Complex subvolcanic magma plumbing system of an alkali basaltic maar-diatreme volcano (Elie Ness, Fife, Scotland)

T. M. Gernon a,∗ , B. G. J. Upton b , R. Ugra a , C. Yücel c , R. N. Taylor a ,
H. Elliott a †

a Ocean and Earth Science, University of Southampton, Southampton SO14 3ZH, U.K.

b School of GeoSciences, University of Edinburgh, Edinburgh EH9 3JW, UK.

c Department of Mining Engineering, Gümüşhane University, TR-29000, Gümüşhane, Turkey.

† now at: Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE, UK.

Abstract

Alkali basaltic diatremes such as Elie Ness (Fife, Scotland) expose a range of volcanic lithofacies that points to a complex, multi-stage emplacement history. Here, basanites contain phenocrysts including pyrope garnet and sub-calcic augites from depths of ∼60 km. Volcanic rocks from all units, pyroclastic and hypabyssal, are characterised by rare earth element (REE) patterns that show continuous enrichment from heavy REE (HREE) to light REE (LREE), and high Zr/Y that are consistent with retention of garnet in the mantle source during melting of peridotite in a garnet lherzolite facies. Erupted garnets are euhedral and unresorbed, signifying rapid ascent through the lithosphere. The magmas also transported abundant pyroxenitic clasts, cognate with the basanite host, from shallower depths (∼35–40 km). These clasts exhibit wide variation in texture, mode and mineralogy, consistent with growth from a range of compositionally diverse melts. Further, clinopyroxene phenocrysts from both the hypabyssal and pyroclastic units exhibit a very wide compositional range, indicative of polybaric fractionation and magma mixing. This is attributed to stalling of earlier magmas in the lower crust—principally from ∼22–28 km—as indicated by pyroxene thermobarometry. Many clinopyroxenes display chemical zoning profiles, occasionally with mantles and rims of higher magnesium number (Mg#) suggesting the magmas were mobilised by juvenile basanite magma. The tuffs also contain alkali feldspar megacrysts together with Fe-clinopyroxene, zircon and related salic xenoliths, of the ‘anorthoclaseite suite’—inferred to have crystallised at upper mantle to lower crustal depths from salic magma in advance of the mafic host magmas. Despite evidence for entrainment of heterogeneous crystal mushes, the rapidly ascending melts experienced negligible crustal contamination. The complex association of phenocrysts, megacrysts and autoliths at Elie Ness indicates thorough mixing in a dynamic system immediately prior to explosive diatreme-forming eruptions. DOI: 10.1016/j.lithos.2016.08.001

Key words: Alkali basalt, diatreme, clinopyroxene, pyroxenite, magma, eruption

Manuscript accepted for publication in Lithos 15 August 2016
1 Introduction

Basaltic volcanism takes place in all tectonic settings and accounts for an estimated 80% of all igneous activity at the Earth’s surface (Parfitt, 2004). Basaltic magmas are generated as a consequence of partial melting of mantle peridotite (see Hirose and Kushiro, 1993). Such low degree melts then segregate from the refractory residue, and mobilised by thermochemical processes, ascend through the lower lithosphere. Many batches of basaltic melt stall in the ‘deep crustal hot zone’ (sensu Annen et al., 2006), where prolonged interaction with crustal rocks can occur, yet others ascend rapidly from the source experiencing negligible crustal interaction (e.g. Cortés et al., 2015). One possible explanation for this contrasted behaviour is that progressive melt accretion to the conduit walls results in later magmas becoming increasingly shielded from crustal contamination (cf. Tepley et al., 2000).

 Maar-diатremе volcanoes—an important class of basaltic landform—are formed as a consequence of rapid magma ascent and explosive eruptions (see Sparks et al., 2006; White and Ross, 2011). Typically these consist of a diverging tephra-filled pipe linking a syn-eruptive crater floor to a hypabyssal ‘feeder’ system at depth (e.g. Lorenz and Kurszlaukis, 2007; Gernon et al., 2013; Elliott et al., 2015). Ascending basaltic melts are liable to exploit crustal weaknesses, commonly resulting in diatreme localisation along major structural features (e.g. Kurszlaukis and Barnett, 2003; Jelsma et al., 2009; White and Ross, 2011; Son et al., 2012; Brown and Valentine, 2013).

 Most maar-diатremеs contain lithic fragments (‘xenoliths’) entrained from the feeder dyke or conduit walls at a range of crustal levels, and occasionally from the upper mantle. Such xenoliths commonly disaggregate during ascent or eruption, liberating crystal fragments or ‘xenocrysts’ into the host magma. The study of xenoliths, xenocrysts and other crystal fragments from deeply eroded maar-diатremеs can yield crucial evidence on the origin, interactions and ascent mechanisms of their parent melts (e.g. Zajacz et al., 2007; Ashchepkov et al., 2011; Yücel et al., 2014).

Geochemical and mineralogical constraints are even more powerful when combined with a physical volcanological understanding of diatreme emplacement, thus yielding insights into the spatio-temporal evolution of the magmas. Here we present data from crystal and lithic inclusions in dykes and pyroclastic deposits of the well-exposed Elie Ness diatreme, SE Scotland (Fig. 1), which records a transition from an initially magmatic eruption style to a dominantly phreatomagmatic mode of eruption (Gernon et al., 2013). We examine and discuss the geochemistry of the different igneous rock units confined to the

* Corresponding author

Email address: Thomas.Gernon@noc.soton.ac.uk (T. M. Gernon).
diatreme, together with the origin and significance of associated (diverse) cognate xenoliths (i.e. autoliths) and lithic inclusions. Our data and observations indicate that the parental magmas originated by low-degree partial melting of a garnet lherzolite source and ascended rapidly, mixing magma batches arrested at various depths, yet experiencing negligible crustal contamination. Our study highlights the complexity of the pre-eruptive magma plumbing system fuelling maar-diatreme volcanism.

2 Geological setting

The Elie Ness diatreme, erupted at ∼290 Ma (Monaghan and Pringle, 2004), is one of >100 diatremes and associated intrusions in Fife and the Lothians, SE Scotland (Fig. 1a–b). These were emplaced during a major phase of Permo-Carboniferous rifting and magmatism across Europe (see Wilson et al., 2004, and references therein). Elie Ness, together with neighbouring diatremes at Elie Harbour, Ardross, Coalyard Hill, Ruddon’s Point and Newark, lies along the NE-SW trending Ardross Fault (Fig. 1b)—a right-lateral strike-slip fault, active throughout the late Palaeozoic—inferred to have been exploited by basanitic magmas (Francis and Hopgood, 1970).

The Elie Ness diatreme exposes a stratigraphic thickness of >250 m of tuffs and lapilli tuffs (see Fig. 1c). The deposits are subdivided into three lithofacies associations (LFA, see Gernon et al., 2013). LFA1 is confined to the eastern part of the diatreme (Fig. 1c), and dominantly consists of massive lapilli tuffs, locally containing abundant pyroclastic autoliths and country rock breccias. The tuffs are structureless and poorly to moderately sorted, consisting mainly of juvenile vesicular ash and scoria. Locally, the tuffs comprise sub-vertical lapilli pipes and pod-like accumulations of lapilli. LFA1 is interpreted to represent a pyroclastic deposit formed within the diatreme, mixed with subsided and disrupted pyroclastic material, likely sourced from the overlying (now-eroded) tephra ring (Gernon et al., 2013).

LFA2 dominates most of the pipe-fill at current levels (Fig. 1c), and forms a repetitive succession of massive and well-stratified lapilli tuffs and basalt tuff breccias. The massive lapilli tuffs (on average 0.5–2 m thick) typically infill scour channels developed in underlying strata, and contain abundant angular lithic clasts and blocks. Typically these are overlain by well-bedded (lapilli-) tuffs with diffuse parallel and low-angle cross-stratification, bomb sag structures and rare accretionary lapilli. LFA2 is interpreted to represent a sequence of dilute pyroclastic density current deposits, representing a protracted phase of highly pulsatory phreatomagmatic eruptions, many of which were potentially sourced from a neighbouring vent to the east (Gernon et al., 2013).
LFA3 comprises a series of minor discordant intrusions, including a 500 m wide basanitic breccia pipe to the west (Fig. 1c), and a number of volcaniclastic and magmatic dykes of basaltic and trachybasaltic composition. The breccia pipes are thought to relate to debris-jet emplacement, linked to a feeder dyke that interacted with groundwater at some level within the diatreme. The dykes signify an episode of passive magma intrusion during the waning phase of volcanism at Elie Ness (Gernon et al., 2013).

3 Analytical methods

The Elie Ness diatreme was mapped at a scale of 1:2,270 (Fig. 1c). The lithofacies were recorded on graphic logs of a cumulative total of ~250 m strata, enabling correlation of beds based on grain-size, texture, composition and sedimentary structures (Gernon et al., 2013). Representative samples were collected from regular intervals across the diatreme (Fig. 1c), capturing the different lithofacies and intrusive bodies. A total of twenty polished thin sections were analysed using optical and scanning electron microscopy (SEM: Leo 1450 VP, operated at 25 keV using energy-dispersive X-ray spectroscopy (EDS)).

Whole-rock major elements were analysed using X-ray fluorescence (XRF) (Panalytical Magix-Pro WD-XRF fitted with a 4kW Rh X-ray tube) at the University of Southampton. Calibration was via 20+ international geochemical reference samples. Solution inductively coupled plasma mass spectrometry (ICP-MS) was performed to determine the concentration of incompatible elements using a ThermoScientific XSeries2 at the University of Southampton; samples were prepared following the standard procedure of silicate rock dissolution by HF digest (adapted from Beauchemin, 2008).

Major element analysis of zoned and unzoned pyroxene crystals from selected samples (5, 10, 14 & 17) was carried out using a Cameca SX-100 electron probe micro-analyser (EPMA) in the School of Earth Sciences at the University of Bristol. Analyses were performed using operating conditions of 15 kV and 80 nA and a focused spot size of 1 µm. Earlier analyses by B.G.J.U. on sample 1L were performed at the Department of Geology and Geophysics, University of Edinburgh, on a Cambridge Scientific Instruments Microscan 5 electron-probe micro-analyser using the wavelength dispersive method. Pure elements, oxides and simple silicate compositions were used as standards. The operating conditions were 200 kV, using a sample current of 30 nA.
4 Results | Erupted rocks of the Elie Ness diatreme

4.1 Alkali basalts, trachybasalts and basanites

The rocks investigated in this study are classified as basalts, trachybasalts and basanites (Fig. 2a; see Table 1). Together with a suite of similar, albeit older (i.e. Lower Carboniferous) volcanics in Scotland (Smedley, 1988), the rocks are classified as alkaline basalts (Fig. 2b) on the basis of their Nb/Y versus Zr/TiO\textsubscript{2} compositions (sensu Winchester and Floyd, 1977), and as within-plate alkali basalts based on Nb-Zr-Y (Meschede, 1986). Whole-rock analyses of representative tuffs and minor intrusives at Elie Ness show a limited compositional range with MgO between 8.7 and 10.8 wt.% (Table 1; see also Table 5.1 in Wallis, 1989). Indeed, the total alkali and silica contents are broadly comparable to other Permo-Carboniferous volcanics in Scotland (Fig. 2a), which include the Passage Group lavas, Ayrshire sills, Mauchline group, Fife and Lothian sills and basanite lavas, and the Highland dykes (Wallis, 1989).

All LFA samples have Zr/Nb \leq 5 (Fig. 3a; Tables 1–2), and Zr/Y–Nb/Y that place the samples above the MORB field in the mantle plume array (Fig. 3b). The Nb-Zr-Y contents (Figs. 2a–3) are again comparable to those of the aforementioned Permo-Carboniferous volcanics described by Wallis (1989).

The chondrite-normalised rare earth element (REE) patterns for all samples are characterised by a progressive enrichment from Lu through to La (Figs. 4a–c) with La\textsubscript{n}/Yb\textsubscript{n} typically in the range 14–27. Abundances of La are around 80–200 times chondrite. Primitive mantle-normalised trace elements (Figs. 4d–f) also reflect an enrichment towards the more incompatible elements. This is particularly apparent in the progressively higher normalised abundances between Y and Nb. Sr is an exception in that it generates a dip relative to Ce–Nd in LFA1 and LFA2 (Figs. 4d–e).

The strongly negative Ba anomaly observed in one sample (S4, Fig. 4d) is most readily explained by Ba mobility during basalt alteration; indeed this sample shows evidence of sericitic alteration, which is a potential sink for Ba and may lead to erratic barium abundances (Du Bray et al., 1995). Similarly, the fact that Pb concentrations are scattered, yet are dispersed around the Ce\textsubscript{n} and Nd\textsubscript{n} values (Figs. 4d–f), is consistent with hydrothermal alteration. For example, the porous breccia pipe (S10)—more susceptible to fluid flow—exhibits a positive Pb anomaly, whereas the coherent dyke (S17) lies directly between Ce\textsubscript{n} and Nd\textsubscript{n} (Fig. 4f) presumably as it was less accessible to hydrothermal fluids.
4.2 Xenoliths and crystals | observations and review

The basalts, trachybasalts and basanites—pyroclastics and intrusives—contain abundant xenoliths and crystals (xenocrysts and phenocrysts), akin to many Permo-Carboniferous volcanics in Scotland (e.g. Chapman, 1976; Upton et al., 1998, 2003, 2009). The diatreme contains two categories of highly contrasted cognate materials: (a) pyrope garnets (colloquially referred to as ‘Elie rubies’) and sub-calcic augites that are likely representative of a high-pressure (∼2 GPa) phenocyst assemblage, and (b) a suite of pyroxenite and related aultoliths, together with alkali feldspar megacrysts and co-magmatic felsic rocks. This second category is thought to represent products that crystallised in the vicinity of the crust-mantle discontinuity at ∼35–40 km depth (Bamford et al., 1978; Upton et al., 1983). In the intrusive bodies (LFA3, Fig. 1c), accidental xenoliths are rare and generally restricted to metagabbro and quartz-feldspathic gneiss probably of lower to mid-crustal derivation.

In this section, we summarise the pertinent characteristics of xenolith and crystal assemblages recorded at Elie Ness, combining empirical observations of these fragments in thin section, and drawing extensively on published accounts, including exhaustive studies by Chapman (1976) and Upton et al. (2003).

4.2.1 Garnet crystals and their significance

The pyrope garnet crystals are typically <1 mm but up to ∼50 mm in diameter (Fig. 5a), commonly exhibiting euhedral form (i.e. rhombic dodecahedron with bevelled edges, occasionally with faces of the octahedron; see Upton et al., 2003). The garnets are titaniferous (∼0.4 wt.% TiO₂) and have low Cr₂O₃ contents (0.01–0.19 wt.%) (Chapman, 1976; Upton et al., 2003). Sub-calcic augites also occur, and their compositional similarity to those co-crystallised with titanian pyrope in the Kakanui diatreme (New Zealand; Dickey, 1968) suggest that these might similarly have been in equilibrium with garnet. The pressure at which the pyrope and sub-calcic augite were in equilibrium with melt is inferred to have been approximately 2 GPa (Colvine, 1968; Chapman, 1974a, 1976; Upton et al., 2003).

4.2.2 Pyroxenite xenoliths: a synthesis

Lustrous black ultramafic xenoliths, with diameters up to ∼50 mm occur in the tuffs and intrusions (Fig. 5b-c), and are interpreted as cognate cumulates (see Chapman, 1976). Most are hornblende pyroxenites, composed largely of salitic augite and pseudomorphs after olivine (carbonated or serpentinised), enveloped by kaersutite oikocrysts up to 10 mm across. Minor accessories
include biotite, apatite and opaque oxides. The pyroxenites display a wide va-
riety of textures and modes, ranging from olivine-kaersutite clinopyroxenites
through olivine-free hornblende pyroxenites via hornblende pyroxenites with
late sodic feldspar to amphibole-free varieties with biotite and/or sodic plagio-
clase. On textural and mineralogical criteria, the cumulate nodules have been
subdivided into five types, collectively thought to represent a differentiation
series (refer to Chapman, 1974a, 1976).

Olivine and clinopyroxene are inferred to represent cumulus phases, whilst
kaersutitic amphibole, biotite and sodic feldspar were intercumulus. The kaer-
sutite oikocrysts (Fig. 6a) constitute up to 40 modal%. Chlorite in some pyrox-
enites (Fig. 6b) is presumed to be pseudomorphous after intercumulus glass,
and—if so—indicates that these pyroxenites were still above their solidus at
the time of entrainment. Calcitic ocelli, typically chlorite-rimmed (Fig. 6c),
also occur in both late-stage amphiboles and the inferred glassy residues (Fig.
6b).

With loss of olivine and then pyroxene, this suite of xenoliths is inferred to
grade into less frequent biotite-rich ultramafic xenoliths (Fig. 6d). Olivine py-
roxenites and clinopyroxenites lacking hydrous phases also occur, but again
are rare. Some pyroxenites contain pseudomorphs after idiomorphic olivine
enclosed in well-equilibrated mosaics of equigranular augite and hornblende
showing 120° triple junctions. In other pyroxenites, larger augite crystals are
surrounded by smaller pyroxene neoblasts (Fig. 6e), whilst elsewhere the py-
roxenes have been partially replaced by secondary amphibole along cleavage
planes and grain boundaries (Chapman, 1976). The hornblendites in some of
the basanites may have grown as metasomatized pyroxenites in which the py-
roxenes were wholly replaced by kaersutite. Some pyroxenes and olivines are
idiomorphic and occasionally euhedral. Pyroxenes in the Elie Ness autoliths
commonly show oscillatory zonation and some exhibit hourglass zoning (Fig.
6f).

4.2.3 Anorthoclase xenoliths and zircon

Feldspars (anorthoclase, K-albite and sanidine) occur as discrete crystals,
and as xenoliths dominated by Na-rich feldspar. Anorthoclase megacrysts,
up to several cm across, occur in the tuffs and minor intrusives. Scarce zir-
con megacrysts (>10 mm diameter) are regarded as co-magmatic with the
anorthoclase/albitite xenoliths (see Irving and Frey, 1984; Hinton and Up-
ton, 1991). Oscillatory zoning in the zircons corresponds to abrupt changes
in REE, Th and U contents, suggesting dynamic growth conditions in these
melts, as recorded in other Scottish megacrysts (Hinton and Upton, 1991;
Upton et al., 1999). Similar zircons in the neighbouring Coalyard Hill vent ex-
hibit quasi-euhedral morphologies, and their association with ‘anorthoclase’
xenoliths suggest they grew in a felsic magma, which subsequently mixed with
the basanite (Chapman and Powell, 1976). The Elie Ness tuffs also contain
(rare) coarse-grained polycrystalline anorthoclaseite and albite clasts com-
posed mainly of sodic feldspar, comparable to those in other diatremes along
the Ardross Fault.

4.2.4 Alkali feldspar megacrysts: observations and review

Alkali feldspar cleavage fragments are presumed to be derivative from coarse
anorthoclase rocks comparable to those found as xenoliths (Aspen et al.,
1990; Upton et al., 2009). Electron microprobe analysis of the feldspars yield
a composition of $\sim An_{1.8} Ab_{80.1} Or_{17.7} Cn_{0.1}$; however, these megacrysts span the
broadest compositional range yet seen in any of the Scottish localities, ranging
from K-albite via sodic anorthoclase, to nearly pure sanidine (i.e. $Or_{7.5}–Or_{99}$).
Commonly there is a patchy replacement of ‘primary’ anorthoclase by more
potassic feldspar, and late high-K feldspar veinlets. These bilaterally symmet-
rical veinlets (nearly pure $KAlSi_3O_8$) are similar to those described from an
anorthoclase xenolith in the Southern Uplands (Upton et al., 1999, 2011).
Most of the discrete feldspar crystals are likely to represent cleavage fragments
from (pegmatitic) anorthoclase veins or dykes, although through analogy
with the neighbouring Coalyard Hill diatreme, some might represent high-
pressure phenocrysts in evolved melts that were intercepted by the basanitic
host magmas (Chapman and Powell, 1976; Aspen et al., 1990; Upton et al.,
2011).

5 Clinopyroxene and alkali feldspar analysis

Clinopyroxenes and some alkali feldspars from the tuffs, breccias and dykes
(Fig. 1c) were analysed by electron-microprobe (see methods). Whilst some
pyroxenes retain idiomorphic form, the majority of the pyroxene crystals (and
alkali feldspars) were cleavage fragments. According to the International Min-
eralogical Association (Morimoto et al., 1988) the pyroxenes (Table 3) are
subdivided mainly as diopsides and augites (Fig. 7), with magnesium numbers
($Mg\# = Mg/(Mg + Fe_{tot})$) ranging from 0.49 to 0.84. Some clinopyroxenes
have high Wo contents ($>Wo_{50}$), and a few extreme compositions with high
$Fe/Mg$ and $Na_2O$ are hedenbergite (Fig. 7).

Zoned clinopyroxenes are abundant in LFA3, and of comparatively low abun-
dance in both pyroclastic lithofacies associations (LFAs 1–2), where they are
more fragmented. In many cases, the clinopyroxenes are strongly zoned (see
Table 3; Fig. 8; Supplementary Fig. 1), with discrete crystals showing normal
and reverse zonation. Although numerous crystals exhibit cores with more
primitive compositions (i.e. relatively high Mg\# and Cr$_2$O$_3$, e.g. S10-34, Table 3; Supplementary Fig. 2), in some cases the mantles and rims of the clinopyroxenes exhibit higher Mg\# (dark areas in the BSE images) relative to their cores (e.g. S17-40, Fig. 8, and S10-71, S10-73 & S17-81, see Supplementary Fig. 2).

The wide range of clinopyroxene compositions is shown in plots of CaO vs. Al$_2$O$_3$ and Na$_2$O vs. Al$_2$O$_3$ (Figs. 9a,d) with CaO ranging from $\sim$16 to $>$24 wt.\%, Al$_2$O$_3$ from $\sim$1 to $>$15 wt.\% and Na$_2$O from $\sim$0.5–3.4 wt.\%. Wide scatter is seen in plots of TiO$_2$ vs. Al$_2$O$_3$ and Al$_2$O$_3$ vs. SiO$_2$ (Figs. 9b,c) with crude positive and negative correlations respectively (TiO$_2$ contents vary from $\sim$0.1–$>$4 wt.\%). A closer (negative) correlation is shown for MgO vs. FeO (Fig. 9e) with MgO ranging from $\sim$7–17 wt.\% and total iron (as FeO) from $\sim$3–17 wt.\%. The few clinopyroxenes exhibiting comparatively high Fe/Mg and Na contents are comparable to those of megacrysts and anorthoclasites described from other Scottish localities (refer to p. 948 of Upton et al., 2009). Indeed, they are also compositionally similar to clinopyroxene megacrysts and xenoliths from Highland intrusions of comparable age (i.e. Colonsay, Stob a’ Ghrianain and Streap Comlaidh, see Wallis, 1989).

The clinopyroxenes are subdivided further using Mg\# vs. Cr$_2$O$_3$ (Fig. 10a), Mg\# vs. TiO$_2$ (Fig. 10b), and Ti (apfu) vs. Al (apfu) (Fig. 10c). High Cr$_2$O$_3$ and Mg\# reflect more primitive compositions (Fig. 10a), and it can be seen that the majority of these correspond to crystal cores (Fig. 10d). They display negative trends in Mg\# vs. TiO$_2$ but positive trends in Al$_{tot}$ vs. Ti (apfu) (Fig. 10 b–c) from the most primitive to the most evolved compositions (cf. Jankovics et al., 2012).

In general, the rims to zoned clinopyroxene have comparably low Cr$_2$O$_3$ (typically $<$0.1 wt.\%; Fig. 10d), high Mg\# (typically of the order 0.7–0.8; Fig. 10d–e), high TiO$_2$ (typically $>$2 wt.\%, Fig. 10e), and high Al$_2$O$_3$ (Table 3), with Ti:Al values typically in the range 0.25–0.4. In contrast, the majority of cores generally exhibit higher Cr$_2$O$_3$ ($\sim$50% $>$0.1 wt.\%), lower TiO$_2$ (most $\leq$2 wt.\%), moderate to high Mg\# (Fig. 10d–e; Supplementary Fig. 2) and Ti:Al values mostly of the order 0.125–0.25 (Fig. 10f). Some crystals exhibit ragged cores (e.g. S10-57), whereas other cores resemble euhedral phenocrysts (S17-12, Fig. 10e).

Finally, the feldspar cleavage fragments have compositions ranging from albite and anorthoclases to sanidines (Na$_2$O: $\sim$0–11.5 wt.\%; K$_2$O: $\sim$1–$\sim$17 wt.\%; Fig. 9f).
5.1 Pyroxene thermobarometry

The temperature and pressure, and hence crystallisation depth of volcanic rocks can be estimated using clinopyroxene compositions (Nimis, 1995; Nimis and Ulmer, 1998; Nimis and Taylor, 2000) and clinopyroxene–liquid equilibria (Putirka et al., 1996, 2003). More quantitative P-T estimates using clinopyroxene composition have been re-evaluated by Putirka (2008); by using Fe–Mg exchange and \( K_D(\text{Fe–Mg})_{\text{cpx–liq}} \), this yielded an equilibrium constant = 0.27 ± 0.03.

Quantitative pressure and temperature estimates for the Elie Ness pyroxenes were obtained using the clinopyroxene-only and clinopyroxene-liquid barometric and thermometric equations of Putirka (2008). The parent liquid compositions were approximated using whole-rock (XRF) compositions. The equilibrium constants were calculated for clinopyroxene compositions from the basanitic breccia pipe (sample 10) and trachybasaltic dyke (sample 17); two clinopyroxene compositions were identified as being in equilibrium with the melt, according to the Putirka equilibrium constant (0.27 ± 0.3) (Table 4). In contrast, clinopyroxene crystals from the tuffs were found not to be in equilibrium with the melt; this is perhaps not surprising given that the tuffs comprise a complex mixture of pyroclastic and magmatic deposits from a variety of sources (e.g. mass wasting of crater walls; Gernon et al., 2013). The calculated results of clinopyroxenes from the breccia pipe (Table 4) reveal high mean pressures of 0.7 ± 0.16 GPa and temperatures of 1166 ± 43 °C. The P and T estimates for the dyke are within error of this at 0.9 ± 0.27 GPa and 1188 ± 72 °C (Table 4), corresponding to approximate crystallisation depths of 22–28 km.

6 Discussion | Complexity of the magma ‘supply chain’

6.1 Petrogenesis

The Elie Ness parental magmas are assumed to have an asthenospheric origin (>70 km Wallis, 1989). The high MgO contents (> 8 wt.%) of all sampled basaltic hosts (Table 1; see Wallis, 1989) indicate that they represent relatively primitive magmas that have not experienced significant fractionation and are close to parental melt compositions. High Zr/Y and Nb/Y (Fig. 3), alongside the generally high incompatible element contents, provide evidence for small degrees of partial melting (<5%). The REE patterns, progressively enriched from Lu to La, and the high Zr/Y are consistent with retention of garnet in the mantle source. As garnet is considered to be a phenocryst phase in Elie Ness,
it is inferred that the HREE were retained either during garnet crystallisation and accumulation during magma ascent, or were held in garnet during melting of peridotite in a garnet lherzolite facies.

Negative Sr in the trace element patterns (Figs. 4d–f) is extremely unlikely to relate to plagioclase fractionation, given the absence of feldspar as a crystallising phase in the basanitic magmas (with their low Ca/Al ratios), and the absence of a negative Eu anomaly (Fig. 4a–c). Hence the Sr concentration may be a feature of the mantle source (akin to kimberlites; e.g. Le Roex et al., 2003) or crustal contamination (e.g. Elburg and Soesoo, 1999). Given the primitive nature of the samples and the lack of any other indications of crustal contamination such as Th/La $\gtrsim 0.15$, coupled with relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7032–0.7049) and high $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (0.5122–0.5126) (see Wallis, 1989), the low Sr is most likely a mantle characteristic. Pb concentrations are not systematically enriched relative to equivalently incompatible REE (Fig. 4), indicating a negligible role for crustal contamination.

The pyrope garnets and low-Ca augites are inferred to represent high-pressure phenocrysts that crystallised from basaltic melts deep in the lithospheric mantle ($\sim$50–60 km; Fig. 11) (Colvine, 1968; Chapman, 1976; Upton et al., 2003). The survival of garnet (Donaldson, 1984) points to very rapid ascent rates, which for alkali basaltic magmas containing peridotite xenoliths, is estimated to be of the order of 10 ms$^{-1}$ (Kuo and Kirkpatrick, 1985)—broadly comparable to rates obtained from studies of garnet dissolution in kimberlites (Canil and Fedortchouk, 1999). Rapid ascent of such crystal-laden magmas invokes the presence of an exsolved fluid phase, perhaps linked to decompression-induced CO$_2$ exsolution during magma ascent (cf. Stoppa, 1996; Stoppa et al., 2003; Mattsson and Tripoli, 2011).

6.2 Clinopyroxene variability

The very broad compositional range exhibited by clinopyroxenes (Figs. 9a–e & 10) indicates a wide range of pressures, temperatures and magma compositions, and in summary, can be considered in three categories:

(1) Crystals derived from fragmentation of pyroxenitic cumulates. From the petrographic indications that some pyroxenites were above their solidus temperatures at the time of entrainment, they are assumed to be cognate to the host magma (cf. Chapman, 1976). The comparative abundance of pyroxenite autoliths at different stratigraphic levels in the tuffs implies energetic pulses of magma through the protolith sequence.

(2) Discrete Na-rich pyroxene crystals (Fig. 9d), known from other Scottish xenolith/megacryst suites, compositionally resemble those found in
anorthoclase-pyroxene-magnetite-apatite associations. Accordingly these are regarded as part of the ‘anorthosites suite’ (sensu Upton et al., 1999).

(3) Phenocrysts crystallised under a variety of conditions ranging from deep lithospheric to near surface. Pyroxene thermobarometry suggests that crystallisation of a subset of these pyroxenes (i.e. late effusive eruptive phase of LFA3) commenced in lower-crustal magma reservoirs at ∼22–28 km, broadly equivalent to the depth of mafic reservoirs in modern-day rift settings (e.g. Ronga et al., 2009).

The clinopyroxene crystal fragments exhibit a very wide compositional range in both the intrusive and extrusive rocks (Fig. 9a–e), pointing to extremely thorough mixing of magma batches from various depths, probably within a lower-crustal reservoir prior to eruption (cf. Montagna et al., 2015). Fractional crystallisation of magmas is indicated by the Fe/Mg variation (Fig. 9e), whilst the variation in Ca-Tschermak’s molecule, suggested by the variance in SiO₂, CaO and Al₂O₃ (Figs. 9a–c), points to a polybaric evolution. This can be explained by the presence of a stock-work of semi-independent magma reservoirs beneath the diatreme (cf. Yücel et al., 2014), which were disturbed and entrained by the rapidly ascending basanite magma.

Elsewhere, high Mg and Cr clinopyroxenes have been interpreted as xenocrysts that formed in the mantle or deep crust (e.g. Barton and van Bergen, 1981; Zhu and Ogasawara, 2004; Akinin et al., 2005; Zhang et al., 2007), or as reflecting high-pressure fractionation and mixing processes during the same magmatic episode (e.g. Wass, 1979; Duda and Schmincke, 1985; Fodor et al., 1995). Compositional changes observed within individual clinopyroxene crystals (Figs. 8, 10d–f, Supplementary Figs. 1–2) can be interpreted as step zoning and show multiple growth events in some cases from more mafic magmas (e.g. Duda and Schmincke, 1985; Streck et al., 2007; Streck, 2008), probably indicting periodic replenishment of the shallower magma reservoir by primitive basaltic melts (cf. Streck et al., 2002). However, several clinopyroxene crystals show complex oscillatory zoning and many also record a shift from primitive to more evolved melts (see Figs. 10d–f & Supplementary Figs. 1–2). Further, the presence of both normally and reversely zoned clinopyroxenes within the same rock sample is consistent with magma mixing and/or an increase in temperature and Mg/Fe²⁺ ratio (Anderson, 1974; Pe-Piper, 1984).

6.3 Regional variability in diatreme composition

It is noteworthy that the nearby basanitic Elie Harbour diatreme (see Fig. 1b) did not erupt any xenoliths, autoliths or high-pressure phenocrysts. Further, the absence of upper mantle lherzolite xenoliths at Elie Ness is enigmatic since
these are present in several neighbouring basanitic diatremes that also contain analogous pyroxenitic xenoliths and anorthoclase debris (e.g. Coalyard Hill; Chapman, 1974b, and Ruddon’s Point). One possible explanation is that the Elie Ness magmas crystallising garnet and sub-calcic augite did not have the erosive capability to entrain pieces of their sidewalls, but were sufficiently energised at near-Moho levels (possibly due to copious CO₂ exsolution) to disaggregate and transport pyroxenite and ‘anorthoclase suite’ fragments to surface levels.

Significant mineralogical differences within the East Fife cluster may suggest that eruptions sampled the deep lithosphere on length-scales of individual diatremes, as documented in monogenetic volcanoes in modern rift systems, where the distribution of melt is similarly controlled by large-scale lithospheric structures (Rooney et al., 2011). Speculatively, movement along major structures such as the Ardross Fault might have provided a pathway for magmas to traverse the lithospheric mantle, without tearing peridotite from the conduit margins. Nonetheless, evidence for negligible crustal contamination is most readily explained by rapidly ascending magmas exploiting the same pathway—at least from mid to upper crustal levels—with accreted material insulating magmas from crustal contamination (cf. Tepley et al., 2000).

6.4 Implication for physical volcanological emplacement

Our data and petrological constraints provide a ‘cradle-to-grave’ insight into the deep and shallow magma plumbing systems fuelling alkali basaltic maar-diatreme eruptions. Accordingly, the three lithofacies associations (Fig. 1c) capture different stages in the life-cycle of a maar-diatreme volcano (Fig. 12). For instance, LFA1 constitutes vent-filling massive lapilli tuffs, inferred to represent an early eruptive phase driven primarily by magmatic volatiles (Gernon et al., 2013). Given that LFA1 represents progressive infilling and mixing of the diatreme through repetitive eruptive bursts and subsidence of pyroclastic material (cf. Gernon et al., 2009), it is not surprising that these samples show significant variation in chondrite-normalised REE patterns (Figs. 4a–c) and primitive mantle-normalised trace element patterns (Figs. 4d–f).

In contrast, LFA2 (overlying LFA1) shows very little variation in REE and trace element patterns (Fig. 4), which is surprising, given the samples were collected through a sequence of >50 bedded tuffs and lapilli tuffs (Fig. 1c) with a cumulative thickness of >65 m (Gernon et al., 2013). The assemblage of structures and nature of pyroclasts (Gernon et al., 2013) are consistent with small pulsatory phreatomagmatic eruptions (see Lorenz, 1986; White and Ross, 2011), resulting from high-level interactions between ascending magmas and external water. However, volcanism was necessarily driven by magmatic
volatiles (see Sparks et al., 2006) to explain the preservation of unstable mineral phases. Geochemical similarities between a neighbouring vent to the east (S8, Fig. 1c) and the majority of tuff packages from LFA2, supports the hypothesis that many flows were derived from an external source ∼200 m to the east (Gernon et al., 2013).

The late-stage coherent trachybasaltic and basanitic dykes of LFA3 (Fig. 1c) exhibit the most considerable variability in REE and trace element concentrations (Tables 1–2, Fig. 4). These relatively shallow magmas (i.e. ∼22–28 km), containing abundant zoned clinopyroxenes (e.g. Fig. 8), were likely destabilised by deep-sourced basanite magma involved in the eruption of LFAs 1–2 (Fig. 12). Given the abundance of mafic phases including clinopyroxene and amphibole in the LFA3 intrusives, the observed chemical heterogeneity is very likely due to the accumulation of entrained mafic phases—a process invoked to explain similar patterns in Spanish lamprophyres (Ubide et al., 2014). The shift towards effusive activity recorded by LFA3 reflects a lesser role for phreatomagmatism during the waning stages of eruption (Gernon et al., 2013).

7 Concluding remarks

Elie Ness is remarkable for the complex assemblage of lithic inclusions, crystals—and inferentially former melts—signifying a wide range of pressures, temperatures and melt compositions. For all of these components to have been evacuated in the explosive tuff-forming eruptions requires a culminating flux of basanite magma through the subvolcanic plumbing system, that evacuated magmas in differing stages of evolution. We propose that energetic magma flows transport the deep crystals, disaggregate and entrain earlier-formed ‘anorthoclase suite’ xenoliths approximately at Moho levels (produced from several previous replenishments of ‘underplated’ chambers, Fig. 11), and then flush out minor pockets in which preexisting magma batches had been equilibrating at lower pressures (i.e. depths of ∼22–28 km; Fig. 11). Based on the euhedral, unresorbed form of garnets—combined with the preservation state of alkali feldspars and ‘anorthoclase suite’ inclusions—transport from the lithospheric mantle to the surface was necessarily very rapid (order of hours to days) (cf. Canil and Fedortchouk, 1999). An initially explosive phase driven by magmatic volatiles, involving diatreme excavation and pyroclastic infill processes, was followed by pulsatory phreatomagmatic eruptions and a final effusive stage (Fig. 12), with remarkably little bulk geochemical variation occurring throughout the eruptive life-cycle.
Acknowledgements

Gernon was supported by the Clough and Mykura Fund of the Geological Society of Edinburgh, and the Timothy Jefferson Fund of the Geological Society of London. We thank Stuart Kearns and Matthew Cooper for their assistance with the EPMA and XRF respectively. Figure 12 was illustrated by Gary Hincks. We thank Andrew Kerr for his editorial assistance, and Aniko Batki and Teresa Ubide for very helpful comments that greatly improved the manuscript.

References


Gernon, T. M., Gilbertson, M. A., Sparks, R. S. J., Field, M., 2009. The role of


Putirka, K. D., 2008. Thermometers and barometers for volcanic systems. Reviews in Mineralogy and Geochemistry 69 (1), 61–120.

Putirka, K. D., Mikaelian, H., Ryerson, F., Shaw, H., 2003. New clinopyroxene-
liquid thermobarometers for mafic, evolved, and volatile-bearing lava compositions, with applications to lavas from Tibet and the Snake River Plain, Idaho. American Mineralogist 88 (10), 1542–1554.


Scottish alkali basalts: derivatives of deep crustal intrusions and small-melt fractions from the upper mantle. Mineralogical Magazine 73 (6), 943–956.


Zhu, Y., Ogasawara, Y., 2004. Clinopyroxene phenocrysts (with green salite cores) in trachybasalts: implications for two magma chambers under the
Figure Captions

**Figure 1 |** a. Inset map of Scotland showing location of east Fife. b. Simplified geological map of east Fife showing the main diatremes and intrusions, including Elie Ness (EN) and Elie Harbour (EH) (Lst.: limestone; Sst.: sandstone). c. Geological map of the Elie Ness diatreme showing stratigraphy and three lithofacies associations (modified after Gernon et al., 2013). Sample numbers, shown in circles, correspond to sampled locality; note that blue circles signify sampled dykes; numbers shown in red signify samples also used for pyroxene analysis; these were collected from pyroclastic deposits (1L, 5, 14), a basanitic breccia pipe (10) and a trachybasaltic dyke (17). Sample 8 is a tuff from a small neighbouring diatreme ~150 m to the east (not shown). Location of sample 1L is approximate.

**Figure 2 |** a. TAS classification of selected volcanic rocks from Elie Ness (Table 1), plotted alongside published compositions of similar alkaline volcanic rocks in Scotland, of Lower Carboniferous (Smedley, 1988), Upper Carboniferous (Macdonald et al., 1981), and Permo-Carboniferous* (Wallis, 1989) age, and nearby diatremes in east Fife (Chapman, 1976). b. Classification of the Elie Ness volcanic rocks using the Nb/Y vs. Zr/TiO$_2$ diagram of Winchester and Floyd (1977), plotted alongside other Scottish volcanics (Smedley, 1988; Wallis, 1989). *Please note that these represent mean values (see Table 5.1 of Wallis, 1989).

**Figure 3 |** a. Zr–Nb plot (sensu Leat et al., 1986) showing the composition of all Elie Ness volcanic rocks (Tables 1 & 2) determined in this study. For comparison, the compositions of similar diatremes in Limerick, Ireland (Elliott, 2015) and Permo-Carboniferous alkaline volcanics in Scotland (Smedley, 1988; Wallis, 1989) are also shown. b. Zr/Y vs. Nb/Y plot (sensu Fitton et al., 1997) comparing Elie Ness basalts with alkali basalts from the Scottish and Irish Carboniferous (see (a) for key to symbols). Fractional melting curves are shown for spinel and garnet lherzolite according to Fitton et al. (1997).

**Figure 4 |** a–c.: C1 chondrite normalised (McDonough and Sun, 1995) REE plots for LFAs 1–3. d–f.: Primitive mantle-normalised (McDonough and Sun, 1995) multi-trace element distribution diagrams.

**Figure 5 |** Field photographs of (a) a pyrope megacryst from Elie Ness (© BGS); (b) pyroxenitic cumulate, and (c) pyroxenite megacryst coated in a thin layer of juvenile vesicular basalt. All these features occur within a ~65
m thick sequence of pyroclastic (lapilli) tuffs of the Elie Ness diatreme (see Gernon et al., 2013).

**Figure 6** | Photomicrographs of cumulate nodules from the Elie Ness diatreme (photomicrographs are ~2.2 mm wide). a. Coarse kaersutite (Kt) pyroxenite comprising idiomorphic augite (Au) prisms up to 3 mm with patchy zonation; b. amphibole pyroxenite comprising ~50% idiomorphic to subhedral amphibole (<2 mm), augite (pale dull green and present as small “granulated” crystals) and interstitial chlorite (Ch) (after glass) with quench feldspar and spherical globules of calcite surrounded by chlorite; c. sub-spherical ‘ocelli’ of calcite (Ca) with chloritic rims within a coarse amphibole pyroxenite; d. coarse-grained biotite pyroxenite comprising colourless augite and subhedral biotite (Bt); e. amphibole pyroxenite containing large (up to 3 mm) subhe-dral pyroxenes with oscillatory zoning, neoblast-type augites, anhedral kaer-sutite, possible pseudomorphs after olivine, and anhedral late-stage oligoclase (An_{10.2}Ab_{84.8}Or_{5.0}—An_{12.5}Ab_{83.2}Or_{4.3}); f. Idiomorphic augite exhibiting hour-glass zoning within a coarse amphibole pyroxenite (same sample as (c) above).

**Figure 7** | Clinopyroxene classification diagram (Morimoto et al., 1988) of sampled volcanic rocks from Elie Ness (see Fig. 1c for locations).

**Figure 8** | Zoning profiles showing compositional variations within a clinopyroxene crystal (S17-40) from a trachybasaltic dyke (S17, see Fig. 1c); back-scattered electron image; note: c = core, r = rim.

**Figure 9** | Plots a.–e. correspond to pyroxene analyses (n = 634); a. CaO vs. Al_2O_3 plotted for pyroxenes from three samples of pyroclastic lapilli tuffs from different locations across the diatreme (see Fig. 1c), a basanite dyke and a breccia pipe (see Fig. 1c); also plotted are the compositions of pyroxenitic cu-mulates and clinopyroxene crystals from Chapman (1974b), and clinopyroxene megacrysts and xenoliths from Highland intrusions described by Wallis (1989); b. TiO_2 vs. Al_2O_3; c. Al_2O_3 vs. SiO_2; d. Na_2O vs. Al_2O_3; e. MgO vs. FeO. Plot f. showing Na_2O vs. K_2O, is from alkali feldspars in a sample of lapilli tuff (S1L; Fig. 1b).

**Figure 10** | Clinopyroxene compositions of selected volcanic rocks from Elie Ness (see Fig. 1c); a. Mg# vs. Cr_2O_3 (wt.% and Ti (apfu) vs. Al (apfu); d.–f. plot the same variables as a.–c., above, however discriminate the cores (filled symbols, N = 33) and rims (empty symbols, N = 33) of all zoned clinopyroxene crystals (note the change in symbols); e. provides several examples of zoned clinopyroxene crystals and their corresponding compositions. Note that for S5, N = 2; S10, N = 17, S14, N = 5; and S17, N = 9.

**Figure 11** | Cartoon illustrating the deep crustal structure beneath the Midland Valley of Scotland during late Carboniferous to Permian times. (1)
Basaltic parent melt rises from the asthenospheric mantle (~60–70 km), crystallising high-pressure phenocrysts including pyrope garnets, and rapidly ascends to the surface, possibly exploiting lithospheric structures. (2) These magmas then incorporate trapped ‘anorthoclase suite’ pegmatites, representing small fraction melts from large volumes of mantle peridotite. (3) Fuelled by \( \text{CO}_2 \) exsolution, the ‘mixed’ magma rises rapidly entraining xenoliths of lower crustal granulite facies metabasic lithologies, whilst also flushing out pockets of magma that had been equilibrating at lower pressures—principally between 22–28 km. (4) The magma erupts explosively forming a maar-diатreme, driven by magmatic volatiles and later influenced by interaction with meteoric water giving rise to phreatomagmatic explosions. Note GM: geophysical Moho; PM: petrological Moho.

**Figure 12** | Schematic summary of the structure and lithofacies associations of the Elie Ness maar-diатreme, highlighting the key depositional processes and geochemical relationships between the major units; modified after Gernon et al. (2013).

**Supplementary Figure Captions**

**Figure S1** | Backscattered electron (BSE) images (taken with a Cameca SX100 electron microprobe) of zoned clinopyroxene crystals from samples 5, 10 and 17 (sample numbers shown, see Fig. 1c for locations); note the zoning traverses shown correspond to \( \text{Mg}^\# \) profiles in Fig. S2. The horizontal scale bar beneath each image is 100 \( \mu \text{m} \).

**Figure S2** | Normalised zoning profiles showing variations in \( \text{Mg}^\# \) across clinopyroxene crystals depicted in Fig. S1 (note there are no images for S10-18 and S17-81).
Tables

<table>
<thead>
<tr>
<th>Sample No. Lithofacies</th>
<th>S1 Lapilli tuff</th>
<th>S5 Lapilli tuff</th>
<th>S8 Lapilli tuff</th>
<th>S10 Breccia Pipe</th>
<th>S17 Dyke</th>
<th>JA-2 Measured</th>
<th>JA-2 Recom. value</th>
<th>BRR-1 Measured</th>
<th>BRR-2 Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>[w%]</td>
<td>UN1</td>
<td>UN2</td>
<td>UN3</td>
<td>UN4</td>
<td>UN5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TD2</td>
<td>2.16</td>
<td>2.26</td>
<td>2.27</td>
<td>2.77</td>
<td>2.39</td>
<td>-</td>
<td>-</td>
<td>49.28</td>
<td>49.82</td>
</tr>
<tr>
<td>AD2033</td>
<td>15.56</td>
<td>14.74</td>
<td>12.23</td>
<td>14.07</td>
<td>13.54</td>
<td>-</td>
<td>-</td>
<td>1.02</td>
<td>1.03</td>
</tr>
<tr>
<td>MnO</td>
<td>0.25</td>
<td>0.20</td>
<td>0.17</td>
<td>0.47</td>
<td>0.37</td>
<td>-</td>
<td>-</td>
<td>0.10</td>
<td>0.14</td>
</tr>
<tr>
<td>MgO</td>
<td>9.96</td>
<td>8.75</td>
<td>9.39</td>
<td>9.18</td>
<td>10.86</td>
<td>-</td>
<td>-</td>
<td>8.49</td>
<td>8.57</td>
</tr>
<tr>
<td>CaO</td>
<td>6.32</td>
<td>6.97</td>
<td>10.50</td>
<td>8.70</td>
<td>7.08</td>
<td>-</td>
<td>-</td>
<td>11.74</td>
<td>11.95</td>
</tr>
<tr>
<td>Na2O</td>
<td>1.98</td>
<td>1.33</td>
<td>2.00</td>
<td>1.26</td>
<td>1.52</td>
<td>-</td>
<td>-</td>
<td>1.92</td>
<td>1.97</td>
</tr>
<tr>
<td>K2O</td>
<td>2.80</td>
<td>3.32</td>
<td>1.37</td>
<td>4.09</td>
<td>3.37</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>P2O5</td>
<td>0.47</td>
<td>0.69</td>
<td>0.59</td>
<td>0.62</td>
<td>0.53</td>
<td>-</td>
<td>-</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>Total</td>
<td>100.07</td>
<td>98.97</td>
<td>99.70</td>
<td>100.09</td>
<td>100.07</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LCl</td>
<td>9.52</td>
<td>9.54</td>
<td>12.41</td>
<td>4.23</td>
<td>4.57</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(continued)

Table 1

Major and trace element data for selected Elie Ness volcanics, samples 1, 5, 8, 10 & 17 (see Fig. 1c for locations). Major elements measured by XRF and trace elements by ICP-MS at the University of Southampton (see methods). Analyses of International standard JA-2 (Imai et al., 1995) and Southampton internal basalt standard BRR-1 (Murton et al., 2002) are presented with consensus values for these rocks. Further whole-rock analyses of comparable volcanics in this area are reported in Table 5.1 (and the appendix) of Wallis (1989).
Table 2. Trace element data for all other Elie Ness volcanics in this study (see Fig. 1c for locations). Trace elements measured by ICP-MS at the University of Southampton (see methods). Analyses of International standard JA-2 (Imai et al., 1995) and Southampton internal basalt standard BRR-1 (Murton et al., 2002) are presented with consensus values for these rocks.
Table 3. Representative microprobe analysis of clinopyroxene from Elie Ness (see Fig. 1c for sample locations). Asterix denotes crystal shown in Fig. 8.
Table 4
Quantitative pressure and temperature estimates for selected clinopyroxene crystals from Elie Ness, using the barometric and thermometric equations of Putirka (2008).
Lithofacies:

- **Volcaniclastic dykes**: steeply-inclined, discordant bodies.
- **Monolithic breccia**: clast-supported, structureless with angular clasts (block-rich).
- **Bedded (lapilli-) tuffs**: diffuse parallel & cross-stratified, scour & impact structures. Associated with massive, thick-bedded lapilli-tuffs.
- **Basalt tuff breccias**: block-rich, poorly-sorted, clast-supported, with occasional autholiths.
- **Massive autolith-bearing lapilli tuffs**: juvenile vesicular ash grains, pelletal lapilli. Local breccias (MLTb).
- **Massive lapilli tuffs**: locally crudely-bedded, with juvenile scoria. Local breccias (MLTb).
- **Crudely-bedded volcaniclastic tuffs**: sandstone-rich, very heterogeneous. Local breccias (basalt & sand-stone).

---

**Figure 1**

Map of Scotland showing different terranes and geological features. The map is color-coded to distinguish various rock types and features such as dykes, tuffs, vents, and faults.

---

**C** Country rock: cross-bedded sandstones of the "Millstone Grit" Series

- **Bedding**
  - horizontal
  - inclined
  - vertical

- **Faults**
  - observed
  - inferred

- **Folds**
  - synform
  - antiform

- **Dykes**
  - observed
  - inferred

- **Geography**
  - coastline (low tide)
  - beach / embankment

---

**LARGO BAY**

- **SUF**

---

**FIRTH OF FORTH**

- **EH**

---

**Midland Valley Terrane**

- **Grampian Highland Terrane**

---

**Northern Highland Terrane**

- **Hebridean Terrane**

---

**Southern Upland Terrane**

- **EN**

---

**Hebridean Terrane**

- **AF**

---

**Vents**

- **Calc. Sst.**
  - Lower Lst.
  - Upper Lst.
  - Millstone Grit
Generally silica undersaturated

Generally silica-saturated

Generally silica oversaturated

Basalt Basaltic andesite

Andesite Dacite

Rhyolite

Phonolite

Foidite

Phonotephrite

Picrobasalt

Trachyandesite

Phonolite

Trachyte/dacite

Subalkaline basalt

Alkaline basalt

Comendite/pantellerite

Basanite/nephelinite

Na$_2$O + K$_2$O (wt.%)

SiO$_2$ (wt.%)

Zr/TiO$_2$ *0.0001

Nb/Y

Upper Carboniferous Scottish volcanics (MacDonald, 1981)

Lower Carboniferous Scottish volcanics (Smedley, 1988)

Fife vents (Chapman, 1976)

Permo-Carboniferous Scottish volcanics* (Wallis, 1989)

LFA1

LFA2

LFA3

this study

Figure 2
Figure 3

Scottish volcanics (Smedley, 1988)
Scottish volcanics (Wallis, 1989)
Limerick diatremes (Elliott, 2015)

LFA1
LFA2 (this study)
LFA3

Scottish volcanics (Wallis, 1989)

Figure 3
Figure 4

(a) LFA1

(b) LFA2

(c) LFA3

(d) LFA1

(e) LFA2

(f) LFA3
Figure 7

- **LFA2**: S1L (lapilli tuff) and S14 (lapilli tuff)
- **LFA3**: + S10 (basanitic pipe) and S17 (trachybasaltic dyke)

- Points represent samples with compositions:
  - **Wo**: 0-100
  - **En**: 0-100
  - **Fs**: 0-100

- Key minerals:
  - Diopside
  - Hedenbergite
  - Augite
  - Pigeonite
  - Clinoenstatite
  - Clinoferrrosilite

- Sample count: n = 634
Figure 8

[Graph showing the distribution of Na₂O, CaO, Mg#, Al₂O₃/TiO₂ along the distance (μm) from c to r, with a 100 μm scale.]
Figure 9

Al₂O₃ (wt.%)
MgO (wt.%)

0 5 10 15

6 8 10 12 14 16 18 20

16 18 20 22 24

S5 (lapilli tuff)
S14 (lapilli tuff)

Al₂O₃ (wt.%)

FeO (wt.%)

Na₂O (wt.%)

K₂O (wt.%)

y = 11.6 - 0.7x
R² = 0.94

LFA2

S1L (lapilli tuff)
S14 (lapilli tuff)
S5 (lapilli tuff)
LFA3

Pyroxenitic cumulates
Cpx. crystals
Cpx. megacrysts & xenoliths (Wallis, 1989)
Scotland c. 290 Ma

Maar diatreme eruptions

Figure 11

Depth, km

0

20

40

60

70

Lithospheric mantle

Lower crustal granulite facies metabasic rocks

Layered ultramafic cumulates

Sp. lherzolites

GM

PM

Lithospheric mantle

Asthen. mantle

Parent melt (small fraction)
Mass-wasting of maar-crater walls

Contamination of Elie Ness by pyroclastic surges from neighbouring vent

LFA1 | vent-filling massive lapilli tuffs | considerable variation in REE and trace element patterns

LFA2 | pyroclastic surge deposits | remarkably consistent REE and trace element patterns

LFA3 | late-stage intrusives and breccia pipes | most geochemically diverse LFA (entrained mafic phases?)

S8 | neighbouring pipe | geochemically near-identical to LFA2

Figure 12