Melting, Differentiation and Degassing at the Pantelleria Volcano, Italy

DAVID A. NEAVE¹*, GARETH FABBRO^{1,2}, RICHARD A. HERD³, CHIARA M. PETRONE^{1,4} AND MARIE EDMONDS^{1,5}

¹DEPARTMENT OF EARTH SCIENCES, UNIVERSITY OF CAMBRIDGE, DOWNING STREET, CAMBRIDGE CB2 3EQ, UK
 ²UNIVERSITÉ BLAISE PASCAL, LABORATOIRE MAGMAS ET VOLCANS, CLERMONT-FERRAND, FRANCE
 ³SCHOOL OF ENVIRONMENTAL SCIENCES, UNIVERSITY OF EAST ANGLIA, NORWICH NR4 7TJ, UK
 ⁴NATURAL HISTORY MUSEUM, CROMWELL ROAD, LONDON SW7 5BD, UK
 ⁵COMET+, DEPARTMENT OF EARTH SCIENCES, UNIVERSITY OF CAMBRIDGE, DOWNING STREET, CAMBRIDGE CB2 3EQ, UK

RECEIVED MARCH 5, 2011; ACCEPTED NOVEMBER 30, 2011

We present the results of the first systematic study of melt compositions at Pantelleria, based on both melt inclusions and matrix glasses in pantellerites from 10 eruptions during the last eruptive cycle (<45 kyr). We present major and trace element compositions, as well as data on the volatiles sulphur (S), fluorine (F), chlorine (Cl), water (H_2O) , carbon dioxide (CO₂) and lithium (Li) Rare earth element (REE) compositions were inverted using the program INVMEL to establish the melt fraction vs depth relationship in the Pantellerian mantle source region. Inversion indicates that melts are generated by $\sim 1.7\%$ melting of a light rare earth element (*LREE*)-enriched mantle source. The source lies principally within the spinel-garnet transition zone, which, on the basis of trace element ratios, shows some affinity to the source of North African magmatism. Major and trace element data indicate a gap in melt compositions at intermediate compositions, consistent with previously published whole-rock data. This gap rules out the possibility of explaining chemical variability in the Pantelleria lavas merely by changes in the crystal content of the magmas. Principal component analysis of major element glass compositions shows that the liquid line of descent for mafic melt compositions is controlled by clinopyroxene, plagioclase, magnetite and olivine crystallization. Alkali feldspar, clinopyroxene, ilmenite and olivine or aenigmatite crystallization controls the liquid line of descent for the silicic melt compositions, with aenigmatite broadly replacing olivine in the most evolved magmas. Trace element modelling indicates that 96% fractional crystallization is required to generate pantellerites from alkali basalts at Pantelleria (through trachytes, generated after 76% fractional crystallization). We have measured pantellerite volatile concentrations in melt inclusions and in matrix glasses from a variety of eruptions. Melt inclusions, on average, contain 350 ppm S, 3500 ppm F and 9000 ppm Cl. We have measured up to $4.9 \text{ wt \%} H_2O$ and 150 ppm CO_2 in melt inclusions. Li- H_2O systematics and Cl abundances in melt inclusions are consistent with partitioning of Li and Cl into a subcritical hydrosaline fluid at low pressures. The volatiles H_2O and CO_2 are used to estimate melt equilibration pressures, which reach a maximum of 1.5 kbar. Temperatures of 800°C are calculated for the most evolved pantellerites, using published feldspar-melt geothermometers, and up to $870^{\circ}C$ for the least evolved samples. Low melt viscosities are calculated for the range of pantellerite compositions observed and may account for rapid differentiation by crystal settling. Stable density stratification of the magma chamber is reflected in the eruption of generally progressively more fractionated compositions after the Green Tuff eruption during the last eruptive cycle. Some anomalies in this trend may be explained by variation in the relative rates of eruption vs fractionation. The density stratification is expected to be enhanced and further stabilized by the efficient migration of a fluid phase to the roof of the magma chamber. The sulphur data are used in combination with published experimental partitioning data for peralkaline rhyolites to estimate the sulphur yield to the atmosphere for a large pantelleritic eruption similar to the Green Tuff. This is expected to be markedly higher than for a similar-sized metaluminous

*Corresponding author. Telephone: +44 $\,(0)$ 1223 333400. Fax: 01223 333450. E-mail: dan
27@cam.ac.uk

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rhyolitic or dacitic eruption, mainly owing to the higher bulk sulphur content, lower fluid—melt partition coefficients, and rapid differentiation and vapour phase segregation in the magma chamber.

KEY WORDS: fractional crystallization; sulphur; pantellerite; peralkaline rhyolite; viscosity; degassing

INTRODUCTION

Pantelleria Island is the type locality for pantellerite, a type of peralkaline rhyolite that contains phenocrysts of sodic pyroxene, alkali feldspar and aenigmatite. Pantellerites are also found outside Pantelleria: in continental rift settings such as the Afar Triangle, Ethiopia and the East African Rift, Kenya (Barberi et al., 1975; Webster et al., 1993; Ren et al., 2006), on ocean islands such as the Azores (Mungall & Martin, 1995) and rarely in back-arc environments such as New Zealand (Ewart et al., 1968). In the Afar, at Fantale, Ethiopia and at Olkaria, Kenya, where continua from basalt to rhyolite are observed, pantellerites are thought to have been formed by extensive fractional crystallization of alkali basalt parent magmas via trachyte (Barberi et al., 1975; Webster et al., 1993; Macdonald, 2006; Ren et al., 2006). In contrast, at Pantelleria a significant Daly Gap is observed between hawaiite and trachyte compositions (Baker, 1968; White et al., 2009).

Two alternative models have been proposed to account for the evolved compositions at Pantelleria: extensive fractional crystallization of parental alkali basalt (Civetta et al., 1998; White et al., 2009); or alternatively, partial melting of alkali gabbro cumulates (on the basis of clinopyroxene chemistry, which suggests different liquid lines of descent for basaltic and silicic magmas; Avanzinelli et al., 2004). Recent major and trace element modelling for a large suite of whole-rock compositions from Pantelleria supports the genesis of pantellerites via fractional crystallization (White et al., 2009) at low pressures (<2 kbar) and an oxygen fugacity of around 1.5 units below the nickel-nickel oxide (NNO) buffer (Di Carlo et al., 2010; Gioncada & Landi, 2010). Significant crustal assimilation during pantellerite genesis is unlikely, given the consistent isotopic compositions (Sr, Nd, Pb) across the Pantellerian suite of rocks (Civetta et al., 1998), but re-melting of crustal gabbros remains a possibility for the generation of trachyte (White *et al.*, 2009).

Here we present new data for a range of matrix glass compositions analysed in 12 samples from 10 eruptions, ranging from alkali basalt to pantellerite. Although whole-rock compositions are undoubtedly useful for evaluating differentiation processes, they are not necessarily representative of melt compositions because of the often extensive crystal content of the magmas; the crystals may be antecrysts, or crystals may have been lost from the bulk magma through crystal settling. We examine the petrographic characteristics of the suite of lavas and pyroclastic rocks and use principal component analysis (PCA) to refine models of fractional crystallization and differentiation. This study is the first to focus on quantifying the geochemical variation in a suite of major and trace elements in melts (now glasses) as opposed to whole-rocks.

Pantellerian magmas are volatile-rich: feldspar and olivine-hosted melt inclusions contain up to 4.5 wt % H₂O, which has been used to estimate a magma chamber pressure of <2 kbar (Gioncada & Landi, 2010; present study). Until this study only one analysis has revealed significant CO₂ in a pantellerite melt inclusion (Lowenstern, 1994); others have demonstrated CO_2 contents up to 1000 ppm in olivine-hosted melt inclusions in alkali basalts (Gioncada & Landi, 2010). Pantellerites are rich in halogens, with chlorine concentrations of up to 9000 ppm (Lowenstern, 1994; White et al., 2009; this study). Sulphur partitioning has been shown to be somewhat suppressed in peralkaline rhyolites, compared with their metaluminous counterparts (Scaillet & Macdonald, 2006). This has important implications for the sulphur output of pantellerite eruptions. We present here feldspar-hosted melt inclusion data for H₂O, CO₂, Li, S, F and Cl, which we use to make more refined estimates of magma chamber depth, and of the volatile output for explosive pantellerite eruptions [using fluid-melt partition coefficients from Scaillet & Macdonald (2006)]. These data show that owing to the more protracted sulphur partitioning into a fluid phase in the magma chamber and more rapid differentiation, pantellerite eruptions have the potential to yield considerable masses of sulphur gases into the atmosphere.

TECTONIC, GEOLOGICAL AND GEOCHEMICAL SETTING

Pantelleria is a volcano of Quaternary age located in the Strait of Sicily Rift Zone in the central Mediterranean (Fig. 1). The volcano is located on the Pelagian block of the African Plate in the foreland of the Maghrebian-Apennine orogenic system that formed as a result of Alpine collision in the Neogene (Butler et al., 1992). Extension has resulted from the NE movement of Sicily away from Africa in the Miocene to early Pliocene (Illies, 1981; Civile et al., 2008). The rift zone comprises three linear depressions in continental crust: the Pantelleria, Linosa and Malta basins, characterized by bathymetric lows of 1317 m, 1529 m and 1731 m respectively (Morelli et al., 1975). Crustal extension has resulted in the Moho depth being reduced from 25 km to 17 km beneath the basins as shown by gravity and seismic studies (Civile et al., 2008, 2010). Seismic reflection profiles show that the basins are bounded by inward-dipping normal faults (Civile et al., 2008, 2010). A thick sediment fill has



Fig. 1. Map showing the location of Pantelleria and other Sicily Strait rift zone volcanoes (Linosa, Graham Bank) in the rifted foreland of the Maghrebian–Apennine orogenic zone between Sicily and Tunisia. The current WNW–ESE extension across the Strait of Sicily is shown from the relative motion of global positioning system (GPS) stations on Sicily and Lampedusa. Map based on Mahood & Hildreth (1986), Butler *et al.* (1992) and Catalano *et al.* (2009).

accumulated in the basins, with up to 2000 m of Pliocene– Pleistocene turbidites, compared with 500 m on the continental platform.

Pantelleria is divided into basaltic northwestern and trachytic-pantelleritic southeastern sections by the SE-dipping Zighidi fault (Catalano et al., 2009). Geodetic and Bouguer gravity anomaly data suggest that the fault penetrates to deep levels in the crust (Behnke et al., 2006). Detailed studies of the geology of the island have been carried out by Cornette et al. (1983), Mahood & Hildreth (1983, 1986) and Civetta et al. (1988). The nomenclature of Mahood & Hildreth (1986) is used in this paper. The major volcanic units are shown in Fig. 2. The ages of eruptions are taken from Mahood & Hildreth (1986) and Civetta et al. (1984), who principally used K/Ar dating methods that are subject to up to ± 10 ka errors. One exception is the 5.5 ka Cuddia Randazzo eruption, which has been dated to a higher accuracy using ¹⁴C methods. The oldest rocks exposed on Pantelleria are 324 ka lavas exposed at Scauri (Mahood & Hildreth, 1986). The volcanic history prior to 100 ka was dominated by emplacement of lava flows (Mahood & Hildreth, 1986). The southeastern section of the island is dominated by two nested calderas, suggesting that the more recent, post ~100 ka, history consists of small eruptions punctuated with catastrophic caldera-forming events. The sequence of catastrophic then minor eruptions can be thought of as a single eruptive cycle. Cornette *et al.* (1983) and Civetta *et al.* (1988) have identified discrete periods of activity within the last 45 ka, forming eruptive cycles super-imposed on this broad-scale cycling.

In this study, we have focused on those eruptions that have taken place during the last eruptive cycle, which started at 45 ka, with the aim of characterizing a sequence of fractionation and degassing within one closed eruptive cycle between Plinian events. The 6 km diameter Cinque Denti caldera formed synchronously with the 45 ka eruption of the Green Tuff, which is chemically zoned, ranging from pantelleritic compositions at its base to trachyte at its top (Civetta et al., 1984, 1988). The Green Tuff covers approximately half of Pantelleria, and has been identified as a composite of flow and fall deposits (Orsi & Sheridan, 1984), with previous researchers identifying it as either an ignimbrite (e.g. Villari, 1974) or a welded fall deposit (e.g. Wolff & Wright, 1981). The intra-caldera trachyte cone of the Montagne Grande-Monte Gibele complex formed after the Green Tuff eruption. Mahood & Hildreth (1986) have dated the formation of this trachyte cone to between 44 and 37 ka. Civetta et al. (1988), however, disputed this date, favouring the 34 ka date from Cornette et al. (1983), with a pause in eruption following the Green Tuff event. An injection of magma led to trapdoor uplift of Montagne



Fig. 2. Geological map of Pantelleria after Mahood & Hildreth (1986). Sample locations are indicated. Key features: (1) the nested Cinque Denti and La Vecchia calderas; (2) the central trachytic complex centred on Montagne Grande; (3) numerous small pantellerite vents, which are mainly located within the Cinque Denti caldera; (4) the restriction of mafic volcanism to the NW part of the island.

Grande between 18 and 3 ka, which was associated with pantelleritic volcanism along the trapdoor faults and hinges (Mahood & Hildreth, 1983; Orsi *et al.*, 1991; Fig. 2). Civetta *et al.* (1988) have identified six cycles of activity since ~45 ka. The Green Tuff and intra-caldera trachytes represent the first and second cycles, with further cycles at ~22, 18–20, 12–14 and $5\cdot3-8$ ka. However, on the basis of uncertainties in the dating and the scope of this study, we do not attempt to place our samples within these high-resolution cycles.

Eruption of basalts in the NW of Pantelleria since 45 ka is thought to have occurred in two main phases, one around Cuddia Bruciata, at 30 ka, and one at Cuddia Rosse at ~10 ka (Cornette *et al.*, 1983; Mahood & Hildreth, 1986; Civetta *et al.*, 1988). Historical basaltic eruptions occurred in 1831 and 1891 (Civetta *et al.*, 1988). Melting most probably reflects adiabatic decompression of the mantle, driven by mantle upwelling resulting from extension. On the basis of the REE chemistry of the basalts, the melting region has been estimated qualitatively to lie in the spinel–garnet transition zone (Civetta *et al.*, 1998). The main aim of this study is to refine our understanding of the melting processes with the first application of a quantitative melting model.

Strontium isotope ratios of the eruptive products are lower than Bulk Earth, whereas Nd isotope ratios, Rb/Sr and light to heavy REE (LREE/HREE) ratios are higher (Civetta et al., 1998). This indicates that the mantle source was originally depleted in incompatible elements but was subsequently re-enriched in some elements such as Rb and the LREE. Depleted mid-ocean ridge basalt (MORB)-source mantle (DMM), high U/Pb mantle (HIMU) and enriched mantle (EM) components (Zindler & Hart, 1986) have been invoked to explain the isotopic data (Civetta et al., 1998). Esperança & Crisci (1995) suggested that the isotopic composition of Pantelleria and the wider rift zone could be explained by mixing of asthenospheric melts with melts from a variably enriched lithosphere. There is some overlap with the MORB field on an Nd-Sr isotope plot, with the Pantellerian lavas being geochemically distinct from those in the Aeolian Arc further to the north (Civetta

et al., 1998). In general, extension-related volcanism in this region is dominated by the eruption of alkali basalts, consistent with intra-continental rifting elsewhere.

METHODS Sample collection, preparation and microanalysis

Samples were collected from units erupted during the past 45 kyr, over the last eruptive cycle as defined by Mahood & Hildreth (1986). Samples of alkali basalt, trachyte, pantelleritic trachyte and pantellerite were collected from 18 units, shown in Fig. 2 and summarized in Table 1. Samples were cut and washed in a sonic bath to remove contaminants, particularly salts from seawater aerosols. Major element composition of phenocrysts and matrix glasses was determined by electron microprobe analysis (EMPA) using a Cameca SX 100 electron microprobe at the Earth Sciences Department at the University of Cambridge. The volatile elements F, Cl and S were also measured in the glasses. A spot size of 10 µm, an operating potential of 15 keV and a beam current of 4 nA for major elements and 60 nA for volatiles and trace elements were used for glass analysis. A focused beam, 15 keV and a beam current of 10 nA for major elements and 100 nA for trace elements were used for phenocryst analysis. Counting times were as follows: 20 s for major elements in glass and phenocrysts; 30 s for trace elements in phenocrysts; 60 s for P, Cr, Mn, Ni, S and Cl in glass; 120 s for F in glass. Standards used were jadeite for Na, periclase for Mg, Si glass for Si, K-feldspar for K, rutile for Ti, fayalite for Fe, corundum for Al, fluorite for F, halite for Cl, pyrite for S, apatite for P, and pure metals for Cr, Mn and Ni.

Trace element compositions of phenocrysts and matrix glasses were analysed in situ by inductively coupled plasma mass spectrometry (ICP-MS) using a Perkin Elmer Elan DRCII system interfaced with a New Wave Research UP213 laser ablation (LA) instrument at the Earth Sciences Department at the University of Cambridge. Spot sizes of $160 \,\mu\text{m}$ were used where possible to improve analytical accuracy by maximizing sample delivery to the mass spectrometer. Some small phenocrysts were analysed using a spot size of $80 \,\mu m$. A laser repetition rate of $10 \,\text{Hz}$ and laser power of $\sim 1 \text{ mJ} (10 \text{ J cm}^{-1})$ were used for the entire study. Total ICP-MS data acquisition lasted 60 s. For each spot the first 20 s was a gas blank, followed by 40 s of laser analysis. There was a 40 s gas rinse-out time after each spot to allow the element signals to return to baseline levels before moving to the next spot. Calcium concentration from the electron microprobe was used as an internal standard for the basaltic samples. Silicon concentration was used for the more evolved samples. The external standard NIST610 was used for calibration, and indicated consistent recovery through the course of analysis and a mean accuracy better than 4% and a mean precision of 3% across the whole suite of elements. For data processing and calculation of concentrations, Glitter software (GEMOC, Australia) was used to process the raw data files containing the signal intensity vs time data (the output from the Elan software). This allows precise selection of blanks and signals, and rapid visualization of the intensity data. Any contaminated or unsatisfactory signals could be easily identified and excluded using Glitter.

The volatiles H_2O , CO_2 and Li were measured in feldspar-hosted melt inclusions and matrix glasses by secondary ion mass spectrometry (SIMS) using a Cameca ims-4f ion probe at the School of Geosciences at the University of Edinburgh. The thin sections were gold-coated and the glasses analysed *in situ*. A 25 µm square area was rastered with a low beam current prior to analysis, to remove the gold coating. Precision of better than 2% was achieved for Li, 25% for CO_2 and 8% for H_2O , using a range of standards, which were analysed at the beginning and end of every analytical session and used to construct a robust calibration curve.

Careful selection of melt inclusions was undertaken when performing both EMPA and SIMS analyses. Glassy feldspar-hosted melt inclusions were used throughout and most were >10 μ m in diameter. Most inclusions analysed contained one or more generations of bubbles (Fig. 3), consistent with studies suggesting the presence of immiscible fluids coexisting with the Pantellerian magmas at crustal depths (Lowenstern, 1994). Melt inclusions with cracks running through them, and those with significant post-entrapment crystallization, were avoided; there were sufficient inclusions that these could be discarded and only fully glassy inclusions analysed.

Computational modelling methods

Melting models were evaluated using the program INVMEL. This code simultaneously inverts melt REE and major element compositions for the best-fitting melt fraction with depth profile for given mantle composition, lithospheric thickness, garnet-in depth and spinel-out depth. A detailed description and theoretical basis have been given by McKenzie & O'Nions (1991). Principal component analysis (PCA) was used to determine the liquid line of descent by simultaneously analysing a suite of major elements. Crystal compositions were then fitted to the first principal component axis to determine the proportion of crystallizing phases using the method of Maclennan et al. (2001). PCA was performed using a subroutine of INVMEL. The mathematical background to using PCA with geochemical data has been discussed by McKenzie & O'Nions (1998) and Slater et al. (2001). Further discussion of the method is given in the online supplementary material available at http://petrology.oxfordjournals.org.

Location	Age* (ka)	Sample	Latitude (°N)	Longitude† (°E)	Sample type	Lithology	Comment
Cuddia Randazzo	5.5 ± 0.01 (¹⁴ C)	09PNL017	36.79973	12·00550	Glassy tephra	Pantellerite	Thin section
Cuddia Randazzo	$5.5\pm0.01~(^{14}C)$	09PNL018	36.79973	12.00550	Pumice	Pantellerite	Hand specimen
Khaggiar Flow	$5.5\pm0.01~(^{14}C)$	09PNL023	36.82106	12.00443	Glassy lava	Pantellerite	Thin section
Punta Tracino	7.56 ± 0.09 (¹⁴ C)	09PNL006	36.79808	12.04626	Glassy lava	Pantellerite	Thin section
Cuddia di Mida	8.95 ± 3	09PNL001	36.78116	11.99308	Glassy tephra	Pantellerite	Thin section
Cuddia di Mida	8.95 ± 3	09PNL027	36.78866	11.99346	Glassy tephra	Pantellerite	Thin section
Cuddia di Mida	8.95 ± 3	09PNL028	36.78866	11.99346	Pumice	Pantellerite	Hand specimen
Monte Gibile (S)	9.45 ± 1	09PNL007	36.76958	11.99340	Glassy lava	Pantellerite	Thin section
Monte Gibile (N)	9.45 ± 1	09PNL008	36.77316	11.98875	Glassy lava	Pantellerite	Hand specimen
Monte Gibile (N)	9.45 ± 1	09PNL012	36.77235	11.98851	Glassy lava	Pantellerite	Thin section
Fossa del Russo	9.45 ± 1	09PNL009	36.76596	11.99863	Glassy lava	Pantellerite	Thin section
Fossa del Russo	9.45 ± 1	09PNL010	36.76703	11.99745	Glassy tephra	Pantellerite	Hand specimen
Cuddia Rosse	<10	09PNL014	36.81833	11.92706	Crystalline lava	Basalt	Hand specimen
Cuddia Rosse	<10	09PNL015	36·81718	11.92760	Basaltic tephra	Basalt	Thin section
Cuddia Mueggen	13±6	09PNL032	36·78915	12·02748	Glassy lava	Pantellerite	Thin section
Cuddia del Moro	16 ± 4	09PNL029	36.79501	12·01313	Glassy lava	Pantellerite	Thin section
Gelfiser	17·6±3	09PNL026	36.81265	11.97791	Glassy lava	Pantellerite	Thin section
Cuddia Bonsulton	18±7	09PNL025	36.80535	11.95828	Glassy lava	Pantellerite	Thin section
Gelkhamar	$23{\cdot}5\pm 3{\cdot}5$	09PNL016	36.80951	11.92968	Glassy lava	Pantelleritic trachyte	Thin section
Youngest flow	28 ± 16	09PNL035	36.78678	12.02443	Crystalline lava	Pantelleritic trachyte	Thin section
Cuddia del Gadir	$28{\cdot}75\pm4{\cdot}75$	09PNL004	36.81266	12.02018	Glassy tephra	Pantellerite	Thin section
Cuddia del Gadir	$28{\cdot}75\pm4{\cdot}75$	09PNL005	36.81266	12.02018	Pumice	Pantellerite	Thin section
Montagne Grande	37.6 ± 10	09PNL011	36·77061	11.99080	Crystalline lava	Trachyte	Hand specimen
Montagne Grande	37.6 ± 10	09PNL030	36.79193	12·01305	Crystalline lava	Trachyte	Thin section
Green Tuff	45 ± 4	09PNL002	36.81995	11.99991	Tuff	Pantellerite	Thin section
Green Tuff	45 ± 4	09PNL003	36.81995	11.99991	Glassy tuff	Pantellerite	Hand specimen
Green Tuff	45 ± 4	09PNL033	36.73615	12.02391	Glassy tuff	Pantellerite	Thin section
Green Tuff	45 ± 4	09PNL034	36.73615	12.02391	Tuff	Pantellerite	Hand specimen
Cuddia Maccotta	?	09PNL021	36.80746	12.01596	Glassy lava	Pantellerite	Hand specimen

Table 1: Location and details of sample localities arranged by eruption age

*Ages of eruptions are averaged K-Ar dates from Mahood & Hildreth (1986) and Civetta *et al.* (1988) (unless marked as a ¹⁴C date).

†Locations west of 12°E use the European Datum 1950 (ED50), UTM 32S projection. Those to the east of 12°E use the ED50, UTM 33S projection. This is consistent with topographic maps from the Instituto Geografico Militare, Italy.

RESULTS

Petrology of the samples

A summary of the phenocryst assemblages in the full suite of analysed samples, as determined by optical microscopy, is given in Table 2.

Alkali basalt scoria (sample 09PNL015) was collected from Cuddia Rosse (Fig. 2) and contains <1% phenocrysts of plagioclase, with subordinate olivine and clinopyroxene.

Trachytes (e.g. sample 09PNL030) were sampled from the lava shield at Montagne Grande and Monte Gibele (Fig. 2); these are holocrystalline and porphyritic, containing 0.5-1.0 mm euhedral phenocrysts of alkali feldspar (25%), often forming glomerocrysts, with irregular inclusions of clinopyroxene (Fig. 3). The alkali feldspar phenocrysts lack prominent zoning and display simple twins. Fayalitic olivine occurs as 0.25-1.0 mm subhedral phenocrysts (1%), associated with Fe–Ti oxides (0.5%), often around degraded rims. Clinopyroxene also occurs as phenocrysts (<0.1%). Examination of crystal inclusion types suggests an order of crystallization: fayalite, clinopyroxene, Fe–Ti oxides, alkali feldspar. The groundmass is highly crystalline and contains 50% lath-like and tabular alkali feldspar. The crystals show some degree of



Fig. 3. Photomicrographs of typical pantellerites from Pantelleria. (a) Euhedral blade of aenigmatite in a glassy matrix. The aenigmatite is opaque to deep red or brown in colour under plane-polarized light. Sample 09PNL027, Cuddia di Mida. (b) Intergrown clinopyroxenes of sodian augite composition in a fine-grained groundmass. Sample 09PNL007, Monte Gibile (S). (c) High-relief grains in the centre are fayalitic olivine. Low-relief grains are alkali feldspar. Numerous melt inclusions are visible in the feldspar grain furthest to the right. Also, the preferred orientation of the feldspar and clinopyroxene microlites in the glassy matrix should be noted. Sample 09PNL017, Cuddia Randazzo. (d) Image showing a feldspar-hosted melt inclusion. Numerous vapour bubbles are visible, consistent with studies invoking immiscible fluids coexisting with Pantelleria magmas at crustal depths (Lowenstern, 1994). Sample 09PNL006, Punto Tracino.

Location	Sample	Phenocrysts	Sample type	Lithology
Cuddia Bandazza		Kan Lany Life Laan Lay	Close tentro	Dontollorito
		$K_{SP} + c_{PX} + ia + aeri + ox$	Glassy teprira	Paritellerite
Punta Tracino	09PNL006	Ksp + cpx + aen + ox	Glassy lava	Pantellerite
Cuddia di Mida	09PNL001	Ksp + aen + cpx + ox	Glassy tephra	Pantellerite
Cuddia di Mida	09PNL027	Ksp + aen + cpx + ox	Glassy tephra	Pantellerite
Monte Gibile (S)	09PNL007	Ksp + cpx + aen + ox	Glassy lava	Pantellerite
Monte Gibile (N)	09PNL012	Ksp + cpx + aen + ox	Glassy lava	Pantellerite
Fossa del Russo	09PNL009	Ksp + cpx + aen + ol + ox	Glassy lava	Pantellerite
Cuddia Rosse	09PNL015	plg+cpx+ol	Basaltic tephra	Basalt
Cuddia Mueggen	09PNL032	Ksp + aen + cpx + ox	Glassy lava	Pantellerite
Gelfiser	09PNL026	Ksp + cpx + aen + ox	Glassy lava	Pantellerite
Gelkhamar	09PNL016	Ksp + cpx + fa + ox	Glassy lava	Pantelleritic trachyte
Cuddia del Gadir	09PNL004	Ksp + fa + aen + cpx + ox	Glassy tephra	Pantellerite
Montagne Grande	09PNL011	Ksp + cpx + fa + ox	Crystalline lava	Trachyte
Green Tuff	09PNL002	Ksp + cpx + aen + ox	Tuff	Pantellerite
Green Tuff	09PNL003	Ksp + cpx + aen + fa + ox	Glassy tuff	Pantellerite

Table 2: Sample phenocryst assemblages in analysed samples determined by optical microscopy

Ksp, alkali feldspar; plg, plagioclase feldspar; cpx, clinopyroxene; ol, olivine; fa, fayalitic olivine; aen, aenigmatite; ox, Fe-Ti oxide. Small grains of quartz are present in the groundmass in small volumes in most samples. The largest grains of quartz occur in the most evolved samples (e.g. 09PNL001 and 09PNL027, Cuddia di Mida), in agreement with White *et al.* (2005).

alignment in most samples. The groundmass texture and crystal alignment are consistent with emplacement in the form of thick, viscous lava flows.

Pantellerites occur in the form of lava domes, cones and shields, mainly around the edges of the caldera, as well as pumice or obsidian pyroclastic deposits from radial vents. Pantelleritic trachyte has an alkali feldspar content of >25%. Obsidian samples are vitrophyric with 0.25-3.0 mm phenocrysts set in a green glassy groundmass containing aligned microlites that define flow banding. Phenocrysts are made up of 10-17% alkali feldspar (frequently zoned, with $\sim 15\%$ forming glomerocrysts), 0.1-10% clinopyroxene (most occurring as <0.5 mm acicular crystals in the groundmass) and 0.1-1.0% aenigmatite (0.25-1.5 mm tabular and bladed phenocrysts) (Fig. 3). Rounded, mostly <0.1 mm Fe-Ti oxides are found in association with, and as inclusions in, alkali feldspar. The order of crystallization is likely to have been clinopyroxene, then alkali feldspar, then aenigmatite. The glass contains aligned acicular microlites of clinopyroxene and rare amphibole and quartz. Small (=0.1 mm) alkali feldspar microlites show hopper-like diffusion-limited growth forms, indicating syn-eruptive formation.

The Green Tuff is an extensive welded ignimbrite erupted at 45 ka, contemporaneous with the formation of the Cinque Denti caldera. This varies in thickness around the caldera edge and is not found within the caldera (Mahood & Hildreth, 1983). Samples were collected at Cala Cinque Denti (09PNL002), with $\sim 20\%$ alkali feldspar-dominated phenocrysts in a glassy groundmass with fiamme and collapsed vesicles, and from the base of a compacted rheomorphic flow at Balata dei Turchi (09PNL033), which comprises $\sim 25\%$ alkali feldspar-dominated phenocrysts in a glassy groundmass with dark streaks where the groundmass is more crystalline.

Major element compositions

All analysed glass samples from the silicic suite are peralkaline, with an agpaitic index greater than unity [AI = molecular ratio (Na₂O + K₂O)/Al₂O₃; Table 3]. Allof the silicic matrix glass compositions plot within the rhyolite field on a total alkalis vs silica (TAS) diagram (Fig. 4; Le Bas et al., 1986) and in the pantellerite field in the classification diagram for peralkaline rhyolites of Macdonald et al. (1974) (Fig. 4). When the phenocryst content is added back to the matrix glass composition to give a whole-rock composition some samples straddle the trachyte-rhyolite boundary, such as 09PNL016 from Gelkhamar (Fig. 4). These rocks are considered as pantelleritic trachytes. They are referred to as such throughout for consistency with prior work (Civetta et al., 1998; White et al., 2009). Table 3 illustrates representative glass compositions and Table 4 representative mineral compositions. Repeat analyses suggest that the matrix glass is largely

Sample: Location:	09PNL015 Cuddia	09PNL016 Gelkhamar	09PNL017 Cuddia	09PNL026 Gelfiser	09PNL027 Cuddia	09PNL032 Cuddia	09PNL033 Green
Lithology:	Rosse Basalt	Pantelleritic	Randazzo Pantellerite	Pantellerite	di Mida Pantellerite	Mueggen Pantellerite	Tuff (base) Pantellerite
Туре:	Matrix	trachyte Matrix	Matrix	Matrix	Matrix	Matrix	Matrix
	giass	91035	giuss	giuss	giuss	giuss	giuss
n (majors):	4	7	7	8	9	3	5
SiO ₂ (wt %)	47·57	69·41	70.28	69.46	70.92	70.95	70.59
TiO ₂	4.39	0.56	0.41	0.32	0.26	0.36	0.47
Al ₂ O ₃	13·15	10.07	8·16	7.44	7.14	7.59	8.45
FeO	14.74	7.53	8.52	8.41	8.70	8.20	8.42
MnO	0.24	0.30	0.36	0.32	0.37	0.34	0.34
MgO	4.30	0.09	0.04	0.047	0.04	0.06	0.09
CaO	9.37	0.49	0.41	0.37	0.34	0.37	0.43
Na ₂ O	3.45	5·15	5.33	6.84	6.88	6.59	6.42
K ₂ 0	1.50	4.87	4.55	4·55	4.50	4.49	4.54
P ₂ O ₅	0.99	0.03	0.02	0.01	0.01	0.02	0.02
F	0.11	0.24	0.26	0.30	0.31	0.29	0.16
CI	0.02	0.70	0.77	0.84	0.90	0.91	0.83
SO ₂	0·11	0.04	0.04	0.03	0.03	0.03	0.04
Total	99.99	99.48	99·15	99.00	100.40	100.20	100.80
AI	0.55	1.48	1.79	2.25	2.34	2·15	1.91
n (traces)	7	5	5	6	5	5	6
Ni (ppm)	27·9	0.1	0.1	0.1	0.5	0.1	0.1
Cu	78·4	0.1	1.0	0.8	0.6	1.3	1.1
Rb	18·3	n.a.	203.3	208.0	227.0	235.3	180.4
Sr	401.0	2.3	4.7	5.2	5.6	5.8	2.5
Υ	27.7	156·1	172.0	178·2	207.7	203.3	156·4
Zr	174·3	330.6	2010.1	2107·2	2425.3	2437.2	1835-3
Nb	42·0	1.2	467·1	480.2	537·3	526·1	397.8
Ba	341.2	0.0	56·4	53·2	60·1	55·0	52·0
La	27.1	86.9	220.2	232.6	265.4	259.3	199·2
Ce	58·3	261.5	429.9	450·8	502·1	491.4	392·0
Pr	7.8	44.4	49.2	51·9	58·5	56.9	45·2
Nd	33·2	201.7	172·1	181.0	204.8	198·5	158·0
Sm	7·2	47.8	32.8	34.5	39.5	37.5	30.1
Eu	2.7	5.8	4.3	4.4	5.1	4.5	4.7
Gd	6.8	40.6	29.6	30.7	35.5	33·7	26.4
Tb	1.0	6.2	4.9	5.1	6.0	5.7	4.4
Dy	5.6	36.3	31.4	32.8	38.2	36.0	28.2
Но	1.1	6.9	6.4	6.8	7.9	7.5	5.8
Er	2.7	17.7	17.7	18.6	21.6	20.7	16·0
Tm	0.4	2.8	2.6	2.7	3.2	3·1	2.3
Yb	2.3	21.8	16.9	17.6	20.4	19.6	15.1
Lu	0.3	4.5	2.4	2.5	2.9	2.9	2.2
Hf	3.9	10.1	44·1	47·2	54·4	53·7	40.1

Table 3: Selection of average matrix glass compositions

(continued)

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09PNL015	09PNL016	09PNL017	09PNL026	09PNL027	09PNL032	09PNL033
Cuddia	Gelkhamar	Cuddia	Gelfiser	Cuddia	Cuddia	Green
Rosse		Randazzo		di Mida	Mueggen	Tuff (base
Basalt	Pantelleritic	Pantellerite	Pantellerite	Pantellerite	Pantellerite	Pantellerite
	trachyte					
Matrix	Matrix	Matrix	Matrix	Matrix	Matrix	Matrix
glass	glass	glass	glass	glass	glass	glass
2.4	0.0	26.2	27.6	30.9	30.2	22.6
1.3	0.3	15·5	16·9	18.4	17·7	13·1
0.8	0.0	12.1	12.9	14.3	14.1	10.6
	09PNL015 Cuddia Rosse Basalt Matrix glass 2·4 1·3 0·8	09PNL015 09PNL016 Cuddia Gelkhamar Rosse Basalt Pantelleritic trachyte Matrix Matrix glass glass 2.4 0.0 1.3 0.3 0.8 0.0	09PNL01509PNL01609PNL017CuddiaGelkhamarCuddiaRosseRandazzoBasaltPantelleriticPantelleritetrachytetrachyteMatrixMatrixMatrixglassglassglass2·40·026·21·30·315·50·80·012·1	09PNL01509PNL01609PNL01709PNL026CuddiaGelkhamarCuddiaGelfiserRosseRandazzoRandazzoBasaltPantelleriticPantelleritetrachytetrachyteRatrixMatrixMatrixMatrixglassglassglass2.40.026.227.61.30.315.516.90.80.012.112.9	09PNL01509PNL01609PNL01709PNL02609PNL027CuddiaGelkhamarCuddiaGelfiserCuddiaRosseRandazzodi MidaBasaltPantelleriticPantelleritePantelleritetrachytetrachytetrachytetrachyteMatrixMatrixMatrixMatrixMatrixglassglassglassglassglass2.40.026.227.630.91.30.315.516.918.40.80.012.112.914.3	09PNL01509PNL01609PNL01709PNL02609PNL02709PNL032CuddiaGelkhamarCuddiaGelfiserCuddiaCuddiaRosseRandazzodi MidaMueggenBasaltPantelleriticPantelleritePantelleritePantelleriteMatrixMatrixMatrixMatrixMatrixMatrixglassglassglassglassglassglassglass2.40.026.227.630.930.21.30.315.516.918.417.70.80.012.112.914.314.1

Table 3: Continued

Major elements and volatiles determined by EMPA and trace elements by LA-ICP-MS (see text for details). The number of analyses used to calculate the averages for major elements and trace elements is given as n (majors) and n (traces) respectively. n.a., not analysed. AI, molecular ratio $(Na_2O + K_2O)/Al_2O_3$

homogeneous within each sample. The standard deviation of repeat analyses is generally much less than 5% of the average value for abundant oxides, such as SiO₂, Al₂O₃, Na₂O and K₂O, in single samples. The entire dataset is available as an Electronic Appendix available from http:// petrology.oxfordjournals.org.

Major element variation diagrams indicate the bimodality of the glass compositions, with a significant gap between 48.0 and 68.4 wt % SiO₂ (Fig. 5), similar to the whole-rock data (49–62 wt %) from previous studies (Civetta *et al.*, 1998; Ferla & Meli, 2006; White *et al.*, 2009). The most glass sample has an MgO content of 5.2 wt %, and is clearly derived from a melt that had undergone significant differentiation since leaving its mantle source region. In general, glass MgO, FeO_t and CaO decrease with increasing SiO₂, whereas Na₂O and K₂O increase. This is indicative of olivine \pm pyroxene \pm Fe–Ti oxide exerting a strong control on the liquid line of descent, in addition to plagioclase. Whole-rock data (White *et al.*, 2009) show displaced trends reflecting their crystal content.

The major element compositions of the phenocrysts show significant variability within the suite of rocks. Plagioclase feldspars in the Cuddia Rosse basalt are anorthite-rich, with compositions in the range An_{57-68} . Trachyte-hosted K-feldspars from Montagne Grande have compositions of $\sim Or_{48}$ with less than 1% anorthite. Pantellerite-hosted K-feldspars have compositions in the range Or_{32-39} . There is a transition from forsteritic olivine in the mafic rocks ($\sim Fo_{80}$; White *et al.*, 2009) to fayalitic olivine in trachytes ($\sim Fo_{28}$) and pantellerites (Fo_{2-11}). Civetta *et al.* (1998) reported a range of olivine compositions of Fo_{86-47} in the Pantelleria basalts, which spans much of the basalt to trachyte variability. Also of note is the transition from magnesium-rich augite in the mafic rocks (~En43Fs12Wo45; White et al., 2009) to iron-rich augite in the trachytes ($\sim En_{30}Fs_{27}Wo_{38}$). Clinopyroxene varies from sodic augite to sodic hedenbergite in pantellerites of low AI (e.g. matrix glass AI=166, 09PNL017, Cuddia Randazzo) to aegerine-augite in high-AI pantellerites (e.g. matrix glass AI = 2.27, 09PNL027, Cuddia di Mida). The clinopyroxene classification used follows the scheme of Morimoto et al. (1988). Aenigmatite is a very iron-rich phase, containing ~41 wt % FeO_t, as well as \sim 9 wt % TiO₂. These observations are consistent with a much more detailed study of the mineral chemistry of the lavas at Pantelleria undertaken by White et al. (2005) as well as more general studies by Civetta et al. (1998) and Avanzinelli et al. (2004). Fe-Ti oxides in the trachytes are predominantly ilmenite, with some magnetite, whereas those in the pantellerites are almost solely ilmenite (White et al., 2005, 2009).

Trace element compositions

Incompatible trace elements show progressive enrichment with SiO_2 content (Fig. 6). Chondrite-normalized REE patterns of glasses and published whole-rock data are shown in Table 3 and Fig. 7. Important features of the chondrite-normalized REE patterns are the increase in concentration from pantelleritic trachyte to pantelleritic compositions, in addition to the deepening of the Eu anomaly (Fig. 7). This is consistent with the high degrees of feldspar crystallization suggested by the major element chemistry. The REE compositions of the constituent minerals are given in Table 4. The trace element compositions



Fig. 4. Upper diagram, total alkalis vs silica (TAS) diagram (Le Bas et al. 1986). Lower diagram, classification of peralkaline rhyolites (Macdonald et al., 1974).

and REE patterns of the glasses are in good agreement with those reported previously by Civetta *et al.* (1998).

Volatile contents

F, Cl and S contents in both matrix glasses and whole-rocks show systematic variations with SiO_2 , AI and incompatible elements (Fig. 8) over the entire lava suite. F and Cl are relatively incompatible, increasing in concentration in more evolved compositions, whereas S shows more complex behaviour (Fig. 8), largely as a result of its decreasing solubility with increasing melt differentiation (Scaillet & Macdonald, 2006). Pantelleritic matrix glasses are very halogen-rich, with F contents in the range

2400–3800 ppm and Cl contents in the range 7800– 9000 ppm, consistent with previous analyses (Lowenstern, 1994; White *et al.*, 2009). Basaltic matrix glass is rich in S, with contents in the range 320–560 ppm. Pantelleritic matrix glasses are much lower in S, containing 80– 280 ppm. The Green Tuff contains less F than the other pantellerite eruptions, and samples from the upper part (09PNL002, Cala Cinque Denti) appear to be depleted in volatiles relative to those at the base (09PNL033, Balata dei Turchi).

 H_2O , CO_2 and Li were measured in feldspar-hosted melt inclusions by SIMS (Table 6 and Fig. 9). Errors are based on repeat analysis of standards at the start and end

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Sample:	09PNL015	09PNL030	09PNL016	09PNL027	09PNL016	09PNL017	09PNL032	09PNL030	09PNL016	09PNL017	09PNL032
Location:	Cuddia	Montagne	Gelkhamar	Cuddia	Gelkhamar	Cuddia	Cuddia	Montagne	Gelkhamar	Cuddia	Cuddia
	Rosse	Grande		di Mida		Randazzo	Mueggen	Grande		Randazzo	Mueggen
Lithology:	Basalt	Trachyte	Pantelleritic trachyte	Pantellerite	Pantelleritic trachyte	Pantellerite	Pantellerite	Trachyte	Pantelleritic trachyte	Pantellerite	Pantellerite
Phase:	Feldspar	Feldspar	Feldspar	Feldspar	Срх	Срх	Срх	Olivine	Olivine	Olivine	Aenigmatite
Type:	Phenocryst	Phenocryst	Phenocryst	Phenocryst	Phenocryst	Phenocryst	Phenocryst	Phenocryst	Phenocryst	Phenocryst	Phenocryst
	core	core	core	core	core	core	core	core	core	core	core
n (majors):	7	2	2	2	4	3	1	2	3	3	2
SiO ₂ (wt %)	51·77	62·96	67·38	67·52	49·22	48·39	49.30	30.95	29.60	29.34	39.77
TiO ₂	0.12	0.01	0.03	0.02	0.40	0.48	0.33	n.m.	n.m.	n.m.	8.64
Al ₂ O ₃	29.26	20.64	18.42	18·39	0.19	0.17	0.13	0.01	0.00	0.00	0.660
FeO	0.82	0.23	0.55	0.66	25·81	28·24	29.24	53·70	64·05	66·18	41·70
MnO	0.00	0.00	0.01	0.00	1.38	1.39	1.10	2·72	3.73	3.81	1.06
MgO	0.14	0.00	0.0	0.00	3.40	1.33	1.12	11·81	2.24	0.82	0.44
CaO	12·99	2.76	0.07	0.04	18.03	17.82	16·75	0.41	0.37	0.34	0.64
Na ₂ O	3.92	8.32	7.46	5.86	1.26	1.57	2.69	0.040	0.04	0.07	6.86
K ₂ O	0.22	2.72	5.48	6.31	0.01	0.00	0.00	n.m.	n.m.	n.m.	0.00
P ₂ O ₅	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
NiO	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	0.000	0.01	0.00	0.04
Total	99·24	97.65	99·41	98·46	99·71	98·38	100.68	99.62	100.04	100.57	99.92
n (traces)	3	n.a.	3	3	3	2	2	n.a.	2	n.a.	1
Ni (ppm)	0.2	n.m.	0.7	0.4	0.1	0.1	0.4	n.m.	b.d.l.	n.m.	0.1
Cu	3.8	n.m.	0.1	0.5	0.1	0.1	0.3	n.m.	0.5	n.m.	0.8
Rb	0.3	n.m.	45·6	60.7	0.0	1.0	34·1	n.m.	0.1	n.m.	0.5
Sr	765·2	n.m.	3.9	1.7	2.3	3.7	12·7	n.m.	0.4	n.m.	0.6
Y	0.5	n.m.	0.0	0.0	156-1	50·2	162·9	n.m.	46.2	n.m.	1.5
Zr	0.4	n.m.	0.1	0.3	330.6	335.1	1221.7	n.m.	0.9	n.m.	154·5
Nb	0.1	n.m.	0.0	0.1	1.2	4·1	28.6	n.m.	0.5	n.m.	236.8
Ba	85·3	n.m.	123.3	45·8	0.0	0.3	4.0	n.m.	0.3	n.m.	0.1
La	0.9	n.m.	0.5	0.0	86.9	46·1	163-4	n.m.	64·7	n.m.	1.2
Ce	1.8	n.m.	0.5	0.1	261·5	134·1	460.0	n.m.	134·3	n.m.	2.9
Pr	0.5	n.m.	0.0	0.0	44.4	22·5	76·5	n.m.	18·2	n.m.	0.4
Nd	0.6	n.m.	0.0	0.0	201.7	99·4	332·1	n.m.	74·6	n.m.	1.7
Sm	0.5	n.m.	b.d.l.	0.0	47·8	21.2	69·6	n.m.	13·9	n.m.	0.3
Eu	0.4	n.m.	0.2	0.0	5.8	2.6	7.9	n.m.	1.6	n.m.	0.0
Gd	0.1	n.m.	0.0	0.0	40.6	16.0	51·8	n.m.	12·2	n.m.	0.3
Tb	0.0	n.m.	b.d.l.	b.d.l.	6.2	2.3	7.4	n.m.	1.7	n.m.	0.1
Dy	0.0	n.m.	0.0	b.d.l.	36.3	12·7	40.8	n.m.	9·5	n.m.	0.3
Ho	0.0	n.m.	0.0	0.0	6.9	2.3	7.6	n.m.	2.0	n.m.	0.1
Er	0.0	n.m.	0.0	0.0	17.7	6.3	20.4	n.m.	5.3	n.m.	0.5
Tm	0.0	n.m.	0.0	b.d.l.	.2·8	1.1	3.6	n.m.	0.8	n.m.	0.1
Yb	b.d.l.	n.m.	0.0	0.0	21.8	10.0	31·5	n.m.	6.2	n.m.	0.2
Lu	b.d.l.	n.m.	0.0	0.0	4.5	2.2	6.9	n.m.	1.2	n.m.	0.1
Hf	0.0	n.m.	0.0	0.0	10.1	9.5	35.1	n.m.	0.0	n.m.	3.7
Та	b.d.l.	n.m.	0.0	0.0	0.0	0.5	1.6	n.m.	0.0	n.m.	17.0

Table 4: Selection of average mineral compositions

(continued)

Sample:	09PNL015	09PNL030	09PNL016	09PNL027	09PNL016	09PNL017	09PNL032	09PNL030	09PNL016	09PNL017	09PNL032
Location:	Cuddia	Montagne	Gelkhamar	Cuddia	Gelkhamar	Cuddia	Cuddia	Montagne	Gelkhamar	Cuddia	Cuddia
	Rosse	Grande		di Mida		Randazzo	Mueggen	Grande		Randazzo	Mueggen
Lithology:	Basalt	Trachyte	Pantelleritic	Pantellerite	Pantelleritic	Pantellerite	Pantellerite	Trachyte	Pantelleritic	Pantellerite	Pantellerite
			trachyte		trachyte				trachyte		
Phase:	Feldspar	Feldspar	Feldspar	Feldspar	Срх	Срх	Срх	Olivine	Olivine	Olivine	Aenigmatite
Type:	Phenocryst	Phenocryst	Phenocryst	Phenocryst	Phenocryst	Phenocryst	Phenocryst	Phenocryst	Phenocryst	Phenocryst	Phenocryst
	core	core	core	core	core	core	core	core	core	core	core
n (majors):	7	2	2	2	4	3	1	2	3	3	2
							4.0				
Pb	b.d.l.	n.m.	0.6	0.1	0.3	0.5	1.2	n.m.	0.0	n.m.	0.1
U	0.0	n.m.	b.d.l.	b.d.l.	0.0	0.1	0.7	n.m.	0.1	n.m.	0.0

Table 4: Continued

Major elements by EMPA and trace elements by LA-ICP-MS (see text for details). The number of analyses used to calculate the averages for major elements and trace elements is given as n (majors) and n (traces) respectively. b.d.l., below detection limit; n.a., not analysed; n.m.,...

of every session and are, in general, small in comparison with the abundances analysed. Isobars are calculated using the chemical solution model for H_2O and CO_2 . Volatilecalc (Newman & Lowenstern, 2002). H₂O ranges from 0 to 4.9 wt %, CO₂ from 0 to 150 ppm and Li from 30 to 80 ppm. The range in H_2O concentrations measured in the melt inclusions results from variability in their last equilibration pressure before sealing, which in some cases (particularly for the so-called 'hourglass inclusions'; Humphreys et al., 2008) takes place during rapid degassing-induced crystallization and crystal rim growth at low pressure. Some inclusions may have lost H⁺ through diffusive re-equilibration through the mineral host (Danushevsky et al., 2002). A 4.9 wt % H₂O content is consistent with Fourier transform IR measurements of 4.5 wt % presented by Gioncada & Landi (2010), as well as an ~ 4 wt % estimate from thermodynamic modelling and phase equilibrium experiments (White et al., 2009; Di Carlo et al., 2010).

Temporal variations in trace element and volatile concentrations

The trace element compositions of the erupted products show variations with time throughout the 45 kyr cycle (Fig. 10). Green Tuff samples (45 ka) have low La and F of ~200 ppm and 0·15 wt % respectively. Samples from Gelkhamar (23·5 ka) exhibit slightly higher values. Those from subsequent eruptions such as Gelfiser (17·5 ka), Cuddia Mueggen (14 ka) and Cuddia di Mida (9 ka) display a smooth increase in La to ~260 ppm, and a more jagged increase in F to ~0·35 wt %. The most recent pantelleritic eruption at Cuddia Randazzo (5·5 ka) has lower La and F contents of 220 ppm and 0·27 wt % respectively.

DISCUSSION

Melting models and the mantle source

Basalt whole-rock major element and REE concentrations (Civetta et al., 1998; White et al., 2009) were used to estimate the depth and degree of melting beneath Pantelleria using the program INVMEL (McKenzie & O'Nions, 1991), which inverts the REE data to find a best-fit relationship between melt fraction and depth, utilizing the partitioning behaviour of the full suite of REE in mantle minerals. Reliable inversions require a primitive basalt with a bulk-rock MgO content of >6 wt %. A primitive mantle source was used for the modelling of the REE concentrations in the Pantelleria basalts that are too high to be recreated by melting a depleted mantle source composition. A lithospheric thickness of 60 km from geophysical studies was used in the favoured inversion (Della Vedova et al., 1987). Melting up to a maximum melt fraction of $\sim 1.7\%$ occurs across a depth range of 60–100 km (Fig. 11). Misfit is minimized when the spinel-garnet transition zone is placed in the depth range 70-90 km. The r.m.s. misfit of the REE fit is 0.083. Melting takes place predominantly in the spinel-garnet transition zone, with the presence of garnet leading to the fractionation of the HREE. This has been previously suggested by Civetta et al. (1998) by comparing the middle REE (MREE)/HREE ratios of the Pantellaria basalts with those of alkali basalts from Hawaii, but is demonstrated quantitatively here.

Inversions performed with different lithospheric thicknesses have larger errors in the degree of misfit. A thickness of 80 km, which is consistent with $\beta = 1.47$ stretching of a 120 km thick lithosphere, as implied from crustal seismic profiles (Civile *et al.*, 2008), combined with a deeper spinel transition zone at 80–100 km, predicts ~1.9% melting



Fig. 5. Harker variation diagrams of matrix glass compositions determined by electron microscope. *Hawaiite and trachyte whole-rock data from White *et al.* (2009), shown for comparison with the glass data. Error bars are as shown.



Fig. 6. Variation of La and Ce contents with SiO_2 for matrix glasses and whole-rocks. *Hawaiite and trachyte whole-rock data from White *et al.* (2009), plotted for comparison with the glass data. Error bars are as shown.



Fig. 7. Chondrite-normalized REE patterns for matrix glasses. The pronounced negative Eu anomaly is indicative of significant feldspar crystallization from the melt. *Trachyte whole-rock data from White *et al.* (2009), shown for comparison with the glass data.

across a depth range of 80–100 km. The r.m.s. misfit of the REE fit is 0.913, in comparison with 0.083 for a 60 km thick lithosphere. However, the similarity of melt fraction estimates from the different inversions indicates robustness in the estimate of $\sim 1.7\%$ melting in the presence of garnet.

Using crude mass balance, it is suggested that the Pantelleria basalts could be generated by $\sim 35\%$ fractional crystallization of a primary melt assuming that the crystallizing assemblage is composed of $\sim 45\%$ forsteritic olivine, $\sim 35\%$ diopside and $\sim 20\%$ anorthite. The primary melt composition (Mg-number = 69) used was determined using the INVMEL melting model. The end-point melt composition used was the Cuddia Rosse matrix glass (09PNL015; Mg-number = 34). The results of the mass balance are likely to reflect the respective crystallization from the primary melt of ultramafic cumulates at depth and mafic cumulates at shallower levels (Maclennan *et al.*, 2001).

Pantelleria basalt values show a high degree of similarity to those from Linosa, a subaerial basaltic volcanic edifice in the Sicily Channel rift zone: Ba/Nb, La/Nb and Ta/Yb of 6.87, 0.74 and 0.83 respectively (Lustrino & Wilson, 2007). They are also similar to those of North African basalts from Algeria and Tunisia (Lustrino & Wilson, 2007). This suggests a close affinity of the parental melts and those supplying the North African volcanic fields. This is consistent with isotopic data presented elsewhere: Pantelleria mafic rocks have ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ lower than Bulk Earth and ¹⁴⁴Nd/¹⁴³Nd greater than Bulk Earth, plotting in the depleted quadrant on a Nd-Sr isotope diagram (Civetta et al., 1998; Francalanci et al., 2004). Esperança & Crisci (1995) have suggested that the isotopic signature may result from mixing of asthenospheric melts with melts from variably enriched lithosphere. Civetta et al. (1998) identified depleted and HIMU-like end members in the Pantelleria mantle source. The isotopic composition of the Pantelleria magmas could thus potentially be explained by the contribution of enriched material (of HIMU-like signature) during melting of a heterogeneous mantle source (Ito & Mahoney, 2005). Low fraction melting at depth, as indicated by the REE inversion, could result in preferential melting of the enriched mantle component, which is more fusible than the ambient depleted mantle.

Characterization of the liquid line of descent

The crystallizing mineral assemblages required to describe the observed liquid line of descent were determined by PCA (e.g. Maclennan *et al.*, 2001). Further discussion of the implementation used here is provided in the supplementary data available at http://petrology.oxfordjournals. org. Major element data for the glasses analysed in this study were used together with whole-rock data (Civetta *et al.*, 1998; White *et al.*, 2009) to calculate the proportion of phases required to move one standard deviation along the principal component axis of each of the three compositional arrays used. The arrays were of mafic, trachytic and pantelleritic composition respectively. Ideally only melt compositions should be used. However, with only one basaltic sample and no glassy trachyte samples



Fig. 8. Variation of F, Cl and S with (a) SiO_{25} (b) Agpaitic Index [AI = (mol Na₂O + mol K₂O)/mol Al₂O₃)] and (c) La for matrix glasses and melt inclusions. *Hawaiite and trachyte whole-rock data from White *et al.* (2009), shown for comparison with the glass data. Error bars are as shown.

available, whole-rock data were used in the mafic and trachytic arrays to construct a complete liquid line of descent. The first principal component axis corresponds to the liquid line of descent. Crystallizing phase compositions were analysed by electron microprobe (this study, Table 4; White *et al.*, 2009). PCA fitting of the data would normally use SiO₂, Al₂O₃, FeO, MgO and CaO data for the liquid line of descent calculation. However, in this case the high alkali and low ferromagnesian content of the pantellerites necessitated the additional use of Na₂O and TiO₂ for the silicic magmas.

Results of the PCA fits suggest that the mafic data array can be explained by the removal of the assemblage 35% plagioclase feldspar (An₇₂), 48% clinopyroxene (En₄₃Fs₁₃Wo₄₄), 5% olivine (Fo₈₀) and 12% magnetite. The trachytic array can be explained by the removal of 64% alkali feldspar (Or₄₈), 15% clinopyroxene (En₃₁ Fs₂₇Wo₄₂), 14% olivine (Fo₂₈) and 7% ilmenite. The pantelleritic array is explained by the removal of 89% alkali feldspar (Or₃₈), 5% clinopyroxene (En₄Fs₄₅Wo₃₅Ae₁₆), 6% aenigmatite and 0.2% ilmenite. The r.m.s. errors for each PCA fit are 0.15, 0.14 and 0.15 respectively.



Fig. 8. Continued.

Crystallization of basaltic magma beneath Pantelleria is dominated by clinopyroxene removal. This is in conflict with the phase abundances observed in the basalt lavas (fsp>cpx>ol), but is consistent with settling of dense phases en route to the surface. In particular, although 12% magnetite is required to reproduce the liquids, magnetite is not this abundant in the rocks and is assumed to have settled out of the liquid prior to eruption. Civetta *et al.* (1998) modelled basalt to trachyte fractionation with feldspar dominant over clinopyroxene in the assemblage, which is consistent with the change in the dominant crystallizing phase from cpx in the basaltic to feldspar in the trachytic arrays.



Fig. 9. Variation of CO_2 and Li with H_2O in melt inclusions and matrix glasses. Isobars in the H_2O vs CO_2 diagram were calculated using Volatilecalc (Newman & Lowenstern, 2002).

Feldspar removal dominates the crystallization of the silicic liquids. The error in the PCA fit to the pantelleritic suite is minimized when feldspar, clinopyroxene, aenigmatite and ilmenite are included in the crystallizing assemblage. This is consistent with the higher resolution study on the phenocrysts by White et al. (2005), which indicates that olivine is stable only at low AI, being replaced by aenigmatite at higher AI. If olivine is also included as a crystallizing phase, the error increases to only 0.18. This is consistent with olivine playing a role in controlling the liquid evolution in low-AI pantellerites. Explanation of the major element trends by alkali feldspar, clinopyroxene and aenigmatite crystallization is in agreement with recent phase equilibrium experiments. These suggest that at the P-T conditions relevant for most pantellerites, these are the only stable phases; minor groundmass quartz and amphibole grow syn-eruptively (Di Carlo et al., 2010).

The results presented here differ slightly from those published previously, especially regarding the importance of clinopyroxene crystallization in mafic liquids and olivine in trachytic liquids (White *et al.*, 2009). PCA fits suggest a greater role for both, with clinopyroxene making up 49% of the mafic crystallizing assemblage rather than 37% (White *et al.*, 2009) and olivine 14% of the trachytic assemblage compared with 2–4% (White *et al.*, 2009). However,



Fig. 10. Variation of F and La in glasses through time. Only silicic glass data are shown. Ages are from Mahood & Hildreth (1986) and Civetta *et al.* (1988). Errors on the K/Ar dating are significant (up to ± 10 ka) leading to a degree of ambiguity in eruption order. (Cross-cutting relationships cannot be used for dating in most instances, because eruptions are spatially distinct) The most recent Cuddia Randazzo eruption has been accurately dated using ¹⁴C.

these discrepancies may arise from the different techniques and samples used [i.e. least-squares modelling by White *et al.* (2009) and PCA fitting in this study] rather than petrological processes. It is also important to recognize that many of the evolved compositions at Pantelleria will have evolved along slightly different liquid lines of descent, and as such the precise crystallizing assemblages will vary.

The Rayleigh fractionation equation was used to determine if the trace element data support differentiation by fractional crystallization for the genesis of the lava suite erupted on Pantelleria:

$$\frac{C_{\rm melt}^i}{C_{\rm melt}^0} = F^{(D-1)} \tag{1}$$

where C^i is the concentration of a given element i in the melt, C^0 the initial concentration of the given element in the melt, F the melt fraction remaining and D the bulk solid/liquid partition coefficient of the given element. Mineral/melt partition coefficients for pantelleritic trachyte and pantellerite compositions were determined from the LA-ICP-MS data (Table 5). Where partition



Fig. 11. Results of REE inversion modelling. (a) Observed chondrite-normalized REE values and inversion results for two lithospheric thickness values. The best-fit solution (r.m.s. error = 0.083) used a 60 km lithospheric thickness from Della Vedova *et al.* (1987). The slight concave-upwards shape of the observed data, which is not replicated in the inversions, may be explained by the presence of amphibole in the melting region. The alternative solution (r.m.s. error = 0.913) shown uses a thicker lithosphere of 80 km. (b) Melt fraction vs depth relationship for the same two solutions as in (a). The lithosphere base, garnet-in and spinel-out horizons are drawn for the best-fit solution. Melting is modelled to start at ~100 km and to have reached ~1.7% at the base of the lithosphere.

coefficients were close to zero, a value of 0.001 was used in the modelling calculations to represent near perfectly incompatible behaviour. Partition coefficients were calculated using average crystal compositions, partly because the large spot size of the laser has an averaging effect across a grain, and average glass compositions located near the mineral analysis sites. Bulk partition coefficients for each element were calculated by weighting each of the mineral/melt partition coefficients using the relevant crystallizing assemblage calculated from PCA. The most incompatible elements (with D < 0.2) are the LREE La and Ce and high field strength elements (HFSE) Zr and Nb, which are used to calculate the degree of fractional crystallization relating single magma compositions (i.e. the

	Alkali bas	alt			Trachyte Pantellerite						
	D _{fsp/melt}	$D_{ m cpx/melt}^*$	$D_{ m ol/melt}^*$	D _{oxide/melt} *	D _{fsp/melt} †	D _{cpx/melt} †	D _{ol/melt} †	D _{oxide/melt} †	D _{fsp/melt}	D _{cpx/melt}	D _{aen/melt}
Ni											
Cu	0.05								0·29	0.58	1.48
Rb	0.02	0.13	0.15	0.15	0.45	0.07	0.08	0.01	0·27	0.02	0.00
Sr	1.91	0.29	0·11	0.11	3·18	0.57	0.02	0.74	0.43	1.09	0·15
Y	0.01								0.00	0.67	0.01
Zr	0.00	0.42	0.29	0.29	0·13	0.69	0.07	0.25	0.00	0.28	0.06
Nb	0.00				0.16				0.00	0.02	0.42
Ba	0·25				5.35				1.01	0.02	0.01
La	0.03	0·27	0.00	0.00	0·16	0.44	0.25	0.47	0.00	0.47	0.01
Ce	0.03	0.39	0.00	0.00	0.12	0.48	0.10	0.07	0.00	0·71	0.01
Pr	0.02	0.80	0.00	0.00	0·11				0.00	1.00	0.01
Nd	0.02	0.74	0.00	0.00	0·11	2.35			0.00	1.26	0.01
Sm	0.02	1.04	0.00	0.00	1.94	2.22	0.10	0.08	0.00	1.39	0.01
Eu	0·14	0.46	0.00	0.00	2.03	1.68	0.16	1.30	0.02	1.41	0.01
Gd	0.01	0.48	0.00	0.00					0.00	1.22	0.01
Tb	0.03	0.58	0.01	0.01	0.04	2.36	0.31	0.90	0.00	1.04	0.01
Dy	0·01	0.96	0.01	0·01	0·11	2.68	0.10		0.00	0.94	0.01
Ho	0.00	1.15	0.01	0.01					0.00	0.85	0.01
Er	0.00	0.55			0·11	2·72			0.00	0·78	0.02
Tm	0.01	0.45	0.10	0.10					0.00	0.89	0.02
Yb	0.00	0.56	0.17	0.17	0.12	2·72	0.35	0.05	0.00	1.17	0.03
Lu	0.00	0.45	0.08	0.08	0.12	3·21	0.44	0.08	0.00	1.72	0.04
Hf	0.00	0.56	0.38	0.38	0.12	0.60	0.02	1.38	0.00	0·36	0.07
Та	0.00	0.10	1.70	1.70	0.03	0.22	0.08	2.38	0.00	0.02	0·51
Pb	0.00								0.01	0.04	0.01
U	0.00	0.03	0.01	0.01	0.03	0.10	0.14	0.29	0.00	0.02	0.01

Table 5: Partition coefficients used in trace element calculations

*Collated from Shimizu (1980), Villemant *et al.* (1981), Fujimaki *et al.* (1984), Zack & Brumm (1998) and Wood & Trigila (2001).

[†]Collated from Nagasawa (1973), Lemarchand *et al.* (1987), Mahood & Stimac (1990) and Villemant *et al.* (1998). Coefficients derived from the present study shown in italics.

degree of magmatic differentiation). The variations of incompatible trace elements suggest that the mafic and silicic lithologies can be explained well by fractional crystallization processes (Fig. 6). We calculate that the trachyte bulk composition of White *et al.* (2009) could be generated by 76% fractional crystallization of the alkali basalt composition. Pantelleritic trachyte can be generated from this trachyte by 77% fractional crystallization. An average pantellerite composition is generated by a further 20% fractional crystallization of the pantelleritic trachyte. The total amount of fractional crystallization required to generate pantellerite from alkali basalt is thus ~96% [similar to the ~95% suggested by White *et al.* (2009) and Civetta *et al.* (1998) based on whole-rock data].

Pre-eruptive magma storage conditions

The pre-eruptive melt temperature of the Cuddia Rosse basalt (09PNL015) was estimated using the clinopyroxene-liquid thermobarometer of Putirka (2008). Clinopyroxene-melt equilibrium was last achieved at a temperature of 1091 \pm 45°C and a pressure of 17 \pm 2 kbar. The observed $K_{\rm D}$ (Fe-Mg)^{cpx-melt} value of 0.264 lies close to the 0.27 value indicative of equilibrium (Putirka, 2008). This pressure range brackets the 2 kbar estimate from volatile equilibria (Gioncada & Landi, 2010). These values are consistent with those calculated from the plagioclaseliquid thermometer of Putirka (2005), which gives a temperature of 1080 \pm 36°C, assuming a 2 kbar pressure of equilibration and an H₂O content of 1.5 wt % (Gioncada

Point	Туре	H ₂ O	Li (ppm)	C0 ₂
		(wt %)		(ppm)
Sample 09PNL006, F	Punta Tracino			
PAN006R4H	Melt inclusion	2.22	37	50
PAN006R4I	Melt inclusion	2.30	30	135
Sample 09PNL007, N	Nonte Gibile (S)			
PAN007R4J	Melt inclusion	2.67	60	59
PAN007R4K	Melt inclusion	3·22	63	-30
PAN007R4L	Melt inclusion	0.78	59	-17
PAN007R4M	Melt inclusion	0.82	60	-31
PAN007R4N	Melt inclusion	1.25	63	0
PAN007R40	Melt inclusion	0.90	69	-7
PAN007R4P	Melt inclusion	0·18	73	245
PAN007R4Q	Melt inclusion	1.59	66	65
PAN007R4U	Melt inclusion	4·01	33	-11
PAN007R4W	Melt inclusion	4.88	28	21
PAN007R4X	Melt inclusion	0.26	70	56
PAN007R4Y	Melt inclusion	0.36	72	-31
PAN007R4Z	Melt inclusion	4·07	43	26
PAN007_R4_AA	Melt inclusion	0.54	78	-11
PAN007_R4_AC	Melt inclusion	0.44	59	-25
PAN007_R4_AB	Matrix glass	0.02	50	-29
Sample 09PNL012, N	Nonte Gibile (N)			
PAN012_R3_C	Melt inclusion	2.68	59	145
PAN012_R3_D	Melt inclusion	2.33	59	100
PAN012R4E	Melt inclusion	0·17	64	36
PAN012R4F	Melt inclusion	0.22	63	7
PAN012R4G	Melt inclusion	0.26	65	13
PAN012R4R	Melt inclusion	1.72	67	50
PAN012R4T	Melt inclusion	0.12	64	29
PAN012_R3_B	Matrix glass	3·18	60	146
Sample 09PNL032, C	Cuddia Mueggen			
PAN032_R4_B	Melt inclusion	0.53	71	35
PAN032R0E	Melt inclusion	0.14	60	-9
PAN032R0A	Matrix glass	0.14	60	-15
PAN032_R4_C	Matrix glass	0·16	62	-17
PAN032R0D	Matrix glass	0·15	62	-3
PAN032R0F	Matrix glass	0·15	60	22

& Landi, 2010). The observed $K_{\rm D}$ (Ab–An) of 0.35 is, however, higher than the expected equilibrium value of 0.1 ±0.11 (Putirka, 2008). Temperatures are similar to the 1079–940°C range presented by Civetta *et al.* (1988) for the mafic suite at Pantelleria.

The pre-eruptive melt temperature for the pantellerites was calculated using the alkali feldspar-liquid thermometer of Putirka (2008), assuming a 15 kbar depth of equilibration (see below) and an H₂O content of 4 wt % based on the SIMS data. Alkali feldspar from the most evolved eruption (Cuddia di Mida, 09PNL027), was last in equilibrium with the melt at $802 \pm 23^{\circ}$ C. Alkali feldspar from the Gelkhamar pantelleritic trachyte (09PNL016) equilibrated at $869 \pm 23^{\circ}$ C, a higher temperature than in the more evolved melts. The $K_{\rm D}$ (Ab–An) of 0.27 is within the 0.25 ± 0.05 bounds indicative of equilibrium (Putirka, 2008). The temperatures presented here are broadly consistent with the 756-888°C range for pantellerites calculated by White et al. (2009) using the QUILF system of Andersen et al. (1993). The temperature of 869°C for Gelkhamar is, however, significantly higher than the \sim 750°C estimated by White *et al.* (2005) with various methods. The 745°C estimate calculated using the cpx-melt thermometer of Putirka et al. (2003) cannot be reproduced with the Gelkamar data presented here because the $K_{\rm D}$ (Fe–Mg)^{cpx–melt} of 0.09 calculated using Putirka (2008) indicates disequilibrium. A lower temperature of $730 \pm 10^{\circ}$ C for the pantelleritic reservoir associated with the Cuddia di Mida cone also was estimated by Di Carlo et al. (2010) based on phase equilibria. Discrepancies therefore exist between temperature estimates obtained by different methods. Thermobarometric calculations are highly sensitive to changes in the composition of the melt and crystals, pressure and water content. Mineral-melt thermometry results will also differ depending on whether a whole-rock or glass analysis is used for the melt. The low temperature ($\leq 800^{\circ}$ C) at which pantellerite evolution occurs is, however, without doubt. The alkali feldsparmelt temperatures are, however, consistent with the almost complete lack of amphibole, which, if present, occurs only as a groundmass phase crystallizing below 700°C (Di Carlo *et al.*, 2010).

The H₂O-CO₂ content of pantelleritic feldspar-hosted melt inclusions can also be used to estimate the pressure of entrapment (Newman & Lowenstern, 2002). A maximum saturation pressure of 1.5 kbar is calculated using the maximum H_2O and corresponding CO_2 values $(4.9 \text{ wt }\% \text{ H}_2\text{O} \text{ and } 52 \text{ ppm } \text{CO}_2)$ and a temperature of 800°C (Fig. 9; Newman & Lowenstern, 2002). The maximum saturation pressure recorded by feldspar-hosted melt inclusions is consistent with the observations that aenigmatite, a major phase in pantellerites, is on the liquidus only at pressures >1 kbar (Di Carlo et al. (2010). Our estimated pressures are higher than the 1kbar estimated by Gioncada & Landi (2010), based on H₂O saturation pressures alone. When converted to a depth, this places a maximum depth for crystallization and melt entrapment at 5.5 km assuming a crustal density of 2700 kg m⁻³. This is in broad alignment with InSAR data showing magma chamber deflation, which may be modelled using a point source 4.8 km below the summit of Montagne Grande (Mattia et al., 2007).

In summary, the alkali basalt erupted to the NW of Pantelleria is likely to have been stored at $\sim 1085^{\circ}$ C and ~ 2 kbar prior to eruption. Assuming an ~ 15 kbar pressure of storage on the basis of their H₂O and CO₂ contents, silicic magmas erupted in the SE show a decrease in temperature from 870° C to 800° C with increasing SiO₂ content and peralkalinity. This is consistent with progressive fractionation and cooling within a shallow magma chamber, centred at ~ 5 km depth, but probably having significant vertical extent.

Behaviour of Li at Pantelleria

It has been observed in various H₂O-rich volcanic systems that Li behaves as a volatile element during magma storage in the shallow crust. Experiments have suggested that Li might diffuse into growing bubbles at least as rapidly as water (Koga et al., 2008). Li exhibits complex behaviour in melts at low pressures, as it can partition both into plagioclase (with a partition coefficient of 0.2-0.3; Bindeman & Davies, 2000; Coogan, 2011) and into a water-rich vapour. Experimental studies of SiO2-rich magmas show that at pressures of 4 kbar and 800–900°C, Li and other alkalis will partition preferentially into an aqueous fluid over the melt (with $D_{\rm Li}^{\rm fluid/melt}$ of ~2–13; Kent et al., 2007). The presence of significant chloride in the system further promotes Li partitioning into the fluid phase (Webster et al., 1989). The Li increase that we observe in the melt inclusions (Fig. 9) is not consistent with fractionation only: REE increases in the pantelleritic melts are not higher than around 20% (Fig. 7), whereas the Li increase across the range of pantelleritic melt inclusions amounts to almost 180% (Fig. 9). Similar enrichments in Li have been observed in H2O-rich melt inclusions at Mount St Helens (Berlo et al., 2004) and have been attributed to shallow-level accumulation of vapour from deeper degassing magma and rapid diffusive equilibration of the melt inclusions. Fluxing by a deep-derived vapour carrying Li and more CO_2 than is in equilibrium with the melt at shallow levels is likely to produce enrichment in CO₂ and depletion in H_2O , similar to what is observed (Fig. 9). It is well known, however, from experimental studies in the NaCl-H₂O system involving coexisting low-salinity vapour and high-salinity brine over the temperature and pressure range characteristic of high-SiO₂ magmas that Li partitions preferentially into the low-Cl vapour. It is likely that the Pantelleria magma chamber contains an immiscible high-NaCl fluid, as proposed by Lowenstern (1994). The Cl contents of the melt inclusions suggest equilibration in the 0.5-1 kbar range, which is consistent with our results, and this pressure range coincides with the region in which one might expect to find both a hydrosaline melt and a low-density (low-salinity) vapour in equilibrium with silicate melt (Lowenstern, 1994). At higher pressures, represented by our melt inclusions with >3 wt % H₂O (equilibrated at pressures >1 kbar), the

immiscible phase field is not present, and only a single supercritical fluid coexists with melt (Lowenstern, 1994). We believe that these phase relations explain two features of our data: why the Cl contents that we have measured in melt inclusions are variable and why we see an apparent Li depletion at high H₂O contents. From Fig. 8, the Cl contents of the melt inclusions range from 0.6 to >1 wt %: the high-Cl melt inclusions are buffered by an immiscible hydrosaline melt and the low-Cl melt inclusions have only a single supercritical fluid in equilibrium with the silicate melt. These ranges in Cl content are exactly consistent with the results of Lowenstern (1994). The melt inclusions with the highest H₂O contents are those that show an apparent Li depletion relative to the H₂O-poor inclusions. We propose that these inclusions have 'locked away' Li in a separate Cl-rich supercritical fluid phase. Upon unmixing of the fluid at lower pressures. Li redistributes itself between silicate melt and low-density vapour, resulting in higher silicate melt Li contents. Although we cannot use these limited Li results to model fluid immiscibility and degassing at Pantelleria, they clearly demonstrate that this system has great potential for future studies of Li behaviour and partitioning.

Magma viscosity and implications for differentiation and stratification

The viscosity of a magma is a primary control on its eruption style, but it also determines the timescale for crystal settling in magma storage reservoirs and hence timescales for magma differentiation and chamber stratification. Viscosity is strongly influenced by melt volatile content and, in the crust, by the bulk crystal content. The (crystal-free) viscosity of each sample was calculated using the empirical scheme of Giordano et al. (2008). Calculations take account of the major element composition, H₂O and F content, and magma temperature. Cl is not included in the viscosity calculations. Major element and fluorine contents are obtained by EMPA. Water content is assumed to be 15 wt % in basaltic rocks, based on analyses by Gioncada & Landi (2010), and in the range 2.5-4.9 wt % in silicic rocks (this study). It is likely that, on average, the less evolved trachytic melts will have lower H₂O contents than the pantellerites. Magma temperatures are those obtained from thermometry calculations (see above). The viscosity of the Cuddia Rosse basaltic melt is 130 Pa s at 1090°C and 1.5 wt % H₂O, which is similar to MORB. At a temperature of 913°C the trachyte melt viscosity ranges from 10^3 to 10^4 Pa s at H₂O concentrations of 2.5–4.9 wt %. At 800°C the Cuddia di Mida pantellerite (09PNL027) melt viscosity lies in the range 5×10^3 to 5×10^4 Pa s for the same range of H₂O. Despite a silica content of \sim 70 wt %, the volatile-rich pantellerites therefore have low pre-eruptive viscosities. The viscosity of volatile-poor pantellerite $(10^4 - 10^5 \text{ Pa s})$ is consistent with that expected for a range of silicic magmas at emplacement or pre-eruption $(10^4-10^5 \text{ Pa s}; \text{ Scaillet et al.}, 1998)$. However, the calculated viscosity of 09PNL027 increases by two orders of magnitude if a temperature of 700°C is used for this magma as suggested by Di Carlo et al. (2010). The viscosity of pantellerites is very highly dependent on temperature, which has implications for eruption dynamics. The confidence of the viscosity estimates is, however, highly dependent on the reliability of the temperature estimates, which are subject to a degree of uncertainty.

High crystal contents can increase magma viscosity significantly (e.g. Lejeune & Richet, 1995); however, little change occurs up to $\sim 40\%$ crystal volume, above which there is a rapid increase in viscosity. All of the pantellerite samples studied here have <20 vol. % phenocrysts. However, some lava samples show evidence of extensive microlite crystallization, which might have occurred in response to H₂O degassing during decompression, as indicated by their very high aspect ratio (Hammer & Rutherford, 2002). This results in a rapid increase in viscosity and yield strength syn-eruption. For example, lava forming the Cuddia Mueggen lava shield (Fig. 2) has minimal groundmass crystallization and <20% phenocrysts, whereas the lava that forms the Monti Gibele domes (Fig. 2) has a highly crystalline groundmass in addition to $\sim 20\%$ phenocrysts.

We have shown, based on both major and trace elements, that silicic melts on Pantelleria are likely to have formed by extensive fractional crystallization of parental basaltic magmas. No melt of intermediate composition (49–62 wt %) has been erupted, producing a Daly Gap between basaltic and silicic suites. Rocks of intermediate composition (i.e. mugearites and benmoreites) are found only as enclaves hosted in the silicic lavas (Civetta et al., 1998; Avanzinelli et al., 2004; Ferla & Meli, 2006). Ferla & Meli (2006) described linear major element trends in enclave compositions that can be explained by mixing of hawaiitic and trachytic melts and not by fractional crystallization processes. Their mixing hypothesis is further supported by evidence that enclave trace element compositions cannot be reproduced by fractional crystallization of a basaltic melt. The presence of mixing and melt mingling textures indicates that mafic and silicic compositions must be present in the same magma reservoir (e.g. Ferla & Meli, 2006), with mixing occurring only at the interface between them (Fig. 12). The low viscosity of peralkaline magmas will allow rapid differentiation to take place through crystal settling in the magma chamber, which might go some way towards explaining the origin of the Daly Gap at Pantelleria, Principal component analysis indicates that large amounts of magnetite and significant olivine crystallize from the Pantelleria basalts. These phases account for 12% and 5% of the crystallizing assemblage respectively. Removal of these low-silica phases

will rapidly drive the remaining melt to a higher silica content. Stokes' settling velocities have been calculated using mineral densities from Deer et al. (1992) at the magmatic conditions calculated above for Pantellerian alkali basalts. This shows that 1mm grains of plagioclase (An_{80}) , augite, olivine (Fo_{80}) and magnetite have settling velocities of 10, 190, 230 and $650 \,\mathrm{m \, a^{-1}}$ respectively. Dense phases such as olivine, clinopyroxene and particularly magnetite thus settle rapidly relative to repose intervals between eruptions and are probably removed from the system after crystallization, and in preference to plagioclase. Rapid crystal fractionation involving magnetite and olivine removal from alkali basalt and hawaiite could explain the presence of a Daly Gap whereby only small volumes of intermediate composition magma are present at any given time. Efficient crystal settling may also aid the generation of pantellerites from trachytes: 1 mm diameter magnetite and clinopyroxene grains have settling velocities an order of magnitude higher in a F-bearing peralkaline silicic melt than in equivalent F-absent per- and metaluminous melts (c. 80 m a^{-1} for a melt containing 4.5 wt % H₂O, 1 wt % F at 800°C; Baker & Vaillancourt, 1995).

The density structure of the magma chamber may also play a role in the generation of a Daly Gap. The magma chamber under the SE of Pantelleria is likely to be highly stratified on the basis of composition and exsolved volatile content. Based on the major element composition of the pantelleritic glasses and assuming melt H₂O concentrations of 4.9 wt %, the pantelleritic melts are of low density, \sim 2380 kg m⁻³. H₂O is included as an oxide (Ochs & Lange, 1999) and the effects of thermal expansion are ignored because they are insignificant in the situation being investigated (Lange, 1997). Using the whole-rock data of White et al. (2009) and assuming a lower water content of 4 wt % on the basis of their being less evolved, trachytic melts have a slightly higher density than the pantellerites ($\sim 2390 \text{ kg m}^{-3}$), largely owing to their higher crystal content. It is possible that an upward-migrating vapour phase may further reduce the density of the upper layers of a volatile-rich magma reservoir, further stabilizing the density stratification (see below). Pantelleria alkali basalt melts, assuming a water content of 1.5 wt % (Gioncada & Landi, 2010), are significantly denser at \sim 2670 kg m⁻³. No mafic compositions have been erupted in SE Pantelleria in the past 45 kyr and possibly longer. This can be explained by the presence of a magma chamber under the area broadly described by the Cinque Denti caldera, which acts a density filter, preventing high-density mafic melts from reaching the surface as suggested by Mahood (1984) and White et al. (2009). The magma chamber would therefore be expected to exhibit compositional stratification with mafic material at the base, overlain by trachyte and capped by pantellerite (Fig. 12). This is



Fig. 12. Summary schematic illustration of the broad structure of the Pantelleria magmatic plumbing system. Key features: (1) magma storage region, with dimensions comparable with the nested calderas, located at 5.5 km depth under the SE of the island; (2) high degrees of stratification within the magma storage region with low-density pantellerite and trachyte magmas overlying mafic rocks; (3) rapid crystal settling and volatile ascent in the magma chamber as a result of low viscosity, which play crucial roles in magmatic differentiation and volatile transport respectively; (4) interface between hawaiite and trachyte melts, at which mixing can occur prior to eruption (e.g. Ferla & Meli, 2006); (5) absence of a large magma storage region in the NW of the island where mafic compositions are erupted from *c*. 7.5 km depth; (6) ultimate derivation of mafic and silicic suites of magmas from the same source.

consistent with temporal variations in the geochemistry of the erupted products through the last volcanic cycle.

The Green Tuff eruption at 45 ka was the most recent Plinian eruption of Pantelleria with an erupted volume of $\sim 7 \text{ km}^3$ dense rock equivalent (DRE) (Wolff & Wright, 1981); this resulted in synchronous collapse of the Cinque Denti caldera (Orsi & Sheridan, 1984; Mahood & Hildreth, 1986). Green Tuff samples (09PNL002 and 09PNL033) were both collected from glassy material towards the base of the Green Tuff and have highly evolved compositions (e.g. $SiO_2 > 70$ wt %), and high incompatible trace elements and halogens (e.g. La ~200 ppm and Cl up to ~9000 ppm). Civetta *et al.* (1998) and White *et al.* (2009) reported that the top of the Green Tuff has a

trachytic composition, suggesting that relatively more primitive material was tapped as the Green Tuff eruption progressed. This can be explained by initial evacuation of the most evolved pantelleritic cap followed by eruption of less evolved trachyte from a deeper zone within a stratified chamber.

The first material erupted following the 45 ka Green Tuff eruption was the Montagne Grande and Monte Gibele trachyte complex at 37 ± 10 ka. The trachyte is characterized by SiO₂ ~63 wt % as well as much lower incompatible trace element concentrations than the Green Tuff (e.g. La \sim 100 ppm; White *et al.*, 2009). It is suggested that eruption rates were too high, and the inter-eruption interval too short, for a highly evolved pantelleritic cap to be re-established by the time of formation of Montagne Grande and Monte Gibele. Subsequent eruptions show an overall increase in the degree of magma evolution until the eruption of Cuddia di Mida (09PNL027) at $\sim 9 \pm 4$ ka. This is recorded in a steady return to SiO₂ >70 wt %, La ~250 ppm and Cl ~9000 ppm. Therefore since the end of trachyte eruption at about $\sim 28 \pm 16$ ka (Mahood & Hildreth, 1986), rates of fractionation have on average exceeded eruption rates until $\sim 9 \pm 4$ ka. Notably, the most recent pantelleritic eruption at Cuddia Randazzo (09PNL017) at 5.5 ka is less evolved than the Cuddia di Mida eruption. This may either represent deeper tapping of the magma chamber, or may indicate that the Cuddia di Mida eruption was significant enough to deplete the magma chamber of most evolved compositions, which were not re-established by the time of the Cuddia Randazzo eruption.

Sulphur output from explosive pantellerite eruptions

The generation of the pantellerites magmas by fractional crystallization is consistent with the S concentrations that we have measured in the melt inclusions, which are consistently >200 ppm and reach 590 ppm (Fig. 8). If the pantellerites had been generated by melting of crustal materials, the bulk S contents might be expected to be much lower (<200 ppm), because lower crustal rocks are inferred to be largely dehydrated and have thus been effectively stripped of S (Scaillet & Macdonald, 2006). The petrogenesis of the pantellerites therefore has implications for the environmental impact of large explosive eruptions on Pantelleria. Based on experimental data, fluid/melt partitioning of S in peralkaline rhyolites is suppressed relative to metaluminous rhyolites (Scaillet & Macdonald, 2006). As a result, a greater fraction of the S remains in the melt under magma storage conditions, as opposed to residing in a fluid phase. Peralkaline rhyolite melts can potentially hold 2-5 times more S than their metaluminous counterparts (Scaillet & Macdonald, 2006). Fluid/melt partition coefficients calculated for peralkaline rhyolites at Eburru are <50 at 15 kbar, 800°C and a bulk S content of 1wt%

(Scaillet & Macdonald, 2006). Using our estimate for the degree of fractional crystallization necessary to evolve pantellerites from the alkali basalts erupted in the north of the island, we can estimate the bulk S content of the pantellerite system, both in the fluid and in the pre-eruptive melt. This allows estimation of the total S output from explosive pantellerite eruptions originating from a gas-rich 'cap' at the roof of the magma chamber.

The H₂O contents of the alkali basalts are around 1.5 wt % at saturation at a pressure of 2 kbar (Gioncada & Landi, 2010). After 90% crystallization, a substantial fluid phase, amounting to ~14 wt % or 10 vol. % at a pressure of 2 kbar, will develop in the magma storage region. In reality, migration of this fluid is likely to occur over long timescales and gas loss is predicted for such high degrees of fractionation from thermodynamic modelling (White et al., 2009). There will also be a substantial amount of CO_2 in the fluid phase; here we assume that the magma chamber fluid comprises \sim 5–10 vol. % CO₂ at a magma chamber pressure of 2 kbar. Melt inclusions in olivine erupted in the alkali basalt contain a mean of 1700 ppm of sulphur (Gioncada & Landi, 2010). After 90% fractional crystallization, we might expect a bulk S content of ${\sim}15\,{\rm wt}\,\%.$ For a temperature of $850^\circ C$ and an fO_2 of NNO -1.5 (Di Carlo *et al.*, 2010), we might expect a fluid/melt partition coefficient of ~40 for sulphur (Scaillet & Macdonald, 2006). We observe S concentrations of 300–600 ppm, with a mean of 350 ppm, in the feldspar-hosted melt inclusions (Fig. 8), which implies that 10 g S per kg magma has partitioned into a vapour. This accounts for \sim 4 vol. % of the fluid phase (or 6.5 wt %). S is likely to exist predominantly as H₂S in the fluid at high pressure. We can use this information to estimate the potential S yield of a typical explosive peralkaline eruption on Pantelleria, of erupted volume 7 km³ (Wolff & Wright, 1981) with a mean magma density of 2500 kg m^{-3} . Assuming there is a fluid phase amounting to 14 wt % prior to eruption, and of that fluid 6.5 wt % is S, then we calculate a syn-eruptive S output of 154 Mt from the pre-eruptive fluid alone. We can also estimate the component from syn-eruptive degassing by exsolution, recorded in the difference in S concentration between the melt inclusions and the matrix glasses. This is an average of 200 ppm (Fig. 8). Using a melt fraction of 50 vol. % for the erupted pantellerite, a melt density of 2400 kg m^{-3} and a degree of fractionation of 3% between the mean melt inclusion composition and the mean matrix glass composition, we calculate a syn-eruptive S degassing (from exsolution) of 1.8 Mt. The estimated total S yield for the explosive eruption associated with the Green Tuff is then 80–160 Mt for a pre-eruptive fluid content of 5-10 vol. %. This is dominated by S contained in the pre-eruptive fluid. The eruption of Pinatubo was slightly larger, erupting around $20 \,\mathrm{km^3}$ DRE and $\sim 9 \,\mathrm{Mt\,S}$ (Wallace & Gerlach, 1994). The S output from these explosive peralkaline eruptions from Pantelleria are likely to have been more significant than their metaluminous and peraluminous rhyolite and dacite counterparts because the melts essentially retain their sulphur contents for longer during melt differentiation owing to the lower fluid/melt partition coefficients (Scaillet & Macdonald, 2006). It is therefore less likely that the S will be lost from the system via fluid migration and diffuse degassing between eruptions. In addition, there is evidence for rapid differentiation owing to the low viscosity of the melts, which means that the fluid phase will develop rapidly. The S is likely to have been emitted in the form of both H₂S and SO₂; the dominant sulphur-bearing gas will depend strongly on oxygen fugacity. It is likely that H₂S emissions will be significant compared with similar rhvolitic eruptions, because this is the dominant sulphur species in vapour at the relatively low oxygen fugacities typical of Pantellerian magmas (Di Carlo et al., 2010). This will be rapidly oxidized to SO₂ in the atmosphere and hence to sulphate aerosol.

Our measurements of Cl, Fand Li (Figs 8 and 9) suggest that the abundance of these volatile elements is controlled by fractionation, partitioning between fluids, and degassing to varying degrees. The degree of Cl and F degassing during eruption is likely to have been small; matrix glasses contain similar concentrations of these elements to the melt inclusions (Fig. 8). This is consistent with previous work, which has shown that HCl degassing is limited for peralkaline melts that are associated with pre-eruptive hydrosaline liquids (Urabe, 1985; Shinohara, 1991; Lowenstern, 1994).

CONCLUSIONS

Based on REE inversion, melt generation in the mantle below Pantelleria is best explained by $\sim 1.7\%$ melting of a primitive mantle source at depths of 60–100 km, mainly within the spinel–garnet transition zone. Pantelleria alkali basalts are generated by $\sim 35\%$ fractional crystallization of the primary melt.

Major and trace element data for glasses indicate a gap in melts of intermediate composition (a Daly Gap), which is consistent with previously published data from Pantelleria based on whole-rocks. Principal component analysis was used to constrain the liquid line of descent and indicates that the major element trends in the mafic melts are controlled by clinopyroxene, plagioclase, magnetite and olivine crystallization. To explain these trends, the crystallizing assemblage must contain ~12% magnetite. Major element trends in the silicic melts are controlled by feldspar, clinopyroxene and fayalitic olivine or aenigmatite. As SiO₂ content increases, feldspar and clinopyroxene become progressively more alkali-rich and sodian respectively. Aenigmatite broadly replaces olivine as a crystallizing phase in the most evolved compositions. Modelling of the trace element compositions indicates that trachyte and pantellerite can be generated by $\sim 76\%$ and $\sim 96\%$ fractional crystallization of alkali basalt respectively. The petrogenesis of the Pantelleria silicic rocks by fractional crystallization rather than by fractional melting is more consistent with their measured compositions. Continua in matrix glass and isotope compositions (Civetta *et al.*, 1998) can be used to rule out crustal assimilation as a mechanism of pantellerite petrogenesis.

Feldspar-hosted melt inclusions contain F and Cl at concentrations of \sim 3500 ppm and 9000 ppm respectively. These are similar to matrix glass values, indicating that F and Cl abundances are controlled by both fractionation and degassing. Li concentrations in melt inclusions decrease with increasing H₂O, which suggests that its distribution is controlled by three-way partitioning between low-density vapour, a high-density hydrosaline fluid, and silicate melt; degassing of Li appears to be limited in the peralkaline system. This is consistent with Cl buffering observed in this study and also used by Lowenstern (1994) to postulate the presence of a Cl-rich fluid phase at low pressures. Feldspar-hosted melt inclusions in pantellerites record pre-eruptive H₂O and CO₂ contents of up to 4.9 wt % and 150 ppm respectively. A maximum pressure for melt inclusion entrapment is calculated using H₂O- CO_2 at 1.5 kbar, which corresponds to a depth of ~5.5 km.

Clinopyroxene-liquid thermometry and CO₂-H₂O equilibria suggest that conditions of alkali basalt storage prior to eruption were ~1090°C and ~2 kbar. Prior to eruption, the most evolved pantellerite was stored at $\sim 800^{\circ}$ C, and the least at $\sim 870^{\circ}$ C, assuming storage at \sim 1.5 kbar. Thermobarometry is broadly consistent with recent phase equilibrium experiments, except for somewhat higher temperature estimates. Using calculated temperatures and volatile contents, pre-eruptive viscosities of alkali basalt melts are in the range $10^1 - 10^2$ Pa s. Pantellerite melt viscosities are in the range $10^3 - 10^4$ Pa s. Lower temperatures determined by other techniques (e.g. White et al., 2009; Di Carlo et al., 2010) still result in comparatively low viscosities of 10⁵-10⁶ Pa s. Low viscosities are the result of the alkali- and volatile-rich composition of the Pantelleria magmas and account for the range in volcanic edifice morphology at Pantelleria.

Silicic melts form by extensive fractional crystallization in a persistent magma chamber under the SE of Pantelleria. The low viscosity of the peralkaline melts is suggested to play a key role in rapid magma differentiation across the Daly Gap by crystal settling. The presence of mafic enclaves in silicic hosts indicates that both compositions are present in the same stratified chamber. It is suggested that stratification results from density reduction in the more evolved melts and enhancement by efficient migration of a fluid phase to the roof of the magma chamber. The magma chamber acts as a density filter that prevents eruption of dense mafic melts in the SE of the island. Mafic magmas in the NW are unlikely to be stored for significant periods in a large magma reservoir. The temporal variation in geochemistry of eruptions from the last volcanic cycle from the Green Tuff eruption can be explained by evacuation and subsequent regeneration of a pantelleritic melt cap in the magma chamber. Anomalies in this trend may be explained by variation in the relative rates of fractionation and eruption.

Published experimental data regarding S fluid/melt partitioning behaviour in peralkaline melts are used with S melt-inclusion data to make estimates of the S yield that would result from eruptions of the order of the Green Tuff eruption. For a 7 km³ eruption, an S yield of 80–160 Mt is estimated, which is significantly larger than the yield expected from a metaluminous or peraluminous eruption of comparable volume. This is the result of partitioning behaviour and high initial S, as well as probably rapid magmatic differentiation and fluid migration. It would be expected that significant amounts of H₂S would be emitted as a result of the low fO_2 of the melt, which would subsequently be oxidized to SO₂ in the atmosphere.

ACKNOWLEDGEMENTS

Sarah Nixon provided advice on using INVMEL, John Maclennan provided assistance with principal component analysis, and Jason Day provided technical support for the LA-ICP-MS analyses. We thank Ray Macdonald, Bruno Scaillet and one anonymous reviewer for expert reviews that have greatly improved the paper.

FUNDING

Fieldwork was supported by Queens' College, Cambridge (D.A.N.), Fitzwilliam College, Cambridge (G.F.), the NERC National Centre for Earth Observation, a University of Cambridge Travel grant (M.E.), a travel grant from the School of Environmental Sciences (R.A.H.) and the Department of Earth Sciences, Cambridge (D.A.N., M.E.).

SUPPLEMENTARY DATA

Supplementary data for this paper are available at *Journal* of *Petrology* online.

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