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Peralkaline Phonolites: Genesis, Magmatic Evolution, and Crustal Storage History

Running title: Evolution of peralkaline phonolites

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ABSTRACT
Peralkaline phonolites are the most evolved products of the evolution of Si-undersaturated magmatic suites. They can be important components of extrusive sequences globally, occurring in all major tectonic settings. Here we review aspects of their petrogenesis and evolution, including their ultimate mantle sources and polybaric liquid-lines-of-descent. There are three main compositional lineages: (i) mafic nephelinite–phonolite, (ii) basanite–phonolite, and (iii) alkali basalt–phonolite. In the majority of cases, the dominant differentiation mechanism has been fractional crystallization. There is no strong evidence for phonolite formation by partial melting of alkali basalts deep in the crust, or for significant crustal contamination. Attention is drawn to the extreme compositions generated by protracted fractionation, with Peralkalinity Indices ≤18. Several natural systems are used to describe the range of high-level magma reservoirs and the internal differentiation processes. Volcanic hazards and the potential environmental impact of eruptions are assessed and the economic potential of phonolites introduced.

Keywords: peralkaline phonolites; tectonic settings; magmatic lineages; extreme compositions; volcanic hazards; economic potential

INTRODUCTION

Macdonald et al. (2021) presented a review of the peralkaline silicic extrusive rocks with a view to assessing, *via* aspects of their formation and evolution, and their importance in the volcanological record. This contribution extends the compositional range of the review to Si-undersaturated parageneses, in particular those that include peralkaline phonolites, the phonolites being broadly equivalent to the rhyolites of the earlier review. It focusses on aspects which complement that review, in following the various evolutionary stages from mantle melting to eruption.

Phonolites occur in hundreds of localities worldwide, being recorded in all major tectonic settings. The complex petrogeneses which the magmatic suites exhibit are providing valuable insights into the nature of, and processes within, their mantle source regions and crustal reservoirs. They can form substantial volumes of eruptive material. For example, the so-called Plateau Phonolites of Kenya (14–11 Ma) have a total volume estimated at 40,000–50,000 km^3 and covered an area of about 40,000 km^2 (Lippard, 1973a). The petrologically and economically important agpaitic plutonic complexes are formed from phonolitic magmas. Phonolites also have some real implications for volcanic hazards, including major threats to life and property. Two of the deadliest eruptions in recorded history, Vesuvius 79 AD and Tambora 1815, were of phonolite-bearing systems. There are also associated

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environmental issues such as effects on climate and the economic potential of phonolites remains to be explored.

A note on nomenclature issues is required here. Many classification schemes of Si-undersaturated suites are based on combinations of compositional and mineralogical data. For example, the term “nephelinite” has been used to refer to rocks with MgO >10 wt% and those with MgO <1 wt%. Phonolites are defined in the TAS classification scheme as occupying a specific area on a total alkalis-SiO_2 plot (Le Bas, 1989). Zaitsev et al. (2012) define phonolite as a volcanic rock containing alkali feldspar and any feldspathoids. The description of a suite as nephelinite – phonolite can, therefore, encompass a large range of compositional variants and phenocryst assemblages. Here we use the term phonolite as referred to in the original papers, accepting that the compositional ranges may be somewhat different in different suites. In some suites, the peralkaline phonolite occurs only as melt inclusions or interstitial glasses and the term is not used as a lithological component. Nevertheless, these systems have evolved to the phonolitic stage and are deemed relevant to this review.

Compositional modifications

As for peralkaline silicic rocks, phonolites have a tendency to be compositionally modified by near-solidus crystallization, devitrification and secondary hydration, important changes including significant loss of Na and F and oxidation. The problem of Na loss is particularly applicable to secondarily hydrated. pumices. For example, in the Furninha Tephra zoned phonolitic deposit, Cape Verde, a positive correlation between oxide totals and Na_2O wt% (Eisele et al., 2016), albeit a little scattered, is consistent with some loss of Na during secondary hydration. Addition of 0.35 wt% Na_2O to the average of five analyses of the 79 AD phonolitic white pumice, Vesuvius (Cioni et al., 1995, Table 1, anal. 1), which have an average of 3.23 wt% LOI, would change the composition from *an*- to *ac*-normative in some melt inclusions in sanidine and leucite. A negative correlation between Na_2O and H_2O+ (≤4.78 wt%) shown by analyses of the Yatta phonolite, Kenya (Wichura et al., 2010) also points strongly to Na loss during hydration. Bryan (2006) acknowledged Na mobilization in the Granadilla phonolites, Tenerife, which have up to 14.83 wt% LOI. Similarly, Holm et al. (2006) recognized the effects of alteration in pyroclastics of Santo Antão, Cape Verde. Thus, the attainment of peralkalinity in certain suites, and details of their further evolution, may be masked by alteration.

	1	2	3	4	5	6
wt%						
SiO_2	38.31	39.02	39.92	43.30	43.80	37.24
TiO_2	3.93	2.93	5.29	2.39	2.65	3.71
Al_2O_3	7.22	10.84	11.46	12.11	12.90	11.04
FeO*	13.27	11.11	12.36	12.69	11.43	11.86
MnO	0.20	0.18	0.18	0.20	0.18	0.71
MgO	15.38	13.18	13.25	12.55	10.40	12.03
CaO	12.88	14.35	10.13	11.25	9.75	15.11
Na_2O	2.67	2.80	2.91	3.27	3.45	3.14
K_2O	1.48	1.31	2.50	1.28	1.03	0.94
P_2O_5	0.91	1.76	0.93	0.63	0.50	0.82
CO_2	0.11					
H_2O	1.59			0.34		
LOI		1.42			1.98	1.69
Sum	97.95	98.90	98.93	100.01	98.07	98.29
FeO* = total Fe as Fe^{2+}						
Mg#	67.4	67.9	65.6	63.8	61.9	64.5
Ni (ppm)	368		321		270	123
Na_2O/K_2O	1.80	2.14	1.16	2.55	3.35	3.34

Table 1. Compositions of primary magmas

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TECTONIC SETTINGS

In the following sections, we assess whether phonolite-bearing suites are associated with a particular tectonic setting or settings and therefore with a specific type of mantle or crust. We also explore the nature of the mantle sources and the conditions under which the primary magmas formed.

Important data sources are the global list of phonolite occurrences at mindat.org/min-48540.html, while Jeffery and Gertisser (2018) have provided a comprehensive review of peralkaline occurrences on Atlantic oceanic islands. The sequences described below were selected because they have features of particular volcanological or petrogenetic significance which are used for discussion in later sections.

Continental intraplate settings

The African continent hosts major occurrences of Si-undersaturated suites. The main occurrences are associated with the Eastern African Rift system in Ethiopia, Kenya/Uganda, and Tanzania, and therefore in areas of domal uplift and active rifting, perhaps plume-related. Three types of phonolites occur in central Kenya. As noted above, the Plateau Phonolites (mid-Miocene) have a total volume estimated at 40,000-50,000 km^3. According to Lippard (1973a), they exceed the total volume of phonolite lavas found elsewhere in the world by several orders of magnitude. In a three-dimensional magnetotelluric study of the Baringo-Bogoria area of central Kenya, Hautot et al. (2000) modelled a resistive layer between 1.5 and 4-5 km depth which they correlated with the Plateau Phonolites. The combined extrusive and intrusive activity made a very significant contribution to crustal growth. The situation has clear analogies with Large Igneous Provinces (LIP), which consist of multiple, rapidly emplaced, large-volume eruptions, each of the order of 10^2-10^3 km^3 of magma (Deegan et al., 2023). The second, so-called Kenya-type phonolites, were erupted in the central rift from the Miocene to Recent; they occur in central volcanic piles and as sequences of flood lava sheets. The third, Gwasi-type (22 Ma–Recent), form minor intrusions and flows associated with nephelinitic volcanoes. In southern Kenya, the nephelinite-carbonatite volcano Shombole has evolved through to phonolites (Peterson, 1989). In Tanzania, magmatism can be divided into two groups; (i) a pre-1-2 Ma alkali basalt-phonolite group, including Tarosero (Braunger et al., 2021), Ngorongoro and Kilimanjaro; and (ii) a post-1-2 Ma nephelinite-phonolite carbonatite group, including the Meru and Kerimasi volcanoes (Dawson, 2008). It also includes Ol Doinyo Lengai (Figure 1a), the only active carbonatite volcano in the world, whose flanks are dominated by nephelinites and phonolites.

Alkaline suites of late-Cretaceous - Paleogene age are widespread throughout western Africa from Namibia to the southern tip of the continent, a distance of 1500 km. They form hundreds of bodies, each generally <0.1 km^3 in volume, including several phonolite occurrences (Marsh, 1987). It is uncertain whether the magmatism was related to mantle plumes or broad epeirogenic uplift (Marsh, 2010). The late Cenozoic Marie Byrd Land volcanic province, Antarctica, lies across an active volcano-tectonic zone which LeMasurier et al. (2018) consider to be one of the world’s major continental rift systems. The province includes 18 large central volcanoes, eight of which have erupted phonolites. In five of the six shield volcanoes in Marie Byrd Land, phonolitic and pantelleritic lavas have been erupted contemporaneously, or at closely spaced intervals, pointing to contemporaneous generation beneath the volcanoes (LeMasurier et al., 2011). Both magma types were available throughout the ~15 Ma history of the centers. The Mt Erebus volcano in Marie Byrd Land, Antarctica is distinguished by having an active phonolitic lava lake containing 30-40% alkali feldspar phenocrysts (Figure 1b). In the United States, notable occurrences of phonolite are Devils Tower, Missouri Buttes, and the Barlow Canyon area, Crook County, Wyoming, Cripple Creek, Colorado, Balcones magmatic province, Texas, and Beemerville, New Jersey. The Devils Tower intrusion contains peralkaline varieties (Halvorson, 1980) and is one of the most famous landmarks in the American West (Figure 1c).

Among the abundance of alkaline rocks in southern Brazil there are ten agpaitic complexes (Gomes et al., 2021). The largest is Poços de Caldas, a Mesozoic, 33 km wide body consisting mainly of phonolites and nepheline syenites, but with associated ankaratrites and a possible carbonatite. There are

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mineralized pegmatite veins and local, intensive, hydrothermal potassic alteration (Schorscher and Shea, 1992; Guarino et al., 2021). This important complex must be a focus for continued detailed study.

The Late Cretaceous – Holocene Central European Volcanic Province (CEVP) is a trans-European uplift-rift related system which includes several associations of melilitites, foidites or basanites and phonolites (Lustrino and Wilson, 2007). Occurrences in Germany include the Eifel, Vogelsberg, Heidburg, Katzenbuckel, Kaiserstuhl and Hegau volcanic regions (Figure 1d). The Velay volcanic province, Massif Central, France, contains a suite extending from basalts to peralkaline phonolites, including the Suc de Sara dyke, where Pereira et al. (2024) have made a detailed study of melt segregation effects. The Cenozoic Saghro lavas were emplaced in the Anti-Atlas belt of Morocco, part of the West African craton, which formed during the prolonged collision of the African and Eurasian plates beginning at ~80 Ma. (Berger et al., 2009). The nephelinite-peralkaline phonolite suite is among the most Si-undersaturated and alkali-rich of the entire West African Cenozoic volcanic province, including the Canary Islands. The tectonic setting is uncertain, but may have been related to a tectonic control during building of the Atlas Mountains.

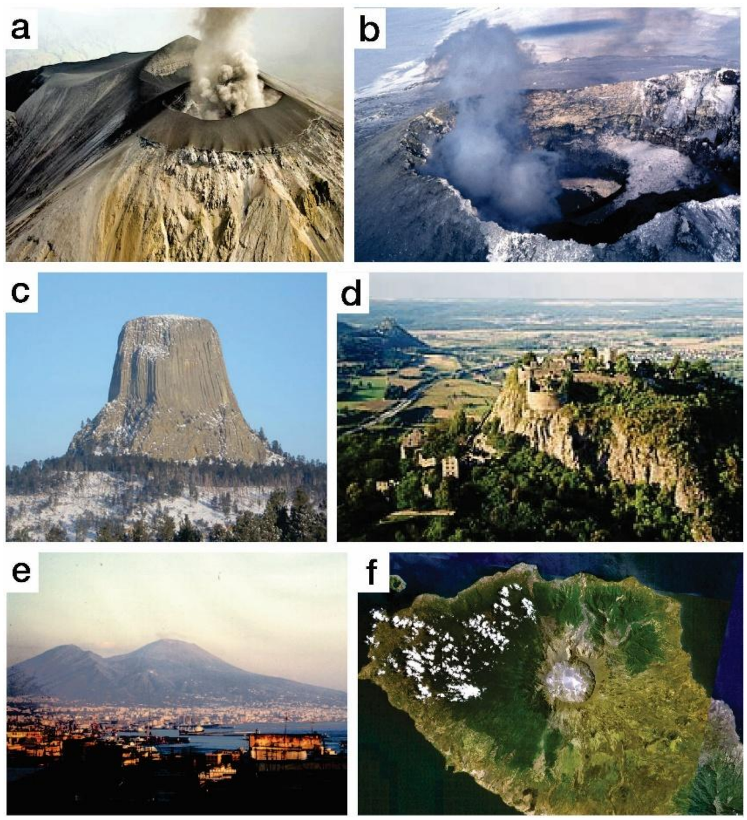

Figure 1

(a) Ash eruption from Ol Doinyo Lengai volcano, Tanzania, seen on 12 March 2008: from the NNE photo by Benoit Wihelmi, 2008 public domain. (b) Degassing at Mt Erebus. Antarctica. GVP image. Smithsonian Institution, public domain. The lava lake is ~200 m wide. (c) Devils Tower, Wyoming, U.S.A. National Park Service image, public domain. (d) Phonolite plug capped by ruined castle, Hohentiel, Hegau, Germany. (e) Somma-Vesuvius volcanic complex viewed over the Bay of Naples. Vesuvius on the right, Somma on the left. Photo; H.E. Belkin, 1975. (f) Tambora volcano, Sumbawa Island, Indonesia. NASA Landsat mosaic by R. Waitt (U.S. Geological Survey), public domain. The caldera is 6 km wide.

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Oceanic islands

Phonolites have been recorded on islands in the Atlantic, Pacific and Indian Oceans, occupying various structural settings. Occurrences in the Atlantic Islands have been reviewed in considerable detail by Jeffery and Gertisser (2018).

The Canary Islands in the NE Atlantic have been related to mantle plumes rising from the core-mantle boundary into the African plate from late Jurassic to Recent times (Hoernle et al., 1995). The recent eruptive history of Tenerife has included the eruption of zoned phonolitic ignimbrites from Las Cañadas Volcanic Edifice, including the Granadilla deposit (600 ka; Bryan (2006)), the El Abrigo caldera-forming eruption (170 ka; Gonzalez-Garcia et al. 2022) and that of Montaña Blanca (~2 ka; Ablay et al.,1995).

The Cameroon Hot Line is a NE-SW-trending tectonomagmatic lineament which penetrates from the Atlantic Ocean into the African continent. It is, therefore, a unique example of an active alkaline alignment developed on both the oceanic and continental domains (Déruelle et al., 2007). Geophysical studies in the oceanic sector have suggested that lithospheric uplift promoted decompression melting and uplift of melts along reactivated fractures related to the opening of the central Atlantic Ocean. Holm et al. (2006) proposed that primary magmas of the Cape Verde Islands were generated in a compositionally heterogeneous, convecting mantle, with no lithospheric input. The heterogeneity was detected in the magma compositions changing with time; for example, magma compositions on Santo Antão from 7.5 to 0.1 Ma changed from an early basanite-phonolite series to a melilite nephelinite-phonolite series. The archipelago of Fernando de Noronha forms part of a chain of seamounts extending eastwards from the Brazilian mainland. Magmatism on the island of Fernando da Cunha has been related to intermittent melting of an enriched mantle source in a “hot spot” (Lopes and Ulbrich, 2015). The island of Trindade lies on an emerged part of the E-W trending Vitória-Trindade Ridge, thought to represent the track left by the Trindade mantle plume on the overlying South American Plate (O’Connor and Duncan, 1990).

In oceanic islands, phonolites usually constitute only a few percent by volume of the volcanic sequences. A notable exception is the island of Brava, in the Cape Verde Archipelago, where phonolites constitute 85% of the eruptives (Madeira et al., 2010). The magmatism was related to a mantle plume impinging on the lithosphere. Another exception is Ua Pou island in the Marquesas, Pacific Ocean, where phonolites cover 65% of the surface (Legendre et al., 2005). The magmatism was related to the movement of the Pacific Plate over a hot spot. Rarotonga, the largest of the Cook Island group in the Pacific, is located near the northwestern end of the Cook-Austral chain, a lineament related, not to a plume-fed hot-spot, but reflecting the intersection of three compositionally distinct mantle sources (Jackson et al., 2020). The island of Kaula is the only center on the Hawaiian Ridge that has erupted phonolites (4.2-4.0 Ma), including peralkaline varieties (Garcia et al., 1986). They erupted during a post-erosional stage of volcanism, similar to other volcanoes on the ridge. Volcanoes of the Comores Archipelago, Indian Ocean, which include Anjouan, may have been built up on a lithospheric plate moving across a hot spot (Flower, 1973). Anjouan contains suites derived from three parental mafic magmas; basanite, alkali basalt, and hypersthene-normative basalt.

Subduction-related

While occurrences of phonolites are uncommon in this setting, two eruptions have been very significant in volcanology. The stratovolcano Somma-Vesuvius, on the west coast of Italy, is part of the Campanian volcanic arc, formed by the convergence of the oceanic sector of the African plate beneath the continental Eurasian plate. Its prime claim to volcanological fame is the eruption of 79 AD which buried the Roman cities of Pompeii and Herculaneum (Figure 1e). The volcano Tambora (Sumbawa, Indonesia) (Figure 1f) is located in the complex zone of convergence of the Sunda and Australian plates. The eruption in 1815 was one of the largest explosive eruptions in historical times, erupting some 30-33 km^3 of trachyandesite-trachyphonolite magmas, largely as alternating or simultaneous

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pumice falls and pyroclastic flows. The most differentiated compositions, preserved as melt inclusions in plagioclase, were phonolitic (Gertisser et al., 2012).

The island of Ischia, in the Gulf of Naples, has erupted lavas and pyroclastics of shoshonitic and peralkaline (trachy)phonolitic composition (Melluso et al., 2014). Some of the phonolites carry such agpaitic minerals as aenigmatite, aegirine and lavenite. Despite the geographical proximity to Vesuvius, the Ischian rocks have sodic tendencies and evolved in a different reservoir.

NATURE OF MANTLE SOURCES

Attempts to determine more fully the nature of the mantle sources of Si-undersaturated suites have mainly used isotopic and trace element compositions of eruptive suites. Various combinations of mantle types have been invoked. The Cameroon Hot Line asthenospheric source had DM (Depleted Mantle) and FOZO (Focus Zone) components (Déruelle et al., 2007), that at Trindade had DMM (Depleted MORB Mantle) or N-MORB (normal-mid-ocean Ridge Mantle) with subordinate EM1 (Enriched Mantle I) signatures (Marques et al., 1999). According to Legendre et al. (2005), the lithospheric mantle source of the Marquesas magmas has both EMII (Enriched Mantle II) and HIMU (High U/Pb ratios) signatures. The plume-derived Santo Antão source has HIMU-OIB components which have varied in proportions with time (Holm et al., 2006). The mantle source for the volcanism on Fernando de Noronha is similar in trace element characteristics to the "typical" OIB source (Weaver, 1990). In Antarctica, Mt Sidley magmas were generated in lithosphere with HIMU-OIB components affected by a mantle plume (Panter et al., 1997). According to Keller et al. (2006), magmas of the Ol Doinyo Lengai volcano in Tanzania have been generated in mantle sources comprising a mixture of HIMU- and EM1-like components. The mantle sources of the Plateau Phonolites in Kenya had HIMU and EM1 and EM2 components (Hay et al.,1995a).

It appears, therefore, that the generation of the primary magmas of Si-undersaturated suites is not critically dependent on the trace element and isotopic characteristics of the sources, although the details of the minor element compositions will influence subsequent formation and fractionation of accessory phases such as titanite and apatite. The sources are broadly similar to those of the peralkaline silicic rocks (Macdonald et al., 2021). However, it has long been known that Si-undersaturated suites are commonly associated with carbonatites (Brögger, 1921). Some recent examples of the association include the Saghro Cenozoic lavas (Berger et al., 2009), East African Rift, Tanzania (Dawson, 2008), Brava Island (Weidendorfer et al., 2016), and the Marie Byrd Land province (LeMasurier et al., 2018). Holm et al. (2006) noted that five of the ten major Cape Verde Islands contained carbonatites, which they suggested is a unique feature of the magmatism. The importance of the presence of CO_2 at the site of melting is that it not only lowers the degrees of partial melting, but makes the initial melts more Si-undersaturated. The role of carbonates in the formation of Si-undersaturated magmas contrasts with that in the oversaturated equivalents; whereas CO_2 may be present in the magmagenesis of silicic suites, it is not normally critical. Furthermore, we are unaware of any *direct* occurrence of a peralkaline silicic suite with carbonatites.

Primary magmas and melting regimes

Estimates from mineral – melt thermobarometry are the main tool used to assess the P-T conditions of formation of primary magmas. The compositions of the partial melts and their variation with P-T-aH$_2$O-aCO$_2$ have also been explored via high P-T experiments on peridotites. As an indication of the range of compositions, selected rocks considered by the original authors to be possible (near-) primary magmas are listed in Table 1. Mg# range from 61.9 to 67.9, Ni contents from 123 to 368 ppm, and SiO_2 from 37.2 to 43.8 wt%. The abundance of P_2O_5 varies from 0.50–1.76 wt% and Na_2O/K_2O ratios vary from 1.2 to 3.5.

The estimated degrees and depths of melting are also variable. On the basis of entrained ultramafic xenoliths, Martin et al. (2013) proposed that the basanite-phonolite magmas of Mount Morning,

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Antarctica, were generated by fractional crystallization in reservoirs within the lithospheric mantle. The presence of mantle-derived fragments and xenocrysts in the Heldburg Phonolite, Germany, led Irving and Price (1981) and Grant et al. (2013) to suggest that the phonolite was formed within the mantle by fractionation of basanitic magma. A similar genesis was proposed for the Phonolite Hill body, Australia, by Irving and Price (1981). Lavas bearing lherzolite xenoliths from Anjouan, with Mg# (100 Mg/(Mg+Fe^{2+}) atomic)) up to 70, were considered by Flower (1973) to be direct mantle-derived melts. According to Holm et al. (2006), primary magmas of Santo Antão were formed by 1–4% melting of peridotite at depths of 90–120 km. The inferred magmas had >12% MgO, but they cautioned that some might be partially olivine-cumulitic. Generation of primary basanitic magmas at Mt Erebus was by partial melting of a five-phase lherzolite at between 4.5 kbars at 1100 °C and 11.2 kbars at 1200 °C, with temperatures based on mineral chemistry (Oppenheimer et al., 2011). Primary basanitic magmas at Mt Sidley formed by ≤2% melting of an asthenospheric source (Panter et al., 1997). Keller et al. (2006) identified olivine melilitites as the primary magmas at Ol Doinyo Lengai, formed by low degrees of melting in the asthenospheric mantle. Primitive melilititic-nephelinitic magmas of the Hegau volcanic region (Central European Volcanic Province) were produced by low-degree partial melting of an amphibole ± phlogopite-bearing garnet peridotite in the upper asthenosphere or lower lithosphere (Binder et al., 2024. Loges et al. (2019) proposed that phonolites from the Spitzberg volcano (CEVP) were formed in several steps. In an initial step, (tephri-) phonolitic melt was formed by reaction between a carbonatitic melt and mantle lherzolite. The silicate melt segregated into a body of unknown size and location. A later pulse of basanite into the body brought to the surface portions of a phonolite-sanidine crystal mush. Suites that can generate phonolitic melts can, therefore, be formed over a wide range of mantle conditions and degrees of melting.

The formation of phonolitic melts by partial melting of lherzolite was demonstrated experimentally by Laporte et al. (2014). They found that phonolites were formed by 0.3– 3.0 wt% melting, depending on the K_2O content of the source lherzolite, at pressures from 1.0–1.5 GPa. They postulated that when a large volume of mantle is enriched in K, low-degree melts resulting from extension could be extracted, yielding bodies large enough to reach the upper crust. This would require the phonolites traversing a range of crustal lithologies with which they are massively out of equilibrium.

MAGMATIC LINEAGES

This section describes the liquid-lines-of-descent of selected magmatic suites involving phonolites. There are basically three magmatic lineages leading to phonolite melts; we have selected eight representative suites to show the variations within and between the lineages and to cover the main tectonic settings; (1) mafic nephelinite–foidites–phonolite (Saghro (Berger et al., 2009); Fernando de Noronha (Weaver, 1990); (2) basanite–phonotephrite–tephriphonolite–phonolite (Santo Antão (COVA suite; Holm et al. 2006); Mount Sidley (Panter et al., 1997); Mt Erebus (Kyle et al., 1992); Anjouan (Flower, 1973), and (3) alkali basalt–hawaiite–mugearite–benmoreite–trachyte–phonolite (Rarotonga high-silica suite; (Thompson et al., 2001); Ua Pou (Bishop and Woolley, 1973).

A common feature of Si-undersaturated systems is that they comprise two or more lineages (Thompson et al., 2001; Holm et al., 2006; Eisele et al., 2016; Wiedendorfer et al., 2016). The different suites may have been erupted at different times during the activity, or may have overlapped in time (Eisele et al., 2016). Whichever, two (or more) mantle sources may have been involved during the activity, or the suites evolved with different volatile contents. For the present discussion, we have specified for each two-source center, which suite we have used. The discussion is divided into two broad sections: mafic parents to phonolites and variations within phonolites.

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Mafic parents to phonolites

Major and minor compositional variations in the suites are shown as MgO plots (Figure 2 a–l). A cursory glance at the plots shows that although all generated peralkaline phonolitic end-members, the evolutionary paths were all to some extent unique.

MgO-SiO_2 trends (Figure 2 a,e,i), are either flat, or increase gently, to MgO values ranging from 4–2 wt%, then increase more steeply to SiO_2 values of 55–60 wt%. Most Al_2O_3 trends (Figure 2 b,f,j) show steady increases with decreasing MgO, with some minor kinks (e.g., at 10 wt% MgO in the Saghro suite). CaO trends vary between the type of suite; in mafic nephelinite-phonolite suites, Ca peaks sharply at high MgO values. In basanite-phonolite suites, it shows fewer sharp peaks at 10 and 6% MgO, whereas in alkali basalt-phonolite suites, it decreases linearly after the peak stage. All trends converge at 1–2 wt% CaO. MgO-FeO* trends (Figure 2 d,h,l) are rather flat in some suites, for example to 7 wt% MgO in Santo Antão and Erebus, steadily decrease in others (Ua Pou), and then drop in all suites down to 3 wt% FeO*. MgO-TiO_2: trends (Figure 2 c,g,k) show gentle decreases (Erebus), increases (Santo Antão, Ua Pou), or are flat (Saghro, Mt Sidley), to MgO values between 6 and 8 wt%, followed by decreases to minimum values around 0.5 wt% TiO_2. In contrast, Fernando de Noronha drops continuously from 14.5 to <0.5 wt% MgO.

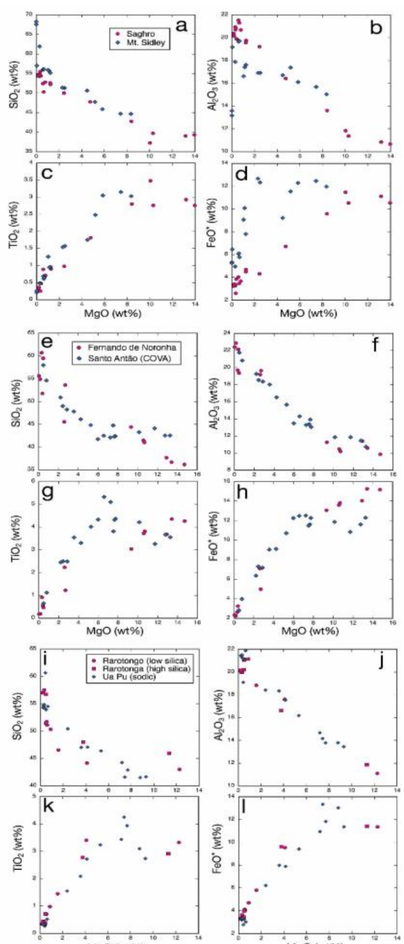

Figure 2
MgO (wt%) plotted against selected oxides for representative suites to show the range of liquid-lines-of-descent.

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The majority of MgO-Na_2O trends show gentle increases for much of the range, with steeper decreases to low MgO values. However, there is considerable scatter at values <2 wt% MgO, at least partly due to Na loss during alteration. MgO-K_2O trends show gentle increases to different MgO values in the range 1–6 wt%), then are steeper to 4.5–6.5 wt% K_2O. MgO-P_2O_5 trends increase variably to peaks at 11–4% MgO and then decrease to nearly zero.

The different trends are a result of different phenocryst assemblages, themselves a function of the composition of the primary magma and the P-T-P_{vol}. history during ascent, for example, the early stages at Saghro were dominated by olivine and clinopyroxene fractionation, accompanied by minor Al-spinel and Ti-magnetite, joined later by alkali feldspar and nepheline (Berger et al., 2009). The compositions of nosean phonolites of the Hegau region (14–11 Ma) can be modelled by fractional crystallization of oxyspinel, olivine, clinopyroxene, mica, feldspathoids, feldspar, titanite and apatite from melilititic-nephelinitic magmas, under relatively oxidizing conditions, fO_2 = FMQ+3 (Binder et al., 2024). The basanite-phonolite sequence at Mt Sidley was generated by fractionation of diopside, olivine, plagioclase, titaniferous magnetite, nepheline ± apatite (Panter et al., 1997). At Rarotonga, the transition from alkali basalt to phonolite was a result of kaersutite + titanaugite + FeTi oxides + plagioclase + apatite fractionation, followed in the phonolites by crystallization of anorthoclase + nepheline + aegirine-augite + FeTi oxides (Thompson et al., 2001).

One aspect of the phenocryst assemblages in Lineages 1 and 2 has received rather scant attention here, *viz.* the occurrence of feldspathoids, including analcite, cancrinite, hauyne, leucite, nepheline, nosean and sodalite. The stability relationships between them are very complex, being functions, *inter alia*, of the nature of the volatiles coexisting with the melts. As such, the phases can in principle be used to trace the role of the volatiles during magma evolution, for example, aCO_2 for cancrinite and aSO_2 for nosean. Unfortunately, very few studies of this kind have been published. A further rationalization used here is that fractionation models have almost invariably ascribed a minor role to the feldspathoids. An exception are the phonolites of the Hegau region, where the fractionation from parental melilitites-nephelinites to phonolites involved removal of up to 9% (unspecified) feldspathoids (Binder et al., 2024).

Within phonolites

Thompson and MacKenzie (1967) appreciated that the Si-undersaturated part of the system $NaAlSO_4$-$KAlSiO_4$-SiO_2 was not a residual system for peralkaline melts. Continued crystallization of alkali feldspar and nepheline would drive melts into peralkaline space better represented by the system $(Na,K)AlSi_3O_8$-$(Na,K)AlSiO_4$-Ac-Ns, where Ac is acmite and Ns is sodium metasilicate. Information that such extended melt trends exist has come from natural rocks and experiments. Andersen et al. (2014) suggested that the maximum Peralkalinity Index (P.I.) reached by most Si-undersaturated suites is 2.5. In their compilation of data from oceanic islands, Jeffery and Gertisser (2018) recorded a maximum P.I. of 1.96, and in the suites discussed above the P.I. values are <1.2. Braunger et al. (2021) described at Tarosero what they termed “agpaitic phonolites” with P.I. up to 1.27. Petrovsky et al. (2012) reported eudialyte-bearing phonolites with P.I. up to 1.5 from the Late Devonian Kontozero carbonatite palaeovolcano, Kola Peninsula. They suggested that the phonolites could represent the melts from which the Lovozero agpaitic complex formed.

However, there are occurrences where higher P.I. values have been recorded. Donaldson and Dawson (1978) reported a pyroxenite nodule from Ol Doinyo Lengai containing residual glass with P.I. up to 5.0. Zaitsev et al. (2012) recognized at Sadiman volcano two subtrends, reaching P.I. > 6.0 and 3.4–4.3 respectively. The phonolite used in experiments by Giehl et al. (2013) has a special significance in that it may represent the parental magma of the Ilímaussaq intrusion, the prime example of an agpaitic complex. The experiments were conducted at T = 950–750 °C, P = 100 MPa, and fO_2 ~Δlog FMQ -3 to +1, and with water contents varying from anhydrous to water-saturated. Under low fO_2 and low aH_2O conditions, the phases synthesized closely matched the natural phenocryst assemblage, *viz*. alkali feldspar, nepheline, hedenbergitic pyroxene, fayalitic olivine and magnetite. The residual melts were driven to increasing peralkalinity (P.I. ≤3.55). In that the lowest temperature experiments (750 °C) still contained 32% glass; it is highly likely that the last few percent of melt would have had much higher P.I..

There are rare cases where fractionation has driven residual melts to extreme peralkalinity. Natural examples include interstitial glasses, melt inclusions in phenocrysts and petrographic proxies. A peralkaline nephelinite (SiO_2 44.13 wt%, P.I. 2.15) from Ol Doinyo Lengai crystallized combeite-sodalite-nepheline-clinopyroxene-titanite-apatite, with enrichment in Na, Fe, Ti, Ba and Sr (but not Si or Al), resulting in a groundmass containing Ba-lamprophyllite, delhayelite and a silicate glass with P.I. up to 15.75 (Dawson and Hill, 1998, Figure 3a). Leucite nephelinites from Nyiragongo volcano contain globules of glass with P.I. up to 18, coexisting with a suite of uncommon minerals including delhayelite (Andersen et al., 2014, Figure 3b). Donaldson and Dawson (1978) reported a pyroxenite nodule from Ol Doinyo Lengai containing residual glass with P.I. up to 5.0 (Figure 3c). Melt inclusions in nepheline from Sadiman have P.I. ≤ 8.9 (Zaitsev et al., 2012). Berger et al. (2009) described, in nephelinites of the Saghro lavas, interstitial "microdomains" comprising nepheline, Sr-rich fluorapatite, sanidine, aegirine and accessory delhayelite (Figure 3d). These are taken as analogues of the Nyiragongo glasses.

Aspects of the compositional variations with P.I. are shown in Figure 4a, b. The sharp drop in Al and increase in Fe is due to very extensive alkali feldspar and nepheline fractionation, as demonstrated experimentally on an Ilímaussaq phonolite by Giehl et al. (2013).

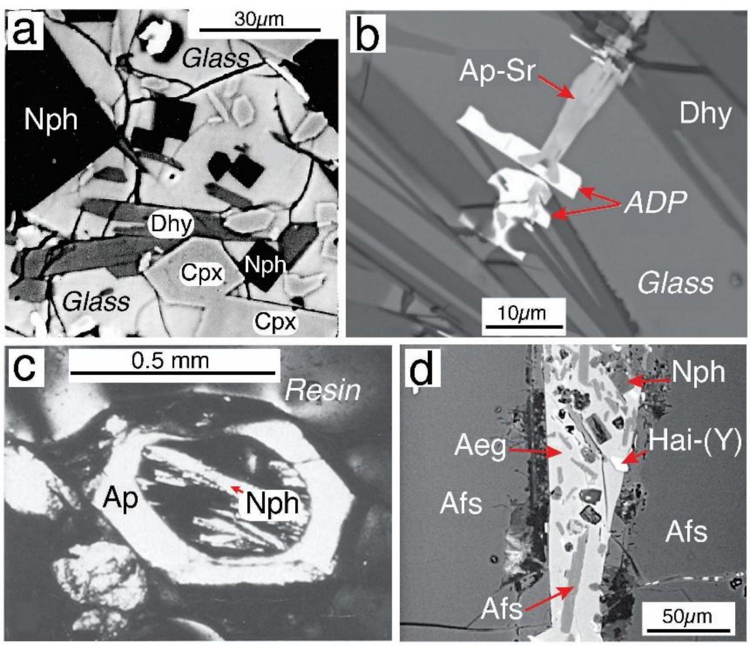

Figure 3

Examples of strongly peralkaline residual melts in phonolitic hosts. (a) Phase resembling delhayelite (Dhy) in patch of groundmass glass (G) with grains of nepheline (Nph) and clinopyroxene (Cpx). Modified from Dawson and Hill (1998). (b) BSE image of glass globule in leucite nephelinite, Nyiragongo. ABP, unnamed alkali-barium phosphate mineral; Dhy, delhayelite; Ap-Sr, Sr-rich apatite. Modified from Andersen et al. (2014). (c) Hollow apatite (Ap) containing isotropic glass from which nepheline (Nph) has crystallized. Embedded in non-isotropic resin. Crossed polarisers. Pyroxenite xenolith, Ol Doinyo Lengai. Modified from Donaldson and Dawson (1978).). (d) Aegirine (Aeg) interstitial to alkali feldspar (Afs) phenocrysts in a microdomain in peralkaline phonolite, Saghro. Inclusions are alkali feldspar (Afs), nepheline (Nph) and hainite (Hai-Y). Modified from Berger et al. (2009).

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The mode of occurrence of the extreme compositions as late melts and the complexity of the associated mineral assemblages has made it difficult to quantify the conditions of formation. Andersen et al. (2014) proposed that the Nyiragongo suite formed at fO_2 below FMQ (-2 to -3) and temperatures ~600 °C. The fractionating assemblage was leucite, nepheline, clinopyroxene and olivine ± apatite. In contrast, Zaitsev et al. (2012) considered that the Sadiman magmas crystallized under relatively oxidizing conditions (>FMQ). In an attempt to explain the extreme peralkalinity at Tarosero, Braunger et al. (2021) proposed that low aH_2O prevented early exsolution of halogens, resulting in a build-up of alkalinity, REE and HFSE. There is some experimental evidence for a delay in water degassing. Using manometric and weight-loss methods, Carroll and Blank (1997) determined H_2O solubility in phonolitic melts to be 4.9 wt% at 1 kb and 850 °C, suggesting that this is higher than in rhyolites (4 wt%) under the same conditions. The greater solubility of water in phonolites means that they can reach greater degrees of fractionation without degassing. In a series of experiments conducted at 50 and 200 MPa and 825 and 850 °C, Larsen and Gardner (2004) also found that phonolitic melts maintained their water contents more efficiently than rhyolites, applying their results to, *inter alia*, Plinian eruptions. However, they cautioned about applying their results to lower temperature phonolites.

These tiny volumes of melt of extreme composition are important petrologically in that they record one end-point of magmatic evolution. It would be of great petrological interest if *rocks* of such compositions could be found, but their mode of occurrence, and their high density due to elevated Fe contents (e.g., 21–23 wt% FeO* in Nyiragongo glasses), make it unlikely that they have ever been erupted as independent melts (Andersen et al., 2014).

DIFFERENTIATION MECHANISMS

In the eight magmatic lineages featured above (Figure 4a, b), fractional crystallization has been considered, on the basis of geochemical modelling, to have been the major differentiation mechanism. The success of the modelling carries, of course, no implications as to the possible complexity of the processes leading to melt-crystal fractionation (Cashman et al., 2017). In addition to the modelling, there are also more direct examples of the process. The Bouzentès alkali basalt lava flow (4.2 Ma) contains hawaiitic segregation sheets containing glassy phonolitic (P.I.≤ 1.36) segregation vesicles (Caroff et al., 1997). The residual melt was formed by crystallization of olivine + clinopyroxene + FeTi oxides + apatite in the hawaiitic magmas. Wolff and Toney (1993) recorded interstitial phonolitic glass in a nepheline syenite xenolith from Tenerife with P.I. in the range 1.81–2.26, making the point that it shows the extent to which peralkaline phonolitic melts can be fractionated in a closed system in this case by crystallization of alkali feldspar, nepheline, sodalite, sodic pyroxene, magnetite, biotite and titanite.

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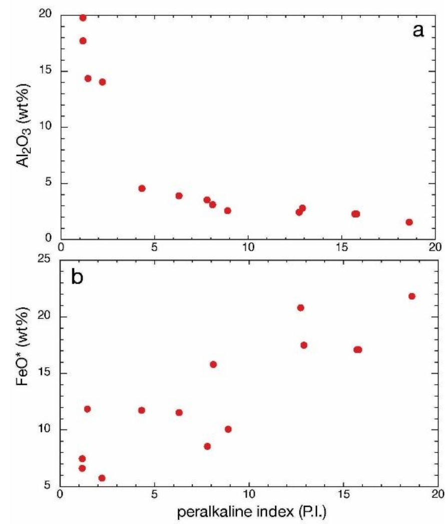

Figure 4
Plots of peralkalinity index (P.I.) versus (a) Al2O3 and (b) FeO (wt%). Data from Donaldson and Dawson, 1978; Krivdik and Tkachuk, 1989; Wolff and Toney, 1993; Caroff et al., 1997: Dawson, 2008; Dawson and Hill, 1998; Zaitsev et al., 2012; Giehl et al., 2013; Andersen et al., 2014.*

Processes other than fractional crystallization have been involved in magma evolution, Magma mingling and mixing have been recognized as ubiquitous in the majority of suites described in this report, resulting, *inter alia*, in expanding the compositional range of the suite, including (partly) filling the Daly gap, and in many cases promoting eruption. For example, Cioni et al. (1995) recognized mixing of three main end-members in the products of the 79 AD eruption of Vesuvius. Panter et al. (!997) described trachyte-phonolite mixing in products of Mt Sidley volcano. Ablay et al. (1998) used mixed basanite-phonolite clasts to identify the process in Montaña Blanca tephra. Nephelinite-phonolite mixing was identified from xenocryst minerals at Saghro (Berger et al., 2009); Holm et al. (2006), on the other hand, argued that mixing was not significant in the Santo Antão eruptives. Although mixed rocks of intermediate composition occur on São Tomé, Déruelle et al. (2007) suggested that mixing was generally very limited.

Contamination of Si-undersaturated suites by crustal rocks does not generally seem to be an important process. Several studies have revealed little or no contamination, including Namibian phonolites (Marsh, 1987), Mt Erebus (Kyle et al., 1992), Mt Sidley (Panter et al., 1997), Saghro (Holm et al., 2006), Cameroon Hot Line (Déruelle et al., 2007), Marie Byrd Land (LeMasurier et al., 2018) and the Hegau region (Binder et al. (2024). As one example of contamination, Legendre et al. (2005) proposed that the peralkaline Group D lavas of Ua Pou were formed by open-system fractional crystallization of tephriphonolite and assimilation of underlying oceanic crust.

A further differentiation process is cumulate recycling. Ellis et al. (2023) refer to a cumulate as a crystal-bearing magma from which some liquid has been lost. Cumulates can be either solid or mushy. In that crystal fractionation involves separation of crystals and melt, “Cumulates are therefore the inescapable complement to magmatic evolution” (Ellis et al., 2023, p. 2). This is especially relevant given the increasing acceptance of models of mush-dominated magma reservoirs (Cashman et al., 2017). Jeffery and Gertisser (2018) make the point that incorporation of cumulate material must be a common process in Atlantic oceanic islands. The cumulates can be recycled by being incorporated into

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magmas without chemical interaction, or may interact with incoming melt, especially if the new magma is hotter than the ambient melt.

Unequivocal geochemical evidence of incorporation of cumulate material, for example alkali feldspar, includes Ba and Eu enrichment and positive Eu anomalies outside those modelled by fractional crystallization (Wolff et al., 2020; Cortes-Calderon et al., 2022; Ellis et al., 2023). In a study of zoned phonolitic ignimbrites on Tenerife, Sliwinski et al. (2015) postulated mushy zones where periodic recharge resulted in strong resorption and embayments of crystals and the generation of Ba-enriched, Zr-depleted melts. Explosive eruptions were able to tap both the modified melts and the mushy cumulates, forming zoned deposits. Petrographic evidence included intense crystal resorption and intergrown textures.

The preservation of melts with compositions modified by cumulate recycling may, however, be a transient feature because the effects may subsequently be overprinted by crystal fractionation. Further fractionation can drive residual melts along a trend (quasi)parallel to, but displaced from, the original magmatic trend. Recognizing the subtle indicators of the various processes may not be possible with the available mineral chemical data set. Undoubtedly, however, cumulate recycling is an important component of the evolution of felsic systems.

A role for crustal melting?

The possibility that phonolites might be formed by partial melting of metasomatically altered alkali basalts was widely promoted by Bailey (1974 and references therein). Similar models have since been proposed by Goles (1976), Hay and Wendlandt (1995), and Hay et al. (1995a, b) for the Plateau Phonolites in Kenya and by Legendre et al. (2005) for the phonolites of Ua Pou. The main lines of evidence used include the scarcity or absence of intermediate members of the suites, the so-called Daly Gap, and the volumetric dominance of evolved over mafic eruptives. As noted earlier, the great majority of recent studies of phonolite-bearing suites have ascribed their formation to protracted fractional crystallization, ascribing Daly Gaps, where present, to combinations of physical controls and rapid differentiation through a short crystallization interval (c.f. Macdonald et al., 2021, section 9).

In an attempt to reproduce the process experimentally, and using an alkali basalt possibly representative of the parental magmas of the Plateau Phonolites, Kaszuba and Wendlandt (2000) found that dehydration melting of the basalt in the presence of a H_2O-CO_2 fluid generated, *inter alia*, tephriphonolitic melts. The most evolved glass, formed at 1025 °C, 0.7 GPa and X_{CO2} 0.22, had 5.73% normative anorthite. They suggested that basalts more alkaline than their starting composition have the potential to produce phonolitic melts. Nevertheless, at this stage there appears to be no strong evidence supporting the melting hypothesis. Such evidence might include, for example, the presence in the more evolved products of xenoliths of partially melted basalts.

MAGMATIC HISTORY: MANTLE TO CRUST

In common with many felsic magmatic systems, phonolitic systems are increasingly being described as “trans-crustal”, meaning that melt is present over a wide region of low velocities extending through the crust (e.g., Cashman et al., 2017; Sparks and Cashman, 2017). As a relevant example, using magnetotelluric data Hill et al. (2022) showed that Mt Erebus is fed by a steep, melt-related conduit of low electrical resistivity originating in the upper mantle (~75 km depth) (Figure 5). On reaching the lower crust the conduit shifts position laterally before rising to shallow storage reservoirs.

The starting point of a polybaric history is normally recorded in primary magmas. As noted earlier, such magmas are relatively rare in the volcanological record, indicating that they have experienced fractionation en route to the upper crust. Many studies of Si-undersaturated suites have recognized periods of magma residence in the deep crust at or near the Moho, consistent with models of trans-crustal systems. Oppenheimer et al. (2011) postulated large volumes of basanitic magma at 20 km depth beneath Mt Erebus. Gonzalez-Garcia et al. (2022) argued that Abrigo tephrites resided at or near the Moho at 410–450 MPa (1050 °C). Ablay et al. (1998) suggested that the parental basanites of Pico Viejo evolved in the lower crust and uppermost mantle at 6–12 kbar pressure. Tarosero volcano has experienced multi-level fractionation at depths between 40 km and the shallow crust (Braunger et al., 2021).

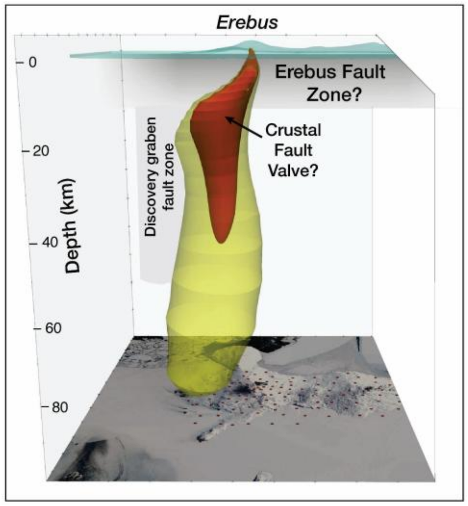

Figure 5
Model of trans-crustal conduit feeding the Mt Erebus system (Modified from Hill et al., 2022).

These periods of repose at various pressures are commonly recorded in studies of xenoliths, which document the polybaric mineral assemblages. Mattioli et al. (1997) reported from the Sete Cidades volcano, São Miguel, Azores, "plutonic nodules" of dunites, wehrlites, pyroxenites and olivine gabbros interpreted as having grown as early, high-temperature cumulates, and a suite of pyroxene hornblendite, kaersutite gabbro and diorite nodules representing lower-temperature crystallization. Holm et al. (2006) noted that many lavas on Santo Antão carry xenoliths of cumulate rocks derived from crustal magma chambers. Berger et al. (2009) refer to olivine clinopyroxenite xenoliths interpreted as high-pressure cumulates from primitive alkaline magmas at Saghro.

A critically important feature is that during ascent magmas are inevitably prone to degassing. Volatiles affect the physical properties of a magma, such as viscosity and density, and thus magma dynamics. They also affect the compositions and abundances of the crystallizing phases and their stability. A critical part of the evolution of magmatic systems is how the volatiles are retained in the melt or if they are released at various stages. The presence of an active phonolitic lava lake on Mt Erebus has provided a perhaps unique opportunity to trace in some detail the degassing history of the system from mantle source to surface (Figure 1b). Using melt inclusion data and Fourier transform infrared spectroscopic measurements, Oppenheimer et al. (2011) modelled the various levels and mechanisms of CO_2 release and related them to crystallization processes and intensive parameters (Figure 6). Their model can be seen as referring to processes in the crustal section of the conduit shown in Figure 5. Among several important petrological consequences of their model, we note that CO_2 fluxing through a relatively static magma column can produce more extensive crystallization and differentiation than degassing *via* an exsolved gas phase. Oppenheimer et al. (2011) suggest that their technique of tracking gas-melt saturation properties can be applied widely to intraplate alkaline volcanoes, potentially providing important detailed information on the progress of magma evolution.

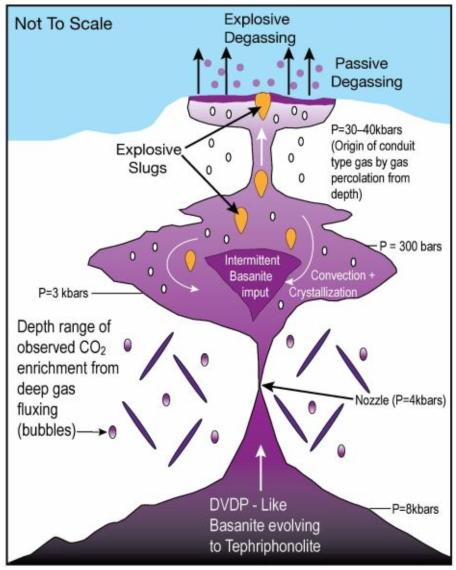

Figure 6
Erebus degassing model (Redrawn from Oppenheimer et al., 2011). DVDP refers to the Dry Valley Drilling Project.

Residence in the upper crust

Evidence for the depths at which phonolitic systems have been emplaced in the upper crust comes from pressure estimates based on mineral equilibria, water solubility models, and geophysical data. The majority of examples are estimated to have been emplaced at depths of 2–5 km. The form of the high-level reservoirs is inferred from geophysical data, comparison with high-level intrusions, and petrological modelling of the relationships between magma types. In this section, we use six models of high-level magma chambers to show the variations in their form and in the processes generating the ranges of magma compositions.

The Laacher See phonolite tephra are the most recent activity (12,880 years before present) at the Laacher See volcano, East Eifel volcanic field, Germany. The deposit (~6.3 km^3) is zoned from a highly evolved, crystal-poor, peralkaline phonolite at the bottom to a crystal-rich phonolite at the top. The zonation is shown in the phenocryst abundances, whole-rock compositions, and matrix glass compositions (Wörner and Schmincke, 1984a, b). There are twelve phenocryst phases, occurring in different proportions in different parts of the tephra: sanidine, plagioclase, hauyne, amphibole, clinopyroxene, titanite, apatite, Ti magnetite, biotite, nepheline, cancrinite and zircon. Mass fractionation models showed that the calculated fractionating assemblages generally agreed well with the observed phenocryst abundances. The exception was the most evolved phonolite, where liquid-state differentiation may have affected the uppermost parts of the reservoir.

Berndt et al. (2001) experimentally determined the phase relationships in three samples of phonolite from the Laacher See Tephra. Most differentiation was thought to have taken place under water-undersaturated conditions although they did not preclude the existence of a fluid phase rich in S, Cl and CO_2 in the upper parts of the chamber. Temperatures ranged from 840–860 °C in the lower parts of the chamber to <760 °C (probably as low as 720 °C) in the upper parts. On the basis of major and trace element zoning in sanidine phenocrysts in the tephra, Ginibre et al. (2004) produced a model of the Laacher See magma chamber which integrated the roles of wall cumulates, convection in the lower two zones, input of basanitic magma, and melt and crystal migration within the chamber (Figure 7a).

Cioni et al. (1995) presented a detailed reconstruction of the magma chamber prior to the 79 AD eruption of Vesuvius (Figure 7b). An uppermost zone, the salic end-member (SEM), consisted of two phonolite layers genetically connected by fractional crystallization. The SEM was underlain by the

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convecting mafic end-member (MEM), seen only as a mixed component in the SEM magmas. The boundary between them was a viscosity-related interface through which melt from the lower layer sometimes penetrated. In an experimental study of the eruption, Scaillet et al. (2008) showed that the phenocryst assemblage, *viz*. sanidine, amphibole, garnet, clinopyroxene, plagioclase and rare leucite, was reproduced at 815 ± 10 °C and 6 wt% dissolved water, matching the 6–7 wt% found in melt inclusions. Vesuvius has also provided a further insight into the evolution of reservoirs; in a study of the four main explosive events of Vesuvius, Scaillet et al. (2008) showed that the reservoir feeding the events has migrated upwards by 9–11 km in the past 18.5 ka.

The Granadilla eruption at 600 ka from the Las Cañadas caldera on Tenerife tapped a reservoir zoned from tephriphonolite to phonolite, across which the temperatures ranged from >940 °C to 790 °C (Bryan, 2006, Figure 7c). Earlier units were erupted through a westerly vent, later units from an easterly vent, pointing to lateral and vertical zonation in the reservoir. Magma mixing characterized the earlier units. The El Abrigo tephriphonolite-phonolite ignimbrite is a product of the largest (>20 km^3 DRE) caldera-forming eruption of the Las Cañadas volcano (~170 ka). Andujar et al. (2008) determined the pre-eruptive conditions of a phonolite from the roof magma ignimbrite, as T = 825 ± 25 °C, P = 130 ± 50 MPa, and fO_2 FMQ ±1. González-Garcia et al. (2022) reconstructed the nature of the pre-eruptive magma chamber, stressing the important roles of magma mixing and melting of a crystal mush (Figure 7d). The parental tephritic magma was stored at or near the Moho (410–450 MPa) at 1050 °C. A sequence of four phonolitic tephras of the Cão Grande Formation, Santo Antão, were erupted from two compositionally zoned reservoirs which showed differences in, *inter alia*, crystal distribution and melt compositions (Eisele et al., 2016). Initially, magmas were derived from a basanitic source. That was followed by activity from two chambers, fed by nephelinitic and basanitic sources, with some interchange between the chambers. Finally, only the nephelinite-sourced chamber was active.

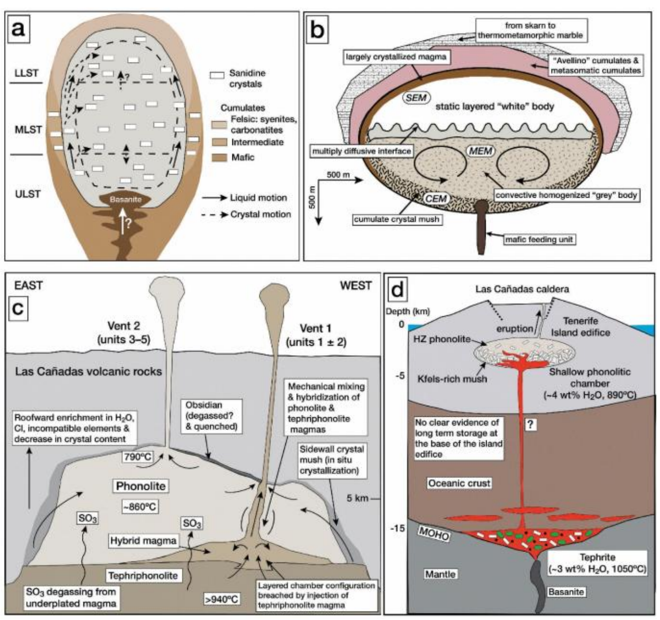

Figure 7

Models of crustal reservoirs of phonolite-bearing systems. (a) Reconstruction of the Laacher See magma chamber before eruption, simplified from Ginibre et al. (2004). (b) Model, after Cioni et al. (1995), of the Vesuvius reservoir prior to the 79 AD eruption. – EM refers to end-members. (c) Model of the Granadilla reservoir prior to the 600 ka eruption. Redrawn from Bryan (2006). (d) Reconstruction of the El Abrigo reservoir prior to the 170 ka eruption. HZ =High Zr. Redrawn from González-Garcia et al. (2022).

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The main explosive eruption (at 2 ka) following the formation of the Las Cañadas caldera came from satellite vents at Montaña Blanca and Pico Viejo. Ablay et al. (1995) recognized three pyroclastic units, followed by emission of lavas and domes. The magmas were erupted from a compositionally (tephrite to phonolite) and thermally (~875 to 755–825 °C) stratified reservoir 3–4 km below Pico Viejo. Unit I was erupted first; when exhausted, Unit II was erupted, initially from the bottom upwards and the remainder from the top downwards. Magma was erupted from Montaña Blanca via a lateral conduit. In the final stages, the presence of mafic tephrites in banded pumices points to the injection of mafic magma into the system.

Following the Montaña Blanca eruption, a composite basanite-phonolite lava flow was erupted from Montaña Reventada at 1100 CE (Wiesmaier et al., 2011). The vent is located at the transition zone between the phonolitic Teide-Pico Viejo complex and the basanitic Northwest rift zone. The occurrence raises the possibility that small-volume phonolitic reservoirs are currently being emplaced at high levels within the Tenerife plumbing system.

The sequences described above point to the complexity of the processes within high-level reservoirs and to the uniqueness of all such systems. The implications for understanding the likely eruptive behavior of any system are manifold. A basic requirement is to interpret correctly the information recorded in the mineralogy of the erupted rocks. Concerning the reliability of the mineralogical record, Ginibre et al. (2004, p. 2220) made the rather provocative statement that "...phenocrysts are not what they are generally assumed to be: crystals formed by cooling in the melt in which they are found. Rather, they record complex processes and many distinct paths and histories of growth". There are, in fact, many examples where the phenocrysts are in equilibrium with the host phonolitic melt, for example, in discussing the alkali feldspar which constitutes 30–40% modally of the Mt Erebus lava lake, Kelly et al. (2008, p.602) note "...the extreme homogeneity of the crystals. Lack of disequilibrium features, --- indicate that the minerals found in the lava and tephra grew from magma with the composition of bulk phonolite". The Ginibre et al. (2004) statement serves, however, to show the huge amount of petrological information to be gained from detailed analysis of phenocryst compositions and textures and their ability to record extremely complicated inter-reservoir processes.

Despite the major advances of the past three decades, major challenges still exist. For example, notwithstanding their considerable volume, the Plateau Phonolites of Kenya are compositionally rather homogeneous in terms of major element compositions (Lippard, 1973b). However, there are significant ranges in minor and trace element contents; for example, Ba 46–819 ppm, Sr 55–1071 ppm and Zr 557–1436 ppm, and there are also some differences in Sr and Pb isotopic characteristics (Hay and Wendlandt, 1995). The ranges may even be extended if associated pumice deposits were to be studied (Lippard, 1973a; Weaver, 1974). Clearly the phonolites have experienced differentiation, a suggestion supported by the observation that a majority of phenocrysts show corroded margins and other resorption features (Lippard, 1973a). It is not known whether this happened in one or more reservoirs, but the fact that individual flows have total volumes up to 300 ± 50 km^3 (Lippard, 1973b) indicates that the reservoirs were large. Determining the form and distribution of the reservoirs is a stimulating challenge, requiring a multi-disciplinary approach. The situation has clear analogies with LIP, which consist of multiple, rapidly emplaced, large-volume eruptions, each of the order of 10^2–10^3 km^3 of magma (Deegan et al., 2023).

Another, volcanologically intriguing, aspect of the Plateau Phonolites is the Yatta flow in eastern Kenya. This single lava flow has an average thickness of 10–15 m and can be traced continuously for nearly 300 km, potentially making it the world's longest lava flow. For most of its course it flowed down a river valley with an average gradient between 1 in 300 and 1 in 500 (Lippard, 1973a; Wichura et al., 2010). A detailed petrological study might provide evidence of the factors which promoted and sustained the flow. Unfortunately, no such study of this singular body seems to have been published.

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VOLCANIC HAZARDS

Eruptions

The most destructive known eruption of a system containing phonolites was that of Tambora, Indonesia, in 1815. Some 5.3–5.8 x 10^{13} g of SO_2 were released within a period of 24 hours, generating between 93 and 118 Tg of stratospheric sulfate aerosols. The aerosol cloud was distributed globally and was responsible for the devastating "year without a summer" in 1816 (Self et al., 2004; Gertisser et al., 2012). An explosive eruption of Vesuvius, on the scale of the 79 AD eruption, would threaten >700,000 people. During the eruption of Niyaragongo volcano in 2002, two flows entered, and partially destroyed, Goma, a town of ~500,000 inhabitants (Favalli et al., 2009).

Given their size, many oceanic islands are in particular danger from explosive eruptions. For example, although phonolite has dominated the youngest activity of the Teide-Pico Viejo system on Tenerife, there has been no eruption from the system for about 2000 years. Ablay et al. (1995) have speculated that there could be a large volume of volatile-rich, evolved magma accumulating in the reservoir. The 2 ka eruption produced ~0.25 km^3 (DRE) of pumice and ~0.18 Mt of F. Similar results from a new eruption would devastate areas within ~20 km of the vent. Eisele et al. (2016) have raised the possibility of future explosive phonolitic eruptions on Santo Antão, either by magma in the reservoir becoming H_2O-oversaturated or by mafic magma injections.

As noted above, a detailed understanding of processes in the magma reservoirs is important in identifying signals of impending eruptions, through for example, combined petrological and geophysical studies (Cashman et al., 2017; Sparks and Cashman, 2017). There are few geophysical studies of Si-undersaturated reservoirs. Furthermore, geophysical studies cannot tell mafic from felsic magma. Scaillet et al. (2008, p.219) were very prescriptive on this issue: "Substantial effort is needed to increase the chemical resolution of geophysical surveys". Magee et al. (2018) have provided a thorough set of guidelines as to how such combined studies might be undertaken.

Environmental hazards

The eruption in 1986 from Lake Nyos, Cameroon, of a toxic cloud of CO_2 resulted in the suffocation of 1,746 people and 3500 livestock in neighboring towns and villages, further raising awareness of the potentially hazardous nature of surface CO_2 emissions. The CO_2-rich nature of much Si-undersaturated magmatism, can result in important CO_2 releases, often manifested as diffuse emissions from the volcano flanks, which Oppenheimer et al. (2011) refer to as the CO_2 pump. Continuous monitoring of such emissions is a prime requirement of human and animal health issues. For example, due to the composition of Ol Doinyo Lengai, there is the potential for CO_2 to be a significant hazard. CO_2 problems may be exacerbated when accompanied by significant SO_2 emissions. Dawson and Hill (1998) recorded SO_3 levels up to 4.55 wt% in glasses in a combeite-lamprophyllite nephelinite from Ol Doinyo Lengai, signaling the possibility of very toxic volcanic plumes. Nyiragongo and Nyamuragira are the fourth largest emitter of SO_2 (~3500 t/day), plus CO_2 and F. More than one million people in the eastern Democratic Republic of Congo are potentially exposed to hazardous effects of the volcanoes.

HCl is one of the major components in heterogeneous reactions in polar stratospheric clouds, and SO_2 forms H_2SO_4 aerosols acting as condensation nuclei in the clouds. Noting that Erebus emits major amounts of stratospheric HCl and SO_2, Zuev et al. (2015) have argued that these gases, along with man-made chlorofluorocarbons, can contribute to the Antarctic ozone depletion. An important aspect is that the ozone depletion can spread over biologically-rich Antarctic waters, with consequences for marine life.

A scientifically important aspect of massive degassing episodes has been the recognition of possible past regional effects. Claessens et al. (2016), for example, recorded a 1.8 Ma period of late Miocene pantelleritic magmatism in central Kenya and argued that S released during the activity may have pushed the vegetation towards a more grass-dominated type by, *inter alia,* decreasing surface temperatures and acidifying lakes. with consequences for the ambient animal life. It is conceivable that

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eruption of the Plateau Phonolites (14–11 Ma; volume 40,000–50,000 km^{3}), with potentially higher concentrations of CO_2 and SO_2, may have had similarly extensive environmental effects. A detailed study of the volatile concentrations in the phonolites, for example, in melt inclusions in phenocrysts, would be informative, as would a complementary study of environmental changes in northern Kenya over that period.

On the botanical theme, a study of vascular plant diversity on La Palma, Canary Islands, Kienle et al. (2022) found higher species richness and abundance on phonolites than on neighboring basalt substrates. One endemic woody species even appears to occur almost exclusively on phonolites. They concluded that phonolites can play an important role for plant diversity on islands. It is interesting to speculate how important this role has been in phonolite occurrences globally; how many plant species owe their existence to phonolite magmatism?

Economic potential

Three types of economic deposits are related to peralkaline phonolites: (i) ore deposits of noble or base metals and commodities, (ii) altered rock and, (iii) their use related to their physical properties. The following give brief examples of these deposit types.

Cripple Creek, Colorado USA is a classic epithermal Au-Te deposit that has been mined since the 1890s from underground operations in its early history. Underground operations ceased in the 1960s and in 1976, Newmont Mining, Inc. began to process oxidized ore in a zero-discharge, valley-type, leach pad to recover gold and silver. In 2015, a rod, ball, and flotation mill were built which processes higher grade, non-oxidized ore (Newmont 2024). Production in 2019 was 322,000 troy ounces of gold (Newmont 2024) with a total production since discovery of approximately 22 million troy ounces as of 2019. Argon ($^{40}Ar/^{39}Ar$) dates indicate two episodes of magmatic activity; tephriphonolite, trachyandesite, and phonolite were emplaced from 32.5 to 31.5 ± 0.1 Ma with a younger phonolite outside the district at 30.9 ± 0.1 Ma (Kelley et al., 1998). Stable isotopic studies of associated silicate phases suggest a largely magmatic origin for early vein fluids (Kelley et al., 1998) related to the hydrothermal system generated by the phonolite intrusions. Eriksson (1987) during a detailed study of the phonolite-dominated continental alkalic suite at Cripple Creek, analyzed 16 phonolite samples and all were peralkaline (P.I = 1.04–1.14). Similar small volumes of peralkaline phonolitic magmas were emplaced along the trend of the Rio Grande rift, New Mexico, USA, although none have the Au-Te endowment of Cripple Creek. Jensen and Barton (2007) compare this off-axis rift magmatism in the beginning stages of regional extension to the styles of phonolitic magmatism in the East African rift.

Economic deposits of fluorite can be formed in various ore-forming environments such as Mississippi Valley-Type, carbonatites, alkaline igneous rocks both silicic and under-saturated, and others (Magotra et al., 2017). Examples of economic fluorite deposits related to undersaturated alkaline igneous rocks are the fluorite deposits in the State of Paraná, Brazil. Jenkins (1987) describes the deposits in the Mato Preto alkaline complex where three large fluorite deposits are related to the hydrothermal system from peralkaline phonolite and carbonatite emplacement during the Cretaceous-Paleocene. The Poços de Caldas massif, the largest alkaline body in the western hemisphere, is located just east of Paraná. Guarino et al. (2021) describe it as an eroded magma chamber formed by different magmatic pulses dominated by peralkaline phonolite. Although, there are fluorite deposits, the main ores related to phonolitic hydrothermal systems are Th, REE, Zr and Mo (Gomes et al., 2021).

The peralkaline Fohberg phonolite (Kaiserstuhl Volcanic Complex, Germany) has been intensely zeolitized by a post-emplacement hydrothermal system. The altered rock contains >40 wt.% zeolite and is mined (as of 2014) for a suite of Na-Ca zeolites (Weisenberger et al., 2014). Gonnardite, thomsonite, mesolite, natrolite and analcime are the main zeolite minerals. The mined products are used for cation exchange, in the concrete and glass industry, in medicinal products, etc.

Phonolite, when unaltered, is tough with a rough vesicular surface and hence has good abrasive properties. During the Roman period, leucite phonolite lava from quarries located near Orvieto (~100

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km north of Rome) were highly prized and in great demand for Pompeian-style millstones and kneading machines (Antonelli et al., 2001; Santi et al., 2003). The Orvieto millstones have been identified by petrography and chemistry and are found throughout Italy as well as Spain, France, Tunisia, and Libya (Santi et al., 2003). The Peralkalinity Index varies from 0.75 for leucite-rich lithologies to 1.03 for those with plagioclase ≥ leucite.

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Source of analyses:
1. olivine melilitite, Ol Doinyo Lengai (Keller et al., 2006, sample OL 199).
2. olivine melilitite, Saghro, Morocco (Berger et al., 2009)
3. melilite nephelinite, Santo Antão, Cape Verde (Holm et al., 2006)
4. basanite, Anjouan, Comores Archipelago (Flower, 1973)
5. basanite, Ua Pou, Marquesas (Legendre et al., 2005)
6. melilitite-nephelinite, Hegau (Binder et al., 2024)

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