used to typify this phase of magmatism [Landi and Rotolo, 2015, Neave, 2020, Perugini *et al.*, 2002]. The flow and pumices were erupted at  $\sim 8$  ka from cones north of Montagna Grande. The compositions range from comenditic trachyte to pantellerite, with overall similarities to the Zinedi Formation (Figure 4b). Neave [2020] has found that there were at least three magma types: trachytes, less evolved pantellerites, and more evolved pantellerites. Compositional variability was generated by accumulation of feldspar into evolved pantellerites, the injection of trachyte magma into less evolved pantellerites and the accumulation of relatively primitive feldspars in trachytic magmas.

Importantly, Neave [2020] proposed that the plumbing system experienced several recharge events prior to eruption and raised the possibility that the three magma types were stored in a com-

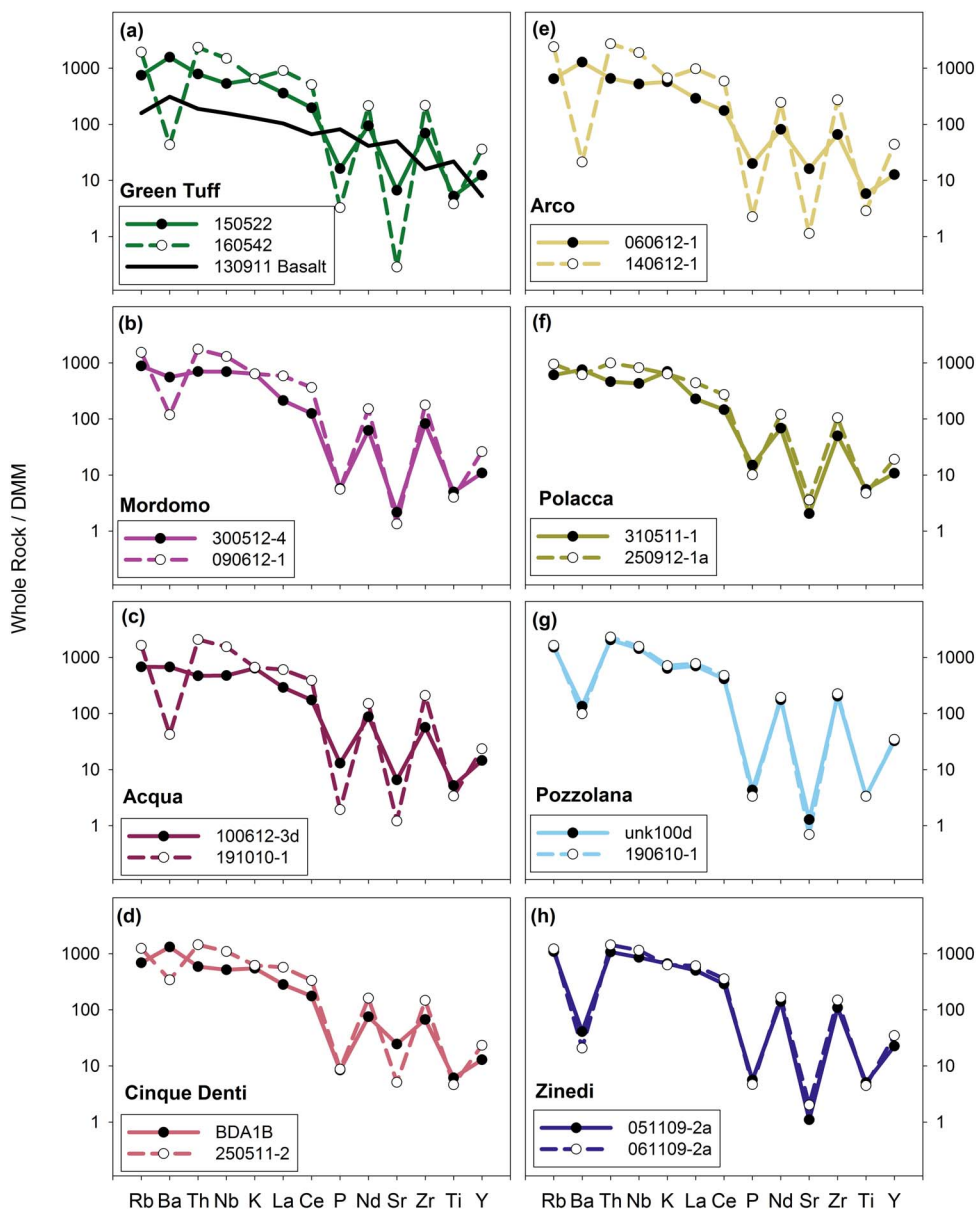


**Figure 7.** Trace element variation diagrams plotted versus Zr. Incompatible trace element ratios calculated from the entire dataset. Green Tuff whole-rock data are from Liszewska *et al.* [2018] and Williams *et al.* [2014].

partmentalized system and followed different LLOD. His cartoon model of the plumbing system comprises an initial stack of three lens-shaped reservoirs connected by dykes. As time progressed, crystal mush erosion connected the upper two reservoirs and the Randazzo and Khaggiar rocks were erupted from this mixed reservoir. The model is in contrast to models of the Green Tuff reservoir, which show a more standard representation of a trachytic mush zone overlain by a stably stratified reservoir zoned from comenditic trachyte to pantellerite [Landi and Rotolo, 2015, Liszewska *et al.*, 2018, Neave *et al.*, 2012]. If the Green Tuff reservoir structure was indeed replaced by another, the change took place in  $\sim 13$  ka or less. Nonetheless, Neave [2020] stressed that the

complexity shown by this small event ( $<0.1$  km<sup>3</sup> DRE) is analogous to that in much bigger peralkaline eruptions, such as the Green Tuff, and in their calc-alkaline counterparts.

Compositional trends for the post-Green Tuff pantellerites are presented in Figure 9. Trachyte lavas are metaluminous to slightly peralkaline (P.I. = 0.90–1.06, with one sample with 1.17 from the “youngest flow” of pantelleritic trachyte on the northeastern flank of Monte Gibeale) and silica-saturated to slightly oversaturated ( $Q^* = 0.0$ –8.75 and 17.8), with  $Q^*$  values and Zr concentrations consistent with the compositional trends of the Green Tuff. Post-caldera pantellerite lavas generally follow the trend of the Green Tuff Formation, but are characterized by higher P.I., Zr,

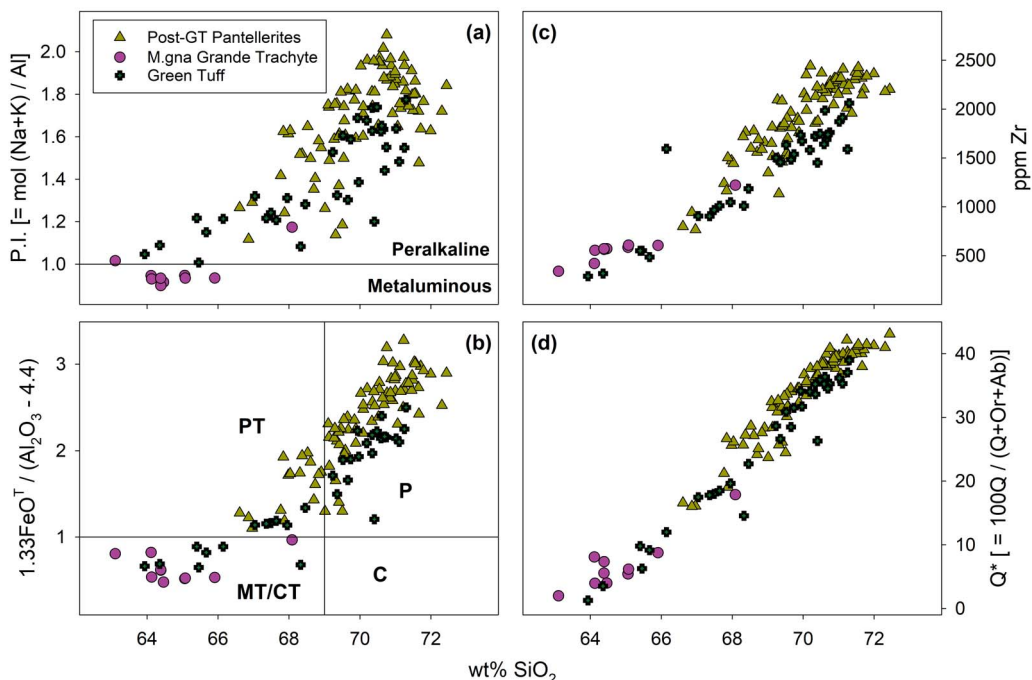


**Figure 8.** Multi-element variation diagrams normalized to depleted MORB mantle [DMM; Salters and Stracke, 2004] for representative least- and most-evolved samples of each formation (see Table 2). Included with the Green Tuff (a) is a sample of pre-Green Tuff basalt (130911; White *et al.*, 2020) for comparison. Green Tuff data are adapted from Liszewska *et al.* [2018].

and  $Q^*$  at a given concentration of  $\text{SiO}_2$ . Both trends terminate at approximately the same value of  $Q^*$ , which may imply that these magma reservoirs were stored at similar depths.

As to the future, based on high-precision  $^{40}\text{Ar}/^{39}\text{Ar}$  ages for activity of the past 20 ka, Scaillet *et al.* [2011]

recognized a long-term (>15 ka) decline in eruptive frequency, from  $3.5 \text{ ka}^{-1}$  to  $0.8 \text{ ka}^{-1}$ . Combined with geodetic evidence that the caldera floor is deflating and subsiding [De Guidi and Monaco, 2009, Mattia *et al.*, 2007], Scaillet *et al.* [2011] proposed that the intracaldera system is on the wane, with no evi-



**Figure 9.** Variation of  $\text{SiO}_2$  with (a) the peralkalinity index [P.I.]; (b) relative variability of  $\text{FeO}^T$  and  $\text{Al}_2\text{O}_3$  (adapted from Macdonald, 1974); (c) concentration of Zr; and (d) silica-oversaturation, as  $Q^* = 100 \cdot Q / (Q + \text{Or} + \text{Ab})$  for the post-Green Tuff trachytes and pantellerites. Green Tuff whole-rock data are from Liszewska *et al.* [2018] and Williams *et al.* [2014]. Other data from Civetta *et al.* [1984, 1998], Perugini *et al.* [2002], Avanzinelli *et al.* [2004], Parker and White [2008], White *et al.* [2005, 2009], Ferla and Meli [2006], Rotolo *et al.* [2007].

dence for a forthcoming eruption. However, in noting the similarities between the current period and pre-Green Tuff inter-ignimbrite periods, Jordan *et al.* [2018] cautioned against assuming that no large, catastrophic eruption will occur in the future, although perhaps not imminently.

The Pantelleria trough, in which the volcano is situated, has high average heat flow ( $94 \pm 21 \text{ mW} \cdot \text{m}^{-2}$ ; Verzhbitsky and Kononov, 2003) and a strong positive Bouguer anomaly (65–103 mGal; Behncke *et al.*, 2006, Civile *et al.*, 2008), features which have been taken to indicate the presence of abundant basaltic magmas at depth [Della Vedova *et al.*, 1995]. Some workers have suggested that there has been asthenospheric upwelling to  $\sim 60 \text{ km}$  [Argnani and Torelli, 2001, Civile *et al.*, 2008, Della Vedova *et al.*, 1995, White *et al.*, 2020]. Ascent of basaltic magma into the Pantescan reservoir, perhaps promoted by increased tensional regional stresses, could result in renewed silicic magmatism.

## 7. Conclusions

- (1) From  $\sim 190$  to 46 ka, the Pantescan plumbing system erupted eight ignimbritic formations from what is inferred to have been a stably stratified reservoir.
- (2) The earliest ignimbrite (Zinedi Fm.) was pantelleritic whereas later ignimbrites had comenditic affinities.
- (3) The Green Tuff eruption at  $45.7 \pm 1.0 \text{ ka}$ , which produced the ninth and last ignimbrite, was apparently considerably more complex than earlier activity, ranging from metaluminous trachytes to pantellerites. It was immediately followed by a suite of trachytes taken to represent a mush zone in the reservoir.
- (4) Magmatism from 25–7 ka was dominated by pantellerites broadly similar in composition to those of the oldest ignimbrite. The upper

part of the plumbing system has shown signs of increasingly open system behaviour.

- (5) All felsic series evolved from a similar basaltic parent along similar LLOD leading to trachyte, with differences in both pressure (depth of the reservoir) and oxygen fugacity (possibly linked to water content) contributing to whether the trachyte evolved to **comendite (under higher pressures and more oxidizing conditions) or to pantellerite (under lower pressures and more reducing conditions)**. Detailed petrogenetic studies of these older comendite units are necessary and ongoing.

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## Supplementary data

Supporting information for this article is available on the journal's website under <https://doi.org/10.5802/crgeos.50> or from the author.

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