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Compositional and thermodynamic variability in a stratified magma chamber: Evidence from the Green Tuff Ignimbrite (Pantelleria, Italy)

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ABSTRACT

The Green Tuff Ignimbrite, Pantelleria, is compositionally zoned from pantellerite at the base to comenditic trachyte at the top, the variation apparently representing an inverted vertical zonation in the pre-eruptive reservoir. The main phenocryst assemblages are alkali feldspar + olivine + clinopyroxene + ilmenite + apatite in the trachytes and alkali feldspar + aenigmatite + clinopyroxene ± quartz in the rhyolites. Thermodynamic modelling indicates that the temperature range was ~900-700°C, fO₂ FMQ-1.5 to FMQ-0.5 and aSiO₂ (relative to quartz saturation) 0.74-1.00. Melt water contents ranged from ~1 wt % in the trachytes to ~4 wt % in the pantellerites. Matrix glass analyses in the more evolved rocks are highly variable, showing that compositional layers in the upper parts of the reservoir, formed by fractional crystallization, were mixed during eruption, the proportion of rhyolitic to trachytic melts increasing towards the top of the reservoir. Some areas of glass have low Al₂O₃ contents (5.16-5.46 wt %) and high FeO* contents (9.66-10.02 wt %), making them the most evolved melts yet reported from Pantelleria. The new glass data stress how whole-rock analyses do not truly reflect the complete range of melt compositions in the pre-eruptive reservoir. The trachytes contain >40% modal phenocrysts, which with relatively high Ba contents and positive Eu anomalies, are considered to have originated in a feldspar-accumulitic layer. Phenocrysts in the trachytes are commonly heavily resorbed, inferred to be a result of heating by influxes of intermediate composition magmas, which, however, were not erupted. It is argued that magma of intermediate composition were present in the Green Tuff reservoir but were efficiently trapped in a crystal-rich layer below the Green Tuff magmas, which was eventually erupted during a resurgent phase as the Montagna Grande Trachyte.

Key words: Green Tuff ignimbrite; Pantelleria; zoned magma reservoir; magma mixing
INTRODUCTION

The island of Pantelleria, located in the Strait of Sicily continental rift system, is a composite, bimodal volcano, with alkali basalt and peralkaline rhyolite end-members. Rocks of intermediate composition, such as mugearites and benmoreites, are rare and in many, perhaps all, cases are products of magma mixing (Ferla & Meli, 2006; Romengo et al., 2012). Despite intensive study since the 1960s, some aspects of the evolution of Pantelleria remain enigmatic, including (i) the location and nature of the magma reservoir(s), (ii) the genetic relationships between the mafic and silicic volcanic rocks, and (iii) the detailed changes in crystallization conditions during magma evolution. The deposit termed the Green Tuff is an important focus in addressing these, and related, problems.

(a) The Green Tuff is compositionally zoned from pantellerite to trachyte, which has been inferred to represent vertical compositional variation within the pre-eruptive magma chamber, with the pantellerites being erupted first. The zonation allows us to examine the genetic relationships between them in the products of one eruption, using whole-rock, matrix glass and mineral chemical data.

(b) The trachytic members show strong textural disequilibrium, which must be related to processes in the lower part of the erupted magma reservoir, such as thermal and/or compositional inputs from more mafic melts via magma mixing. This, in turn, can provide evidence on the material in the sub-trachyte part of the chamber and thus on the existence or otherwise of a composition (Daly) gap in the plumbing system.

(c) The phenocryst assemblages are suitable for estimating such parameters as temperature, $fO_2$ and $aSiO_2$, how they varied with melt composition and inferred depth in the magma chamber prior to eruption and the evidence they provide for a volatile gradient.

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GEOLOGICAL SETTING

Pantelleria is located in the NW-SE trending Strait of Sicily Rift Zone (Fig. 1). The rift cuts
the Pelagian Block, a promontory of the African plate. The crustal thickness under most of the
Block is 25-35 km, thinning to 16-17 km in the rift zone (Civile et al., 2008). The Pantelleria
Trough is one of three basins within the rift; it is a deep trough with a bathymetric low
reaching a depth of -1317 m (Morelli et al., 1975). The trough has a strong positive Bouguer
anomaly (65-103 mgal; Behncke et al. 2006; Civile et al., 2008). It also has a high average
heat flow (94 ± 21 mW/m²; Verzhbitsky & Kononov, 2003), which contrasts with the
continental average of 55 mW/m² but is in line with the fact that southern Italy is a hot spot in
Europe, with an average of 70 mW/m² (Chapman & Pollack, 1975). These features have been
taken to indicate the presence of abundant basaltic magmas at depth (Della Vedova et al.,
1995) and asthenospheric upwelling to ~60 km, which is coincident with the maximum depth
of earthquake foci that have been recorded in this area (Calò and Parisi, 2014). Little is known
of the composition of the submerged part of Pantelleria. Geophysical work by Gantar et al.
(1961) showed that it comprises a large volume of high density rocks (3000 kg/m³). By
analogy with Linosa, a volcanic island some 100 km SE of Pantelleria in the Strait of Sicily,
the rocks may be dominated by basalts and hawaiites (Villari, 1974). The most recent,
basaltic, eruption in the area was submarine and occurred a few kilometres to the NW of the
island in 1891.

At the current level of exposure, Pantelleria is dominated (~94%; Mahood & Stimac, 1986)
by trachytes and rhyolites. Eruption of basalts and hawaiites has been restricted to the
northern part of the island. Furthermore, a well (PPT2) drilled in the northern section
penetrated, at 180 m depth, more than 600 m of basaltic lavas and hyaloclastites cut by
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dolerite dykes (Fulignati et al., 1997). A basaltic component has been recognized in mixed magma rocks from various centres on the island, indicating the continuing presence of mafic magma at depth (Ferla & Meli, 2006; Romengo et al., 2012). Magmatic activity at Pantelleria is undoubtedly basalt-driven, in that basaltic magma is the fundamental source of mass, heat and volatiles in the system.

The Green Tuff forms a thin cover over much of the 83 km$^2$ island, draping all topographic landforms (Fig. 1). High-precision $^{40}$Ar/$^{39}$Ar dating has given an eruption age of 45.7 ± 1.0 ka (2σ) (Scaillet et al., 2013). The volume (in DRE: dense rock equivalent) has been variously estimated as 0.28 km$^3$ (Jordan et al., 2018), 1.5 km$^3$ (Civetta et al., 1988), 3.5 km$^3$ (Mahood & Hildreth, 1986) and 7 km$^3$ (Wolff & Wright, 1981). The range partly reflects uncertainty in the amount of material that fell into the sea: distal ash from the eruption has been identified as far away as the Dodecanese, 1300 km east of Pantelleria (Margari et al., 2007). Taking into account the offshore deposit, Margari et al. (2007) suggested a bulk ash volume of ~10 km$^3$ DRE. The range also reflects the very variable thickness of the Green Tuff, from 30 cm to >10 m in palaeovalleys (Orsi & Sheridan, 1984). The deposit has been variously interpreted as a welded ignimbrite (Villari, 1974), a welded fall deposit (Wolff & Wright, 1981) and a sequence of pyroclastic flow units including welded fall and surge members (Orsi & Sheridan, 1984). Mahood & Hildreth (1986) described the Green Tuff as a Plinian deposit, commencing with fallout beds followed by pyroclastic flows. In the fullest, most recent study Williams et al. (2014) interpreted the Green Tuff as a Plinian fall deposit overlain by a single ignimbrite flow unit.

The location and nature of the eruptive sources of the Green Tuff are debatable. Following Mahood & Hildreth (1986), it has generally been accepted that eruption of the Green Tuff at 45.7 ± 1.0 ka was related to the formation of the Cinque Denti caldera (~30 km$^2$), the younger
of the two calderas on the island (Fig. 1). Wright (1980) argued for a central vent on the
western side of the Cinque Denti caldera, whereas Mahood & Hildreth (1986) located the vent
at the southern end of the caldera or in the Monte Gibele area. Williams et al. (2014)
suggested that the vent was on the northwestern slope of Montagna Grande. In contrast,
Catalano et al. (2014) proposed that the tuff was erupted from fissures superimposed on NNE-
trending normal fault zones within the caldera complex. They further proposed that the
eruption caused only a partial collapse of the southeastern walls of the caldera, the main part
of which had formed earlier, perhaps at ~87 ka. Most recently, Jordan et al. (2018) have
argued that there have been five, or more, periods of caldera collapse on Pantelleria and that
the eruption of the Green Tuff was accompanied by only partial collapse along previously
established faults.

The Green Tuff is continuously zoned from comenditic trachyte at the top to pantellerite at
the bottom, reflecting in reverse order the eruption from a zoned magma chamber (Mahood,
1984; Civetta et al., 1988; Mahood & Hildreth, 1986; Williams et al., 2014). Judging from the
stratigraphic height versus composition profile in Williams et al (2014), the trachyte forms an
estimated 5-10% of the deposit. An important aspect of the Green Tuff, in terms of the
evolution of Pantelleria, is that its eruption marked a peak in melt production and in the
peralkalinity of the magmas, after a long inter-eruptive period following the 85 ka eruptive
episode (Mahood & Hildreth, 1986; Scaillet et al., 2013). On the basis of new $^{40}$Ar/$^{39}$Ar
dating and geodetic evidence of deflation and subsidence of the caldera floor, Scaillet et al.
(2011) proposed that the intracaldera system, in stasis since 7 ka, is on the wane and that there
is no evidence of a forthcoming eruption.

Formation of the Green Tuff was followed by eruption onto the caldera floor of the
volcanic rocks forming Monte Gibele (44-37 ka), which was subsequently uplifted as a
resurgent block and then tilted to form Montagna Grande at ~18 ka (Fig. 1) (Mahood & Hildreth, 1986; Orsi et al., 1991; Lanzo et al., 2013). This edifice is composed dominantly of metaluminous trachytes, with a single recorded example of benmoreite lava (Romengo et al., 2012). K-Ar dates for the trachytes overlap those of the Green Tuff, prompting Mahood & Hildreth (1986) to suggest that the trachytic activity was a continuation of the Green Tuff activity, i.e. it was probably part of the same magmatic system, where continuing eruptions were a response to isostatic compensation for the material ejected during caldera formation. In contrast, Civetta et al. (1988) considered the Green Tuff activity to be a late-stage part of the earliest of six eruptive cycles on Pantelleria, whereas Montagna Grande was the earliest part of a second cycle. However, the existence of the six cycles has been questioned by Scaillet et al. (2011), partly on the basis of newer, high precision $^{40}$Ar/$^{39}$Ar ages. In the activity of the past 20 ka, they recognized a long-term (>15 ka) decline in eruptive frequency associated with a prominent palaeosol horizon marking a volcanic hiatus between 12 and 14 ka.

Using the joint inversion of geodetic data (levelling, EDM and InSAR), Mattia et al. (2007) found that the main caldera is subsiding and proposed that the measured ground deformation pattern can be explained by a simple spherical source located at ~4 km beneath the caldera. The subsidence was related to the cooling of a hydrothermal system beneath the caldera.

Lanzo et al. (2013) combined Cl and H$_2$O solubility data to estimate a confining pressure of about 50 MPa (depth ~2-3 km) for the Green Tuff magma chamber, the shallow depths being consistent with petrological estimates for other pantellerite eruptions on the island (Lowenstern, 1994; White et al., 2005, 2009; Di Carlo et al., 2010; Neave et al., 2012).

**Lithostratigraphy of the Green Tuff**
The Green Tuff is a very complex eruptive unit, showing major lateral and vertical heterogeneity. Primary depositional features have been obscured by various combinations of dense welding, strong rheomorphism and revesiculation. Standard methods of correlation along strike, such as the use of lithofacies, have proved inadequate. For example, Lanzo et al. (2013) divided the tuff into five members on the basis of the clearly visible variations of some megascopic features, including welding, crystal content and rheomorphic structures. Catalano et al. (2014) grouped the many lithofacies in the tuff into three major lithostratigraphic intervals, which show many differences in detail to the Lanzo et al. (2013) scheme.

In an innovative approach, Williams et al. (2014) used compositional variation within the deposit, as exemplified by Zr abundance, as a measure of stratigraphic height. They established a type section on the Monastero scarp (Fig. 1) which shows a continuous decrease of whole-rock Zr contents from ~2000 to 300 ppm with height within the section (Fig. 2). Lateral correlations were then made on the basis of Zr content being a time-marker during eruption of the tuff. It will be shown below that magma mixing was a significant process during eruption of the tuff, such that individual whole-rock analyses may reflect the range and proportions of mixed components. In this report, it is assumed that the highest level in the reservoir being tapped by the eruption of any given magma batch is given by the highest Zr glass content in that sample. The inferred positions of samples are consistent with the field occurrence, where known, e.g. the basal pumice fall, basal vitrophyre and upper vitrophyre (Fig. 2).

**SAMPLING AND ANALYTICAL METHODS**
The aims of this study included determining the range of melt compositions in the Green Tuff, and studying in detail the melt–phenocryst relationships. It was critical, therefore, that, wherever possible, pristine melt (glass) compositions were determined. The only previous study to focus on glass compositions in the Green Tuff is that of Williams et al. (2014). However, as they acknowledge, the beam diameter used in their laser ablation inductively coupled mass spectrometry (LA-ICP-MS) determinations was sufficiently large that their analyses probably included glass and microlites. The electron microprobe technique used here allowed us to focus on areas of clean glass, although the presence of submicroscopic microlites cannot be excluded in every case. Samples were collected from 15 localities (Appendix). Glass was found in 11 samples; certain facies of the tuff, especially strongly welded and trachytic varieties, are completely devitrified. A small number of analyses of glass inclusions in phenocrysts have also been made.

Two whole-rock analyses (samples 090531 and 090533) were made at Activation Laboratories, Ancaster, Ontario, for major elements and Cu, Ni, Pb and Zn by ICP-AES (Code 481) and other trace elements by ICP-MS (Code 4Lithoresearch), F by ion selective electrode (Code 4F-F) and Cl by INAA (Code 4F-Cl). The remaining fifteen whole-rock analyses were made at Bureau Veritas Commodities Canada Ltd (Table 2). Major elements and Cr were analysed by ICP-ES, and trace elements, including REE, by ICP-MS. Mean detection limits on major elements was close to 0.1 wt % whilst the detection limits for trace elements varied from 0.01 to 0.1 ppm.

Mineral compositions were determined by electron microprobe at the Inter-Institute Analytical Complex at the Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw, using a Cameca SX-100 microprobe equipped with four wavelength dispersive spectrometers. The analytical conditions for minerals, except feldspar, were: accelerating
voltage 15 kV and probe current 20-40 nA, with counting times of 20 s on peak and 10 s on each of two background positions. For feldspar, a beam spot diameter of 5 μm was used, to reduce Na loss. For glass analyses, 15 kv and 6-10 nA and a dispersed spot of ~10-20 μm were used. Certain problems can arise with analysis of glass. As well as compositional variations related to incomplete mixing of melts, melts may have been heterogeneous because of (i) proximity to different phenocrysts and (ii) contamination by microlites. In our experience, for example, contamination by feldspar and FeTi-oxide microlites can cause some scatter in Fe and Al abundances. We have attempted to mitigate these problems by analyzing clear pools of matrix glass as far as possible from phenocryst phases.

The ‘PAP’φ(ρZ) program (Pouchou & Pichoir, 1991) was used for corrections. Apatite was analysed using the technique outlined in Macdonald et al. (2008). Estimates of analytical precision (1σ; wt %) for all phases except glass are: Si 0.07, Ti 0.03, Al 0.02, Cr 0.02, Ni 0.03, Fe 0.09, Mn 0.03, Mg 0.04, Ca 0.08, Na 0.01, K 0.01. For glass analyses, the values are Si 0.40, Ti 0.03, Al 0.14, Fe 0.29, Mn 0.12, Mg 0.02, Ca 0.03, Na 0.17, K 0.11, P 0.03, Zr 0.08, Cl 0.03, F 0.08. The numbers of point analyses presented are: phenocrysts: alkali feldspar 501; fayalite 102; hedenbergite 171; FeTi-oxides 27; aenigmatite 58; apatite 10: matrix glass and melt inclusions 145. Representative glass analyses are given in Table 3; the full phenocryst and glass data set is given in Electronic Appendices 1-3 (available at http://www.petrology.oxfordjournals.org).

PETROGRAPHY

Phenocryst assemblages
Phenocryst assemblages are presented in Table 1. Alkali feldspar phenocrysts are present in all samples, its abundance ranging from 30-40 modal% in the comenditic trachytes to <10 modal% in the pantellerites. Mafic phenocrysts are much less abundant, normally occurring in total in amounts less than 5 modal%. Exceptions are clinopyroxene in sample 150521 (~5%) and aenigmatite in 150514 (~2-3%).

Whereas the alkali feldspar phenocrysts in the rhyolites tend to be euhedral to subhedral, homogeneous and up to 3 cm across, those in the trachytes are commonly highly resorbed (c.f. Korringa & Noble, 1972; Troll & Schmincke, 2002; Romengo et al., 2012; D’Oriano et al., 2017) (Fig. 3(a), (b). Resorbed and euhedral crystals are sometimes present together in mixed magma rocks. Olivine phenocrysts occur in the less peralkaline rocks, commonly showing highly resorbed textures (Fig. 3(c)). Clinopyroxene is ubiquitous, varying in form from perfectly euhedral to partially resorbed plates (Fig. 3(d)). Zoning is common, marked by differing shades of green.

Quartz phenocrysts are rounded and up to 1 cm in size. They are found only in the more peralkaline host glasses and appear to have been of relatively late crystallization, consistent with the observation of Di Carlo et al. (2010) from their experimental work on Pantescan pantellerites. Aenigmatite phenocrysts, most commonly forming euhedral prisms, are also restricted to the more peralkaline hosts. Ilmenite occurs throughout the whole-rock compositional range, commonly in association with clinopyroxene and olivine but also as discrete subhedral crystals. Titanomagnetite is scarcer, more texturally variable: it is present as equant microphenocrysts, forms rims to ilmenite phenocrysts and occurs as tiny crystals along the rims of melt inclusions. No exsolution lamellae have been seen. Apatite microphenocrysts occur over the complete whole-rock compositional range, although they are most abundant in the trachytic members. They most commonly form euhedral prismatic
crystals, up to a few tens of µm long, associated with clinopyroxene and olivine phenocrysts.

Pyrrhotite occurs in most samples, usually as small crystals (<20 µm) enclosed in olivine and
clinopyroxene phenocrysts.

As noted above, many samples contain glass of more than one composition and the
phenocryst assemblages reflect those compositional ranges. Taking this into account, some
general observations of phenocryst distribution can be made. The two dominant assemblages
are (i) alkali feldspar + fayalite + hedenbergite + ilmenite + apatite, and (ii) alkali feldspar +
hedenbergite + aenigmatite ± ilmenite ± quartz + apatite. Assemblage (ii) occurs in the more
peralkaline rocks and (i) in the more trachytic types. Samples containing phases more
commonly found in melts of slightly different composition, e.g. fayalite and aenigmatite in
samples 150534 and 150551 (Table 1), contain glass of more than one composition and the
phenocryst assemblages may reflect those compositional ranges. However, it will be shown
below that the assemblage fayalite + ilmenite + aenigmatite may be in equilibrium under very
specific conditions.

Glass

The majority of samples contain two or more varieties of glass, the relationships between
them being very variable. In some cases, the glasses have different colours in plane polarised
light, reflecting differing degrees of devitrification or microvesicularity without significant
compositional differences. In others, the colours reflect magma mixing, which takes several
forms. In Fig. 4(a), rounded blobs of black glass are mingled with a pale brown type. Both
types contain alkali feldspar phenocrysts. Figure 4 (b) shows streaky intermingling of dark
brown and pale glasses, feldspar phenocrysts being more common in the dark variety. Slightly
denser welding in Fig. 4 (c) has resulted in mingling of narrow fiamme, the paler type being more devitrified. The less densely welded sample in Fig. 4 (d) shows pale and slightly deeper brown glasses patchily intermingled along their junction. No relationship between the type of mixing and height within the deposit has been discerned.

Apart from two point analyses in clinopyroxene, all analyses of melt inclusions were made in alkali feldspar phenocrysts (Electronic Appendix 3). The inclusions are similar to those described from the Green Tuff by Lanzo et al. (2013); the dominant forms are ovoidal and subspherical, up to 250 μm across. The analysed inclusions are composed entirely of glass.

PHENOCRYST COMPOSITIONS

*Alkali feldspar* phenocrysts are anorthoclase in the compositional range An$_{10}$Ab$_{70}$Or$_{20}$ to An$_{0}$Ab$_{63}$Or$_{37}$, with an outlier at Or$_{40}$ (Electronic Appendix 1(a)). The Or and Fe contents generally increase with whole-rock peralkalinity. Barium levels (≤0.01 apfu) are detectable only in feldspars with CaO >0.5 wt %. The compositional range within samples is usually small; e.g. in 150511, 150546 and 150551 the range is Or <3. In others, e.g. 150541, a slightly larger range (An$_{6.2}$Ab$_{73.5}$Or$_{20.3}$ to An$_{0.2}$Ab$_{68.2}$Or$_{31.8}$) reflects phenocryst occurrence in glasses of different composition. With the exception of those with higher CaO contents (>0.6 wt %), all the alkali feldspar phenocrysts have peralkalinity indices (P.I. = molar $((\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{Al}_2\text{O}_3)$ in the range 1.0 to 1.14.

*Olivine* phenocryst compositions are in the range Fo$_{6-25}$, the Fo content decreasing with increasing whole-rock peralkalinity (Electronic Appendix 1(b)). They show high abundances of MnO (3.7-4.6 wt %). Calcium levels are moderate, ≤0.75 wt % CaO, and show a positive correlation with Fo, except for sample 150541 where the olivines are relatively Ca-poor.
Zoning is generally small, <1% Fo, except for one strongly resorbed crystal in 150513 where the range is Fo\textsubscript{9.8-6.3}. The clinopyroxene phenocrysts are sodian hedenbergite, ranging from Ca\textsubscript{44}Mg\textsubscript{29}Fe\textsubscript{28} to Ca\textsubscript{37}Mg\textsubscript{9.0}Fe\textsubscript{54} and with Mg-number from 51.0 to 12.5 (calculated with Fe as Fe\textsuperscript{2+}) (Electronic Appendix 1(c)). Mg-numbers decrease with increasing host-rock peralkalinity. Oxidation ratios (Fe\textsuperscript{3+}/(Fe\textsuperscript{3+}+Fe\textsuperscript{2+})) calculated from stoichiometry, range from 0.01 to 0.22 and are negatively correlated with Mg-number. Sodium levels are also negatively correlated with Mg-number, varying from 0.05 to 0.20 apfu. All are peralkaline, in the sense of having Na/Al >1. Zonation within crystals is usually limited (≤En\textsubscript{4}) but in one crystal in 150541 En ranges from 12.8-21.7%. Clinopyroxene-melt exchange coefficients K\textsubscript{d\textsuperscript{Fe-Mg}} (calculated with all Fe as Fe\textsuperscript{2+}) range from 0.11-0.13. This is comparable to values (0.14-0.16) found experimentally in a Pantescan pantellerite by Di Carlo \textit{et al.} (2010) and in Kenyan comendites by Scaillet & Macdonald (2003).

With increasing host-glass peralkalinity, the aenigmatite phenocrysts in the Green Tuff contain more Na and less Ca and Al (c.f. Mahood & Stimac, 1990) (Electronic Appendix 2(a)). The compositional variation can generally be expressed by the coupled substitution Si\textsuperscript{4+} + Na\textsuperscript{+} ↔ Al\textsuperscript{3+} + Ca\textsuperscript{2+} (Kunzmann, 1999) (Fig. 5). The new analyses extend slightly the compositional range on Pantelleria. Ilmenite phenocrysts are in the narrow range X_{ilm} 0.95-0.99, with Nb\textsubscript{2}O\textsubscript{5} levels ≤0.60 wt % and MnO 1.96-3.19 wt % (Electronic Appendix 2 (b)). Limited data are available for magnetite (Electronic Appendix 2(b)). The phase rimming an ilmenite phenocryst in 150513 has the composition X_{usp} 0.47-0.49, the core of a microphenocryst in 150541 is X_{usp} 0.62 and an inclusion in olivine is X_{usp} 0.72-0.76.

Mahood & Stimac (1990) presented analyses of fluorapatite in three Green Tuff rocks spanning the compositional range trachyte to pantellerite. They noted that the REE and Si contents and the La/Ce and La/Y ratios increased, and Ca and P contents decreased, with
increasing host-rock peralkalinity. Our new data (Electronic Appendix 2 (c)) largely confirm their observations, although slightly increasing the britholite component, as measured by REE+Y+Si contents, up to nearly 5%.

GEOCHEMISTRY

Whole-rock compositions

Compositional modification of peralkaline silicic rocks through secondary hydration and/or partial devitrification is well established (e.g. Noble, 1967, 1970; Noble et al., 1967; Baker & Henage, 1977; Weaver et al., 1990). Particularly important is the potential loss of Na which affects the calculation of the P.I. As an alternative measure of peralkalinity, White et al. (2003) introduced the index FK/A (mol. (Fe+K)/Al, with all Fe calculated as Fe$^{2+}$), on the basis that Fe, K and Al are considerably less mobile in aqueous systems than Na and because of the strong positive correlation between P.I. and FK/Al in non-hydrated peralkaline rocks. Plots of FK/Al against P.I. for Green Tuff rocks and glasses show a good positive correlation (Fig. 6). However, some point analyses appear to have Na$_2$O values rather lower than those predicted from the FK/Al values. Loss of Na cannot, therefore, be precluded from all our samples, especially those with high LOI values, e.g. 150542 in Table 2, where secondary hydration was the alteration process. Evidence for the loss of Na in a vapour phase is the presence in 160541 of the rare mineral tuhualite (NaFe$^{3+}$Fe$^{2+}$Si$_6$O$_{15}$), which Bagiński et al. (2018) showed was precipitated in vesicles during and after devitrification of the tuff. Furthermore we cannot preclude some loss of Na under the electron beam, which would be more marked in hydrated glasses.

Classification of the whole-rocks has been made using the scheme for peralkaline silicic rocks of Macdonald (1974). In the scheme, the data form a continuous trend from comenditic trachyte to pantellerite (Fig. 7). Whole-rock compositions are plotted against SiO$_2$ in Fig. 8. With increasing
SiO$_2$, Al$_2$O$_3$, TiO$_2$, MgO, CaO contents decrease and Na$_2$O and F contents increase; K$_2$O peaks at SiO$_2$ $\sim$69 wt % (Fig. 8 (a)). Total Fe decreases to SiO$_2$ $\sim$66 wt % and then increases.

Barium, Sr (and Ni, Sc and V) contents are negatively correlated with SiO$_2$, i.e. are enriched in the trachytic members (Fig. 8 (b)). The incompatible trace elements (ITE; Be, Cs, Hf, Nb, Rb; Ta, Th, U and Zr) generally show positive correlations with SiO$_2$ and P.I. Gallium shows an initial increase and then the trend flattens. An important observation is that data from the Montagna Grande Trachyte overlap with those of the Green Tuff, consistent with a genetic relationship between them (Mahood & Hildreth, 1986).

Chondrite-normalised REE patterns for Green Tuff whole-rocks are shown in Fig. 9 (a). The patterns are LREE-enriched; more trachytic types show gently decreasing values from Gd to Lu, whereas the most peralkaline types have flat patterns between Gd and Lu. Europium anomalies (Eu/Eu*) range from 1.08 in comenditic trachyte 150522 to 0.41 in pantellerite 160541.

**Glass compositions**

Representative matrix glass compositions are given in Table 3 and the full data set in Electronic Appendix 3. The spread in SiO$_2$ values is from 62.8 to 73.7 wt % and the glasses range from comenditic trachyte to pantellerite (Fig. 7). Melt inclusions in phenocrysts cover a similar compositional range (Electronic Appendix 3) and will be discussed in conjunction with the matrix glass.

As noted earlier, alkali migration on devitrification and secondary hydration has affected the melt P.I. but it appears that the glasses, including the trachytic varieties, were all peralkaline. The compositional variations are generally similar to those in the whole-rocks, although the range extends to both more silica-rich and less silica-rich types (Fig. 8 (a)).
may also be noted that the highest Zr abundance (3183 ppm in sample 150544; Electronic Appendix 3) is distinctly higher than the maximum recorded in previous studies of pantescan rocks and glass (2300 ppm; Williams et al., 2014).

On the FeO*-Al$_2$O$_3$ plot (Fig. 7), the glasses show significantly more complexity than the whole-rocks. The sub-horizontal trend across the comenditic trachyte field (Trend 1) shown by samples 150522 and 150534 may be the result of alkali feldspar being the sole liquidus phase in these melts, which results in an increase in FeO*. The change in slope at ~6 wt% FeO* (Trend 2) could mark the onset of clinopyroxene fractionation, after which the glass analyses follow a trend similar to the whole-rock analyses. At ~9 wt% FeO*, two subtrends emerge. Most glass analyses decrease sharply to ~7 wt% FeO* at near-constant (~7-8 wt%) Al$_2$O$_3$ (Trend 3B). The glasses and melt inclusions at ~9 wt% FeO* have a normative composition very similar to the experimentally determined minimum of Carmichael & MacKenzie (1963); we posit that this trend reflects crystallization of aenigmatite along the quartz-feldspar cotectic, which would allow Zr, which is incompatible in all phases (Mahood & Stimac, 1990; Neave et al., 2012) to continue to increase as FeO* decreases and P.I. remains relatively constant (1.83 ± 0.18 for Zr >1500 ppm).

The other trend (Trend 3A) consists solely of glass and melt inclusions in sample 150514, which continue the whole-rock trend to ~10 wt% FeO* and 5.3 wt% Al$_2$O$_3$ (corresponding to P.I. = 2.61 and 2961 ppm Zr) (Table 3 and Electronic Appendix 3). These unusually low Al$_2$O$_3$ contents, high FeO* contents and high P.I. make them the most evolved melts yet recorded from pantelleria (Fig. 7). They are, however, broadly similar to glasses (FeO* 14-15 wt% and Al$_2$O$_3$ 5-6 wt%) formed in the experiments of Di Carlo et al. (2010) and they approach the effective minimum composition for peralkaline silicic magmas (FeO* ~13 wt%, Al$_2$O$_3$ ~5 wt%) proposed by Macdonald et al. (2012). It is possible that pockets of highly
differentiated melt were locally developed in the Green Tuff reservoir, perhaps promoted by unusually high F contents of the magma, as recorded in the glass in 150514 (≤0.9 wt % (Electronic Appendix 3). The high F contents could have lowered melt viscosity and allowed crystal fractionation to continue to slightly lower temperatures.

No new REE data for glass are presented here. However, chondrite-normalized REE patterns for data in Mahood & Stimac (1990), Neave et al. (2012) and Williams et al. (2014) are broadly similar to those in the whole-rocks (Fig. 9 (b)). An unusual feature of several trachytic glass and melt inclusion analyses reported in the literature is positive Eu anomalies (Eu/Eu* = 1.12-1.36), accompanied by Ba concentrations up to 1308 ppm (Mahood & Stimac, 1990; Williams et al., 2014; Romano et al., 2018). Positive Eu anomalies are characteristic of Pantescan basalts that may be parental to these trachytes (Civetta et al., 1998; White et al., 2009). Coupled with low plagioclase/melt partition coefficients for Eu in the basalts (0.13; Neave et al., 2012), it is possible that this is an inherited feature preserved through fractional crystallization (Romano et al., 2018). However, crystal accumulation and resorption have also been suggested as differentiation mechanisms for the trachytes (White et al., 2009) and there is petrographic evidence for such a process in our samples, such as modal alkali feldspar abundances up to 40% (Figs. 3 (a), (b)). Values higher than ~1300 ppm Ba and Eu/Eu* ≈ 1.36 have been observed only in whole-rock trachyte analyses, strongly suggesting that those samples have been affected by such processes.

This raises the question as to the composition of the least evolved trachytic melt in the Green Tuff. This is important because it helps to define the liquid-line-of-descent from intermediate to salic compositions. Williams et al. (2014) presented LA-ICP-MS analyses of trachytic glass with 59.90 wt % SiO₂ and 251 ppm Zr. All analyses in their data set with
positive Eu anomalies have about the same SiO$_2$ and Zr contents. That may well represent, therefore, the trachytic melt parental to the comenditic trachytes.

Chlorine values range continuously from below detection (~250 ppm) in some trachytic glasses to 1.2 wt % (with an outlier at 1.73 wt %) in the pantellerites. Abundances are positively correlated with SiO$_2$ and Zr, indicating progressive enrichment with increased fractionation. Civetta et al. (1988), Lowenstern (1994), Gioncada & Landi (2010) and Lanzo et al. (2013) noted that Cl abundances increase more quickly than Zr in glass in various Pantescan suites, suggesting an upward enrichment mechanism in the reservoir. They also suggested that the fact that Cl levels reached ~1 wt % and then remained constant during further magma evolution, as measured by increases in SiO$_2$ and Zr, pointed to separation of a Cl-bearing fluid phase with which the magmas remained in equilibrium. The new Green Tuff data apparently show a continuing increase of Cl with fractionation, suggesting that Cl remained in the melt phase.

Sulphur abundances (as SO$_3$) range from below detection (~0.03 wt %) to 0.21 wt %, although the great majority of analyses are <0.1 wt %. These values agree with values for Pantescan rocks given by Civetta et al. (1988), Lowenstern (1994), Gioncada & Landi (2010), Neave et al. (2012) and Lanzo et al. (2013). Abundances show a positive, but scattered, correlation with increasing peralkalinity; it is not clear whether the scatter is due to loss of S on devitrification or to variable loss of a magmatic volatile phase.

An important feature of the glass analyses is the range of compositions within individual samples, shown by the SiO$_2$ and Zr ranges in Table 1, denoting the mingling in varying combinations of trachytic and rhyolitic melts. The range within samples varies from 2 to 9 wt % SiO$_2$ and its size is not related to the whole-rock composition. Two examples of the mixing components are shown in Fig. 10. In Fig. 10 (a), a fragment of pale glass with a SiO$_2$ content
of 72-73 wt % contains irregular dark blebs with lower SiO$_2$ contents (65-68 wt %). The photograph of a thin section of 150521 (Fig. 10 (b)) shows textural intermingling of darker and lighter glass components with SiO$_2$ values varying from ~67-71 wt %. Texturally different glasses in the same specimen do not always show such significant compositional differences. For example, the pale and dark glasses shown in Fig. 4 (a) have SiO$_2$ in the ranges 68.7-70.3 and 67.9-70.1 wt %, respectively.

GEOCHEMICAL MODELS

Major-element mass balance models were developed to test the fractional and equilibrium crystallization hypotheses for the origin of compositional zoning and to constrain the relative proportion of the phases involved (Table 4). All calculations were managed with Microsoft Office Excel 2013 and are considered acceptable if $\Sigma r^2 < 1.0$. The first model (A) tests the origin of highly evolved pantellerite glass from comenditic trachyte matrix glass. The most primitive comenditic trachyte glass analyzed for this study was recovered from sample 150522, and has the lowest P.I. (1.09) and FeO* (4.3 wt %) and highest Al$_2$O$_3$ (16.1 wt %) observed; this was chosen as the model parent for Part A. Zirconium concentrations were below the detection limit of the electron probe for this sample. The model daughter selected is an evolved matrix glass at the intersection of two sub-trends recovered from sample 150514 with P.I. = 1.96, 9.5 wt % FeO*, 7.3 wt % Al$_2$O$_3$ and 2591 ppm Zr.

A second, similar model (B) tests the origin of highly evolved pantellerite melt inclusions hosted in alkali feldspar from sample 150514 with a P.I. = 2.61, 10 wt% FeO*, 5.3 wt% Al$_2$O$_3$, and 2961 ppm Zr. Both models use a mineral assemblage from sample 150511, which has a composition intermediate between the model parent and daughter. Model results are
both acceptable ($\Sigma^2 = 0.255$ and 0.240, respectively) and very similar, suggesting that these
highly evolved melts can be produced by 93-94% fractional crystallization of an assemblage
dominated by alkali feldspar (92.5%) with subordinate clinopyroxene and olivine (2.5-3% 
each), ilmenite (~1.5%), and apatite (<1%). This model is largely in agreement with previous
models of fractional crystallization of the peralkaline trachyte-pantellerite suite at Pantelleria,
but also presents the highest estimate for degree of fractional crystallization. The model of
White et al. (2009), for example, suggested 70% fractional crystallization, but from a more
peralkaline parent (P.I. = 1.12, 7.0% FeO*) to a less peralkaline daughter (P.I = 1.91, 7.8%
FeO*). However, this and other models (e.g. Civetta et al., 1998; Neave et al., 2012) all agree
on a dominant role for alkali feldspar (>85% of the fractionating assemblage), with
subordinate olivine, clinopyroxene, Fe-Ti oxide, and apatite, consistent with the observed
mineral assemblages in these samples. Although we lack Zr data for the comenditic trachyte
glass, Williams et al. (2014) report an average value of 255 ppm for one glass sample within
the comenditic trachyte facies of the Green Tuff type section; if we assume bulk $D_{Zr} \approx 0$, then
$F = 0.09-0.10$ (91-90% crystallization) which is consistent with our results.

A curious feature observed in Fig. 7 is a sub-horizontal trend at ~7.5 wt % $\text{Al}_2\text{O}_3$ (Trend
3B) that extends from the end of the main trend (modelled in Part A) to progressively lower
concentrations of FeO* that nonetheless include glasses with the highest concentrations of Zr
measured (up to 3108 ppm) despite near-uniform Zr whole-rock concentrations (1500-1700
ppm). This trend is also manifest in Figures 11 and 12b (next section), where these samples
appear to plot along the experimental alkali feldspar-quartz cotectic (Carmichael &
MacKenzie, 1963). These highly evolved samples have assemblages characterized by a
relatively large volume of aenigmatite (e.g. 2-3% in 150514), along with quartz, alkali
feldspar and clinopyroxene; we suggest that this trend is the result of equilibrium
crystallization of this assemblage. Mass balance modelling of this scheme (Table 4, Part C) suggests its plausibility ($\Sigma r^2 = 0.655$, with 0.221 error from MnO), with a small degree (8%) of late crystallization of an assemblage of aenigmatite and quartz with minor quantities of alkali feldspar and sodian clinopyroxene resulting in a decrease in FeO* with a slight rise in $\text{Al}_2\text{O}_3$ and P.I. An estimate of the degree of crystallization from Zr ratios (assuming $D_{Zr} \approx 0$, as above) between the model daughter and parent suggest about twice as much crystallization (17%, $F = 0.83$) as that determined by major-element mass balance modelling.

Overall, the results of the modelling are consistent with the various magmas having been formed by fractional crystallization of the observed phenocryst assemblages.

### GEOTHERMOMETRY

In Fig. 11, temperatures calculated by (a) QUILF (olivine + clinopyroxene) and (b) by clinopyroxene – glass and clinopyroxene – whole-rock (Putirka et al., 2003) (Table 5) are plotted against Zr contents in the whole-rocks. While the QUILF results yield higher temperatures at given Zr content, it is clear that the least evolved trachytes give ~900°C and the temperatures then decrease to ~700°C in the most peralkaline members. There must, of course, have been local temperature fluctuations due to mixing of magmas from different layers. Oxygen fugacities range from FMQ-0.5 to FMQ-1.5, with an outlier at FMQ-2.2 (Table 5). The temperature and $f_O^2$ estimates are similar to those for Pantescan pantellerites calculated thermodynamically by White et al. (2005, 2009) and determined experimentally by Di Carlo et al. (2010). Thermodynamic values recovered by olivine – clinopyroxene equilibria in the QUILF system are pressure-sensitive, but for an increase (or decrease) of 500 bars of pressure, silica activity changes by only 0.02 units and temperature increases (or
decreases) by only 3°C on average. However, oxygen fugacity, relative to the FMQ buffer, remains relatively unchanged.

Whole-rock (a) and glass (b) analyses have been plotted in the system Q-Ab-Or-H_2O with 8.3 mol% aegirine + 8.3 mol% sodium metasilicate added, P_{H_2O} = 1000 bar, and projected from H_2O + aegirine + sodium metasilicate (Carmichael & MacKenzie, 1963) (Fig. 12). The normative mineralogy was calculated with FeO/FeO* = 0.9, corresponding to oxygen fugacities buffered at FMQ-1 between 700 and 900°C (Sack et al., 1980). The alkali feldspar liquidus surface is plotted as crosses, labelled with the experimentally determined temperature (°C) for that composition. The minimum for this system occurs at Q_{40.5}Or_{34.5}Ab_{25}, with the alkali feldspar-quartz coticet located at approximately Q_{40}. Also shown is the “thermal valley” of Carmichael & MacKenzie (1963), the differentiation path of a system undergoing crystal fractionation of alkali feldspar with a composition of ~Or_{35}. Despite some scatter, temperatures drop from 825°C in the trachytes to 700°C in the most peralkaline whole-rocks, temperatures consistent with those found in Fig. 11, and the rocks generally follow a feldspar fractionation trend. The spread of glass compositions at Or_{40} is consistent with some melts having reached the quartz-feldspar coticet.

The vertical decrease in temperature from the comenditic trachyte to the pantellerite is accompanied by an increase in silica activity relative to quartz saturation (aSiO_2 (Qtz)), calculated by QUILF95, from 0.74 to 1.0, as well as a slight increase in oxygen fugacity relative to the FMQ buffer (Fig. 13). Macdonald et al. (2011) described the antipathetic relationship between fayalitic olivine and aenigmatite as a function of T, P and aSiO_2, with the latter crystallizing at the expense of the former at T <750°C at silica activities close to or at quartz saturation at 150 MPa. Lower pressures extend the stability of aenigmatite to higher temperatures (cf. White et al., 2005; Di Carlo et al., 2010) which is consistent with these results.

Fayalite-bearing rhyolites with ilmenite present as the sole Fe-Ti oxide phase crystallize in T-fO_2 space along the displaced FHQ (fayalite-hematite-quartz) buffer. In this sense, the FHQ buffer is “displaced” from that which would plot for unit activities for all phases. A regression through the T-
$a$SiO$_2$ data was used to calculate the displaced FHQ buffer for ilmenite compositions between $X_{ilm}$ 0.95 and 0.98 in Fig. 13. In our formulation, unit activity is assumed only for fayalite and the curve is displaced to lower $fO_2$ due to much lower hematite activities ($X_{hem} = 0.03-0.05$; activities calculated following Andersen & Lindsley, 1988) and silica activities relative to quartz saturation less than one (interpolated from the linear trend in the previous figure, with silica activities calculated from olivine-clinopyroxene equilibrium using QUILF95).

The Green Tuff broadly follows the FHQ curve, with the magma chamber becoming slightly less reduced roofward relative to the FMQ buffer. A comparison with experimental data from pantelleritic systems, including Eburru, Kenya (Scaillet & Macdonald, 2006) and Pantelleria (Di Carlo et al., 2010), suggests that this may be due to a corresponding volatile gradient from ~1 wt % H$_2$O in the comenditic trachyte to ~4 wt % H$_2$O in the pantellerite. The presence of such a volatile gradient may be supported by FTIR analyses of melt inclusions in the basal pantellerite and uppermost trachyte.

Melt inclusions in the trachyte are comenditic trachyte in composition, with 0.15-1.05 wt % H$_2$O (Romano et al., submitted). Lanzo et al. (2013) reported values of up to 4.2 wt % H$_2$O from feldspar-hosted melt inclusions in the pantelleritic basal fall unit, consistent with values from melt inclusions in compositionally similar pantellerite lavas (up to 4.9 wt % H$_2$O; Gioncada & Landi, 2010; Neave et al., 2012).

Using the model parameters of White et al. (2009), the simplest explanation for a volatile gradient is ~70% fractional crystallization of a comenditic trachyte melt with 1.0-1.5 wt % H$_2$O, which would produce a pantellerite melt with 3.3-4.9 wt % H$_2$O (assuming bulk $D_{H_2O} = 0.01$). This in turn would require 0.3-0.5 wt % H$_2$O in the parental basalts – lower than either the 0.9-1.6 wt % reported by Gioncada & Landi (2010) for melt inclusions in the Cuddie Rosse basalt or the 1.0-1.5 wt % predicted from MELTS modelling (White et al., 2009).

Experimental results on Pantescan basalts also suggest that they must be hydrous ultimately to produce pantelleritic melts (Scaillet et al., 2005), although the MELTS results reported by White et al. (2009) suggest that basalt water concentrations as low as 0.5 wt % would also
produce similar comenditic trachyte. The volatile gradient and accompanying change in oxidation state could also be explained by melt vesiculating, which could result in a reaction between Fe-rich silicate melt and H$_2$O via thermal dissociation and degassing of H$_2$ (cf. Carmichael, 1991; Mungall & Martin, 1995; Scaillet & Macdonald, 2001; White et al., 2005).

**DISCUSSION**

**Nature of Green Tuff reservoir**

Possible relationships in the plumbing system prior to the eruption of the Green Tuff are shown in Fig. 17. A magma reservoir is envisaged with a trachytic crystal mush overlain by a layered pantelleritic upper part of the chamber. Pressure estimates of 100 MPa, which correspond to depths of 3-4 km, were used for all thermodynamic calculations because (1) this is in between the total range of 50-150 MPa estimated by previous workers for the depth of the magma chamber using various methods, and (2) this depth is consistent with geophysical studies of the depth of the magma chamber, e.g. with the model of Mattia et al. (2007), based on geodetic data, placing the top of the reservoir at ~4 km beneath the caldera. The overall depth of the reservoir would have been greater if the Montagna Grande trachytes were part of the magma system; they were erupted from lower layers in the reservoir during resurgence following eruption of the Green Tuff, although the depth of magma being tapped is not known. Major element contents are consistent with such a cogenetic relationship (Fig. 8 (a)) and, although trace element data are rather scarce for Montagna Grande, the trace elements are also consistent; average Zr/Nb ratios, for example, are 4.9 in the Green Tuff and 4.5 in the Montagna Grande trachytes. The speculative gabbroic mush represents the source of the trachytic magmas, squeezed out either by compaction or buoyancy.
Similar models for trachyte – peralkaline rhyolite relationships have been proposed by Troll & Schmincke (2001) for ignimbrite ‘A’, Gran Canaria, and by Sumner & Wolff (2003) for the ‘TL’ ignimbrite, Gran Canaria.

**Origin of compositional zonation**

Previous authors have used geochemical modelling to show that the transition from trachyte to rhyolite at Pantelleria can be satisfactorily modelled by fractionation of an alkali feldspar-olivine-clinopyroxene-oxide ± aenigmatite assemblage (Civetta *et al*., 1988; White *et al*., 2009; Neave *et al*., 2012). The new models presented here are consistent with these earlier models. Experimental studies of Pantescan rocks by Di Carlo *et al*., (2010) and Romano *et al*. (2018) are also consistent with such models. We propose, therefore, that the comenditic trachytes separated from the crystal-rich metaluminous trachytes later erupted as the Montagna Grande Trachyte. Continued fractional crystallization of the trachytic magmas generated pantelleritic melts which separated from the trachytes through buoyancy effects and accumulated towards the roof of the reservoir, finding levels determined by their density.

Some of the compositional variation in the Green Tuff has also been related to alkali feldspar accumulation (Korringa & Noble, 1972; Prosperini *et al*., 1990; White *et al*., 2009).

For example, the so-called low-incompatible trace element (low-ITE) trachytes of White *et al*. (2009) were shown to contain up to 47% modally of alkali feldspar phenocrysts. The new data set provides further evidence that the process was important in the evolution of the Green Tuff. For example, at ~300 ppm Zr, the Eu anomaly increases from 1 to 1.6 (Fig. 14). At the same Zr value, K/Rb ratios rise from ~600 to 1000, Ba contents from ~700-2300 ppm and Sr contents from ~50 to 70 ppm, features consistent with feldspar accumulation in the trachytic rocks. Major- and trace- element models presented by White *et al*. (2009) and Romano *et al*. would...
(2018) suggest that samples affected by accumulation or resorption of alkali feldspar will have Ba >1300 ppm. The process was also locally operative at higher levels in the chamber; sample 150541, with ~35 modal% feldspar phenocrysts, has high Al$_2$O$_3$, Ba and Sr (Fig. 8) contents. However, it has a negative Eu anomaly (Eu/Eu* 0.54) which would require that the accumulating feldspar had a negative anomaly. Yet Mahood & Stimac (1990) argued that all the feldspars in the Green Tuff have strong positive Eu anomalies.

It appears, therefore, that the composition of the comenditic trachyte underlying the pantellerites was modified by variable amounts of feldspar accumulation.

Glass heterogeneity and implications for syneruptive mixing

Density variations in the melts (glasses) have been calculated by the method of Bottinga & Weill (1970) (Fig. 15). Anhydrous densities range from 2480 kg m$^{-3}$ in the trachytes to 2420 kg m$^{-3}$ in the most peralkaline melts. This might imply that the pantelleritic part of the reservoir was stably density-stratified while the higher density and viscosity of the feldspar-rich trachytes prevented them from rising and mixing with the overlying rhyolites. This further implies that eruption of the Green Tuff was triggered by an external mechanism. We suggest that the trigger was an influx of more mafic magma into the trachytic parts of the reservoir which raised temperatures (as seen in the resorption of phenocrysts) and caused trachytic melts to rise and mix with the overlying more evolved melts (c.f. Flude et al., 2008; Romengo et al., 2012). Triggering of the eruption of peralkaline magmas by intrusion of intermediate magmas has been proposed by Sumner & Wolff (2003) for ignimbrite ‘TL’ (Gran Canaria) and by Pimentel et al. (2016) for comenditic trachytes of the AD 1761 eruption at Terceira Island (Azores). The lack of significant compositional zoning in the resorbed phenocrysts is taken to show that the more mafic magma acted as a heat source 26
without physical or chemical mixing, as discussed by D’Oriano et al. (2017) for similar feldspar-rich zones for comenditic trachytes of the Lajes ignimbrite eruption, Terceira Island, Azores.

Models of magma evacuation from compositionally zoned chambers have shown how each successive evacuation draws magma from progressively deeper levels of the chamber, isochemical surfaces being deflected upwards beneath the vents so that several compositional layers can be tapped simultaneously (Blake, 1981; Blake & Ivey, 1986; Spera et al., 1986; Schuraytz et al., 1989; Macdonald et al., 1994). It was noted earlier that many Green Tuff samples show a range of matrix glass compositions, denoting the mingling in varying combinations of trachytic and rhyolitic melts. Importantly, the mingling was very thorough, down to the micron scale, which we ascribe to the small differences in temperature and density between the pantelleritic melts which did not significantly hinder mixing.

The range of SiO$_2$ values in the glasses is matched by variations in Zr (Table 1). It appears, therefore, that the steady increase in Zr values shown with increasing height in the pre-eruptive chamber by Williams et al. (2014) does not simply reflect an increasing degree of fractionation of the melt upwards. Rather, it reflects an increasing proportion of evolved melts in earlier erupted magma batches. Plotting the highest Zr value in each sample, as a measure of the sample’s highest stratigraphic position within the pre-eruptive chamber, against the range of Zr contents in the same glasses, two broad zones can be distinguished (Fig. 16): (i) a zone where the glasses all have rather homogeneous (?) trachytic composition; and (ii) a zone where the glasses are dominantly mixes of rhyolitic-rhyolitic melts. Two barriers to mixing thus existed in the system: one between crystal-rich and crystal-poor comenditic trachytes and one between the trachytes and pantellerites.
An important general point arising from the within-sample ranges in glass composition is that whole-rock analyses do not necessarily give a true indication of the range of melt compositions in the pre-eruptive reservoir; as noted above, the highest whole-rock and glass Zr values are 2300 and 3183 ppm, respectively. This raises the question as to how common this type of fine-scale mingling may be in compositionally zoned silicic systems. Clearly, relevant studies would preferably need to be made in systems preserving significant glassy facies. However, in their absence a careful analysis of the stability relationships of the phenocryst assemblages should provide clues as to the range of host melts.

Significance for the Daly Gap

Models for the formation of the Pantescan suite are broadly divisible into two groups. In one, the trachytes and rhyolites were formed independently of basaltic magma; intermediate compositions (mugearites and benmoreites) are the products of magma mixing (Lowenstern & Mahood, 1991; Avanzinelli et al., 2004; Ferla & Meli, 2006; Romengo et al., 2012). In the other model, the salic rocks were formed by the prolonged crystal fractionation of basaltic magma. The observed scarcity or absence of intermediate rocks results from either a physical or thermodynamic discrimination in the magma reservoirs and their non-eruption (Civetta et al., 1988; White et al., 2009; Neave et al., 2012). One aim of this paper has been to assess whether melts of intermediate composition were present in the Green Tuff magma system. Some of the published evidence is equivocal. Geochemical modelling had shown that the pantellerites of Pantelleria could have been produced by ~95% fractional crystallization of parental alkali basalts, via magmas of intermediate composition. In the modelling of White et al. (2009), melts entered the Daly gap (~50-62 wt % SiO₂) after 30% crystallization, and then stayed there for a further 59% crystallization. In contrast, in experiments made on a Pantescan
basalt at 1 atm and 8 kb, Mahood & Baker (1986) found that residual melts had not reached
the Daly gap after 70% crystallization.

The main approach used here was to carefully relate glass and mineral compositions to
textures. The least evolved glass composition in the new Green Tuff data set has 62.84 wt %
SiO$_2$; similar glass compositions (SiO$_2$ 59.90-62.3 wt %) have been recorded in the Green
Tuff by Mahood & Stimac (1990) and Williams et al. (2014). No clearly intermediate-
composition melts have thus been found.

As an indicator of what mineral compositions might be expected, in their MELTS
modelling of the evolution of Pentescan suites White et al. (2009) found the following
mineral compositions as melts passed through the benmoreite stage (at 1.0% H$_2$O in the
parent, 100 MPa, FMQ-1): plagioclase An$_{60-49}$; olivine Fo$_{47-21}$; clinopyroxene Wo$_{45}$En$_{35-30}$Fs$_{20}$.

For this study, a careful analysis was made of the cores of phenocrysts in the Green Tuff,
on the basis that they may have preserved compositions from earlier stages of magma
evolution. For feldspar, the most “mafic” composition was An$_{7.9}$; for olivine Fo$_{25.4}$; for
clinopyroxene En$_{29}$. The main phenocryst phases thus crystallized from melts more evolved
than benmoreite.

White et al. (2009) described, from post-caldera trachyte lavas of Montagna Grande and
Monte Gibele, anorthoclase phenocrysts (An$_{3.9}$Ab$_{70-71}$Or$_{50-26}$) with cores of resorbed
plagioclase (An$_{34}$Ab$_{62}$Or$_4$). A benmoreitic lava from Montagna Grande, thought to have
formed by mixing of trachytic and mafic magmas, contains feldspar phenocrysts with
resorbed cores of plagioclase (An$_{43.32}$Ab$_{53-63}$Or$_{3.5}$) mantled by oligoclase (An$_{23.25}$Ab$_{66-67}$Or$_{0.1}$)
(Romengo et al., 2012). The occurrence of such calcic compositions as cores suggests that
the feldspars initially crystallized from magmas of intermediate composition and were being
resorbed during subsequent melt evolution. It is possible that if the Montana Grande trachytes
were part of the Green Tuff magma system (Mahood & Hildreth, 1986), benmoreitic magmas may have been trapped in these lower, dense and viscous levels in the chamber and could not rise into the part erupted as the Green Tuff. Many post-Green Tuff pantelleritic eruptives have abundant trachytic enclaves (Prosperini et al., 1990; Ferla & Meli, 2006; Landi & Rotolo, 2015), implying ready intrusion of trachyte to high-levels in these systems. This suggests a remarkable efficiency for the trachyte “trap” zone in the Green Tuff reservoir. It may be noted that Mattia et al. (2007) suggested that trapping of benmoreitic and mugearitic magmas in the chamber due to their relatively high density compared to the more peralkaline rocks and contributed to the high values of the Bouguer anomaly.

In summary, possible relationships in the plumbing system prior to the eruption of the Green Tuff are shown in Fig. 17. The upper part of the erupted reservoir is compositionally zoned pantellerite magma, underlain by feldspar-phyric trachyte. The crystal-rich colourless layer would be erupted during resurgence as the Montagna Grande lavas. The gabbroic mush represents the source of the trachytic magmas, squeezed out either by compaction or buoyancy.

**CONCLUSIONS**

(1) The Green Tuff was erupted from a magma reservoir compositionally zoned from pantellerite (top) to comenditic trachyte (bottom). Conditions within the reservoir are estimated to have been temperature ~900-700 °C, \( f_{O_2} \) FMQ-1.5 to FMQ-0.5 and \( a_{SiO_2} \) (relative to quartz saturation) 0.74-1.00.
(2) The trachytic layer was rich in alkali feldspar phenocrysts and overlay the densely-phyric Montagna Grande Trachyte, which was erupted during resurgence of the caldera whose formation accompanied eruption of the Green Tuff.

(3) Prior to eruption, the Green Tuff magma was layered by crystal fractionation of alkali feldspar- olivine-clinopyroxene-Fe-Ti oxide-apatite assemblages.

(4) During eruption, mingling between layers, especially in the pantellerites, was ubiquitous, at scales down to the micron level, a process revealed only by detailed analysis of within-sample glasses. Whole-rock analyses mask the significance of the mixing.

(5) The new glass analyses have significantly extended the range of melt compositions in the tuff, to those approaching the effective minimum composition for peralkaline silicic melts of Macdonald et al. (2012).

(6) Phenocrysts in the comenditic trachyte are commonly heavily resorbed but only slightly zoned compositionally, indicating perhaps that they were heated by, but did not mix, with influxes of intermediate magmas which were trapped in a lower layer.

ACKNOWLEDGEMENTS

We thank Lidia Jeżak for help with the electron microprobe analyses. Wes LeMasurier, David Neave, Silvio Rotolo and Editor Gerhard Wörner provided extremely detailed and helpful reviews of the manuscript.

REFERENCES

oxides. *American Mineralogist* 73, 714-726.


http://www.petrology.oupjournals.org/


Scaillet, B. & Macdonald, R. (2006). Experimental constraints on pre-eruptive conditions of...


**Figure captions**

**Figure 1.** Locality map showing the distribution of the Green Tuff ignimbrite and the rim faults of the La Vecchia and Cinque Denti calderas. *Sample localities are marked.* Simplified from Scaillet *et al.* (2011).

**Figure 2.** Vertical section through the Green Tuff pumice fall and ignimbrite at the type locality on the Monastero scarp (Fig. 1) where it is ~7.5 m thick. Modified from Williams *et al.* (2014). *The trachytic component is found in the rheomorphic vitrophyre at the top of the deposit (wavy lines). Approximate positions of our samples within the stratigraphy are shown.*
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http://www.petrology.oupjournals.org/
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(c) The experimental results of Scaillet & Macdonald (2006) for Eburru and Di Carlo et al. (2010) for Pantelleria show the strong positive correlation between oxygen fugacity (as $\Delta$FMQ) and melt water content (wt % H$_2$O$_{melh}$).

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166x204mm (300 x 300 DPI)
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134x100mm (300 x 300 DPI)
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180x113mm (300 x 300 DPI)
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## Appendix. Details of analyzed samples

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Datum for all coordinates is WGS84.
Location
Punta Tre Pietre
Punta Tre Pietre
Punta Tre Pietre
Monastero Scarp
Monastero Scarp
Contrada Scirafi
Zinedi Scarp
Cinque Denti Scarp
Cinque Denti Scarp
Khartibucale Scarp
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Monastero Scarp
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p, pantellerite; ct, comenditic trachyte (classification scheme of Macdonald (1974)); +, present but not analyzed.
Table 2. Whole-rock compositions of Green Tuff, Pantelleria

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For Peer Review

http://www.petrology.oupjournals.org/
Table 3. Representative compositions of matrix glasses and melt inclusions in Green Tuff

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Explanation: 1, pale brown glass, sample 150511; 2, dark bleb, 150522; 3, melt inclusion in feldspar, 150522; 4, 5, black blebs of glass, 150534; 6, pale glass, 150534; 7, brown glass, 150542; 8, grey speckled glass, 150544; 9, 10, brown glass, 150551; 11, 12, melt inclusions in feldspar, 150514. FeO*, all Fe as Fe²⁺. bd, below detection. P.I., peralkalinity index (mol. (Na₂O+K₂O)/Al₂O₃).
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</table>

Minerals: Anr, Anorthoclase; Cpx, clinopyroxene; Ol, olivine; Ilm, ilmenite; Ap, apatite; Aen, aenigmatite; Qtz, quartz.

Model results: F, liquid proportion; ²Σ, sum of the squares of the residuals. Apatite and aenigmatite compositions adapted from White et al. (2009).
P.I., Peralkalinity Index (mol. (Na₂O+K₂O)/Al₂O₃)
Table 5. Results of geothermometry and oxygen barometry calculated with QUILF95 (Andersen et al., 1993)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ilmenite</th>
<th>Spinel</th>
<th>Olivine</th>
<th>Augite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X-Hem</td>
<td>X-Gk</td>
<td>X-Py</td>
<td>N-Ti</td>
</tr>
<tr>
<td>160541</td>
<td>0.042</td>
<td>0.013</td>
<td>0.047</td>
<td>0.079</td>
</tr>
<tr>
<td></td>
<td>Calc</td>
<td>0.012</td>
<td>0.009</td>
<td></td>
</tr>
<tr>
<td>150513</td>
<td>0.047</td>
<td>0.024</td>
<td>0.056</td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td>Calc</td>
<td>0.009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150522</td>
<td>Input</td>
<td></td>
<td></td>
<td>0.251</td>
</tr>
<tr>
<td></td>
<td>Calc</td>
<td></td>
<td></td>
<td>0.270</td>
</tr>
<tr>
<td>150534</td>
<td>0.035</td>
<td>0.016</td>
<td>0.044</td>
<td>0.723</td>
</tr>
<tr>
<td></td>
<td>Calc</td>
<td>0.010</td>
<td>0.032</td>
<td>0.126</td>
</tr>
<tr>
<td>150541</td>
<td>Input</td>
<td></td>
<td></td>
<td>0.667</td>
</tr>
<tr>
<td></td>
<td>Calc</td>
<td></td>
<td></td>
<td>0.026</td>
</tr>
<tr>
<td>150551</td>
<td>0.013</td>
<td>0.008</td>
<td>0.042</td>
<td>0.126</td>
</tr>
<tr>
<td></td>
<td>Calc</td>
<td>0.021</td>
<td></td>
<td>0.170</td>
</tr>
<tr>
<td>231</td>
<td>Input</td>
<td></td>
<td></td>
<td>0.719</td>
</tr>
<tr>
<td></td>
<td>Calc</td>
<td></td>
<td></td>
<td>0.058</td>
</tr>
<tr>
<td>226</td>
<td>Input</td>
<td></td>
<td></td>
<td>0.763</td>
</tr>
<tr>
<td></td>
<td>Calc</td>
<td></td>
<td></td>
<td>0.029</td>
</tr>
<tr>
<td>060537</td>
<td>0.039</td>
<td>0.009</td>
<td>0.050</td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>Calc</td>
<td>0.008</td>
<td></td>
<td>0.103</td>
</tr>
</tbody>
</table>

All results are calculated at P = 100 MPa. Entries in italics in the "Input" row signify values that were set as trial values; the values calculated by QUILF95 are in normal font in the "Calc" row. Silica activity is relative to quartz saturation. ΔFMQ = log fO₂ - FMQ(T). Samples 231 and 226 are from mineral analyses reported by Mahood & Stimac (1990); sample 060537 is from mineral analyses reported by White et al. (2009). +, present but not analyzed.