

The Marangudzi Alkaline Ring Complex, Southeastern Zimbabwe: Part I. Mineral Compositions and Formation Conditions of Genetically-Related Gabbro, Nepheline Syenite and Quartz Syenite

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How to cite this paper: Henderson, C. M. B. (2026). The Marangudzi Alkaline Ring Complex, Southeastern Zimbabwe: Part I. Mineral Compositions and Formation Conditions of Genetically-Related Gabbro, Nepheline Syenite and Quartz Syenite. *Journal of Geoscience and Environment Protection*, 14, 55-116.

<https://doi.org/10.4236/gep.2026.1410002>

Received: July 23, 2026

Accepted: October 11, 2026

Published: October 14, 2026

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Abstract

The Marangudzi gabbro is intruded by quartz syenite, nepheline monzonite and nepheline syenite “ring” units. Ortho-cumulate gabbros are richer in intercumulus primary biotite (Ti, Ba-rich) and alkali feldspar than mesocumulates. Clino- and ortho-pyroxenes are present, indicating transitional tholeiitic/alkaline basalt affinities. Least-evolved orthogabbros contain olivine (Mg/(Mg + Fe + Mn) *mg*# 62), clinopyroxene (*mg*#78), orthopyroxene (*mg*#67), plagioclase (*An* 92), with intercumulus Ti-Ba-rich biotite (*mg*#69, TiO₂ 5.6, BaO 0.8 wt.%) and alkali feldspar (Or 88, BaO 1.1%). The rock series nepheline monzonite—nepheline-bearing syenite—foyaite probably formed by fractionation of parental K-Ti-Ba-rich alkaline basalt, as reflected in decreasing *mg*#, *An* and Ba with evolution. Late-intruded leuco-malignites (± pseudoleucites) have minerals less evolved than those in nepheline-bearing-syenites/foyaite. The main quartz syenite mafic mineral is hastingsite/edenite with ~2% TiO₂ and higher Si/Al than amphiboles in undersaturated rocks. Mineral compositions suggest that a parental magma intruded at ~1150°C, with olivine, plagioclase progressively equilibrating over the temperature range from 1000°C to 950°C with biotite at ~900°C ± 50°C in the gabbros and early nepheline monzonites. Feldspar/amphibole data give ~880°C for amphibole equilibration in nepheline monzonite, while biotite shows similar textural relations but calculated formation temperatures of 750°C suggest subsolidus re-equilibration. For nepheline-bearing syenites and foyaite, feldspar and amphibole over the range from ~900°C to 850°C to subsolidus (720°C nepheline-bearing-syenites) and 620°C (microfoyaite). Leuco-malignite amphiboles suggest magmatic formation formed from ~900°C

to 850°C. Feldspar and amphibole in the quartz syenites suggest late magmatic/solidus (800°C - 750°C), with biotite re-equilibrating subsolidus at ~675°C, and with magnetite-ilmenite subsolidus at ~600°C (log f_{O_2} -18 bar) in all rocks.

Keywords

Marangudzi Alkaline Complex, Microprobe Analyses, K-Rich Gabbro, Nepheline Monzonites/Syenites, Quartz Syenites, Ba-Ti-Rich Oxybiotite, Ti-Rich Oxohastingsites, Ba-Rich Alkali Feldspars, Geothermometry

1. Introduction

The Marangudzi igneous complex is one of the Mesozoic rift-related ring complexes in the Nuanetsi (now Mwenezi) Igneous Province, Zimbabwe, as part of the Karoo Large Igneous Province (LIP); Marangudzi and several other Mwenezi ring complexes are exposed near the central axis of a triple-junction feature (Cox et al., 1965; Duncan & Marsh, 2006). Duncan and Marsh (2006) described these Karoo volcanics as the “Lebombo sub-province” with regions to the north and south termed the “Drakensberg sub-province”; the associated eastern region consists of Dronning Maud Land, Antarctica [see Figure 1 in Harris et al. (2026)]. Cox et al. (1967) demonstrated that a northern Karoo province had tholeiitic basalts enriched in K, Ti, P and Ba, while Cox (1972) reported that the Karoo cycle was initiated by eruption of potassium-rich picritic magma, sourced in the mantle. Indeed, the Karoo LIP formed at a time of major tectonic change culminating in the break-up of Gondwana, with an overall time span of 200 to 90 Ma (Storey, 1995).

Marangudzi is located in the south-eastern part of Zimbabwe, 80 km east of Beitbridge (Figure 1), with field relations/petrography described by Rees (1960) and Gifford (1961) (Supplementary file S.1, see the section after Conclusions for details of remote file access). The complex covers ~80 sq. km and is composed essentially of a biotite-bearing gabbro mass intruded by ring dykes of oversaturated rocks, cone sheets of potassic undersaturated rocks and a radial suite of phonolitic dykes (Figure 1). Henderson (1964) studied the mineralogy, petrology and geochemistry of Marangudzi samples chosen by Rees and Gifford as representing the different intrusive units (Figure 1 and Figure 2). Electron microprobe and more sophisticated trace element research carried out since then by the author together with petrographic information are summarised here (see Supplementary file S.2 for details).

The complex intrudes the Proterozoic (2700 Ma) basement of the Central Zone of the Limpopo orogenic belt (Cox et al., 1965); Gough et al. (1964) suggested a K/Ar biotite and amphibole age of 190 ± 10 Ma for Marangudzi, and Landoll et al. (1989) concluded that stepwise-heating $^{40}\text{Ar}/^{39}\text{Ar}$ analyses of amphiboles and biotites gave a reliable cooling age of 178.1 ± 1.8 Ma which is adopted here as the intrusion age for the complex. This age is within error of the dates for Sabi-Limpopo and North Lebombo samples [Period P2; see Figure 5 in Luttinen et al.

(2022)]. Thus, this magmatic episode occurred within the rift-related 178 - 184 Ma volcanic and sub-volcanic igneous activity of the Lebombo region (Duncan & Marsh, 2006).

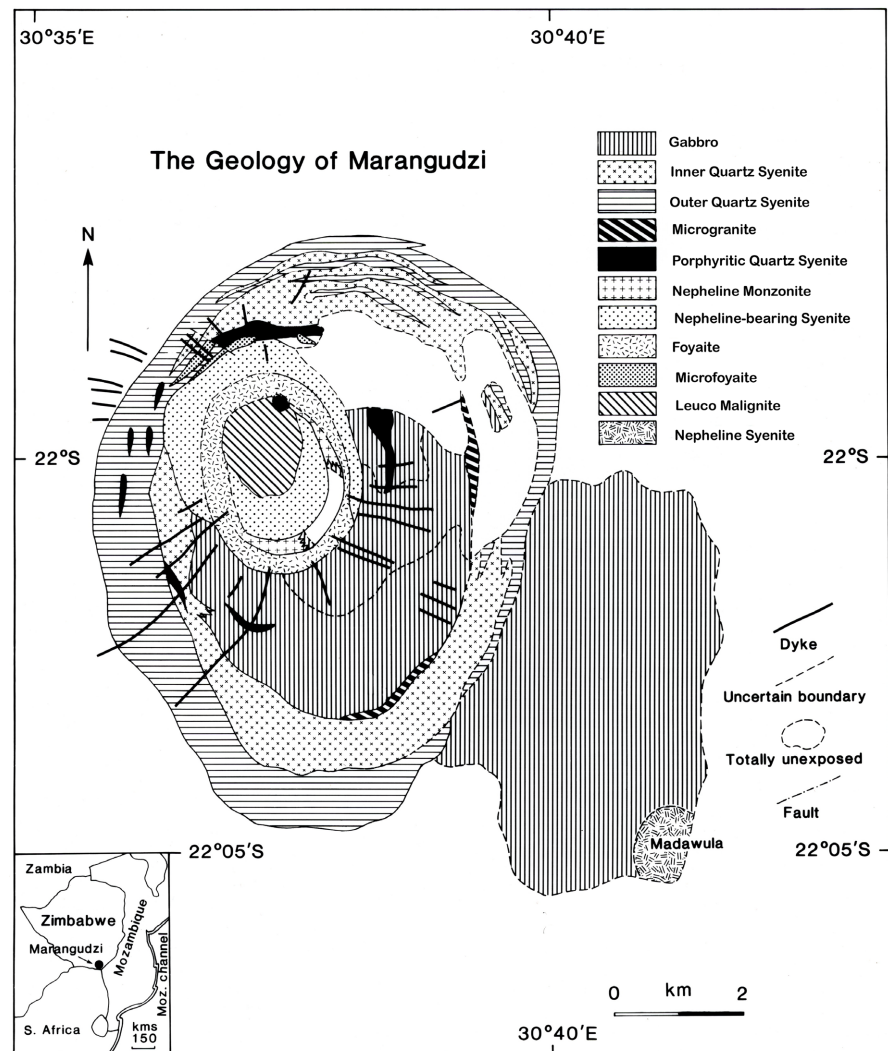


Figure 1. Geological map of the Marangudzi “ring”-complex, southeast Zimbabwe. Madawula is a separate alkaline intrusion to the southeast. The key lists the units in order of intrusion with the oldest at the top.

Foland et al. (1993) reviewed the processes involved in the formation of co-genetic silica-undersaturated and silica-oversaturated rock series in sub-volcanic alkaline ring complexes. In that work the Sr- and Nd-isotope data and selected whole-rock major element compositions for Marangudzi syenitic rocks (Landoll, 1987; Landoll et al., 1989) were briefly reviewed showing inversely-correlated, initial Sr and Nd isotope ratios consistent with an initial parental magma derived from an enriched- or heterogeneous-mantle source; as is reported for other Karoo-related magmas (Hawkesworth et al., 1984; Ellam & Cox, 1991; Howarth et al., 2023; Harris et al., 2026). In addition, Foland et al. (1993) suggested that quartz

syenites could have up to 25 wt.% of crustal components.

The purpose of this and subsequent contributions is to describe the mineralogy, geochemistry, and petrogenesis of the various rock series, within the constraints of the available Marangudzi mineralogical, petrological and isotope-geochemical dataset. Although the literature includes detailed isotope research regarding the possible upper-mantle parentage of LIP rock series, there is still no overall consensus regarding petrogenetic mechanisms. Thus, this paper is concerned specifically with summarising the principal field relations and petrography of the rock suite and providing mineralogical and geo-thermometric/barometric data to provide a foundation for petrogenetic models to be developed further in a subsequent paper (in preparation).

2. Field Relations and Rock Types

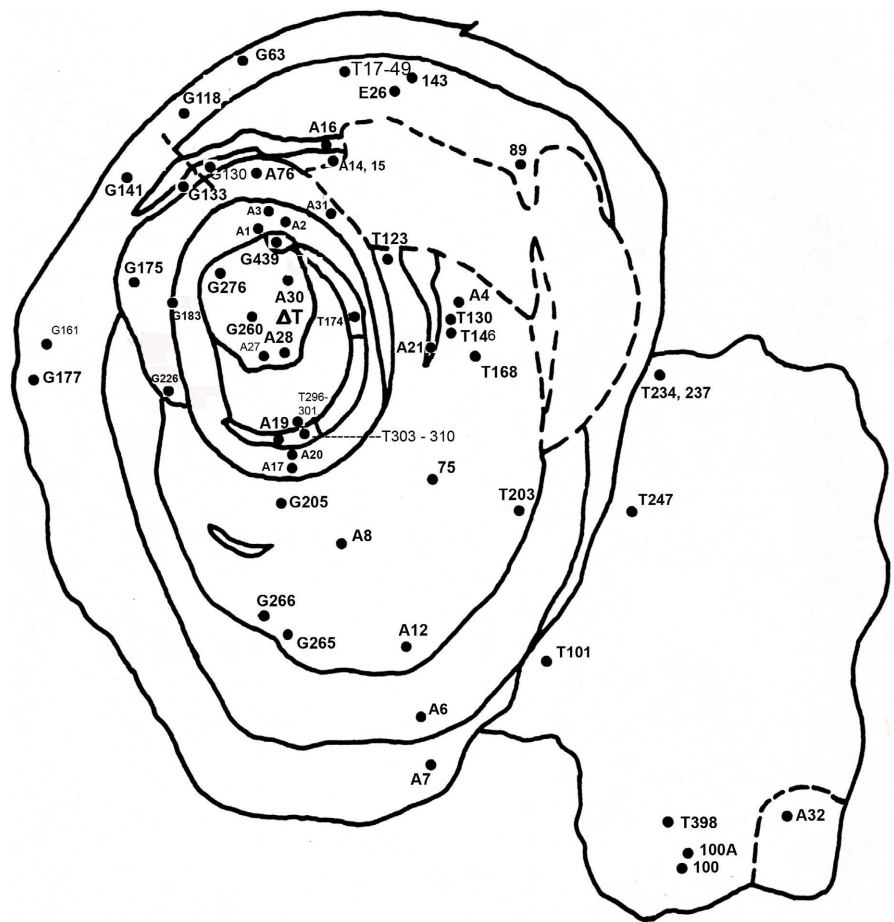


Figure 2. Simplified geological map of the Marangudzi intrusion; the boundaries between the different rock units are taken schematically from **Figure 1**. Details of representative rock-type samples labelled on the figure are provided in **Table 1**, the petrography text and mineral composition tables. Small font sample labels denote approximate positions.

This section summarises the field relations and petrography of the intrusive units, with Supplementary files S.1 and S.2 providing additional information. Note that

field relationship information is only available in the unpublished Ph.D. theses of [Rees \(1960\)](#) and [Gifford \(1961\)](#). The Marangudzi gabbro sheet-like intrusion is poorly exposed on a peneplain with the best exposures occurring near Madawula hill ([Figure 1](#) and [Figure 2](#)). The silica-undersaturated and -oversaturated ring units outcrop in the Marangudzi Hills where the undersaturated rock units and their inter-relationships are variably exposed. The oversaturated rocks are exposed in kopjes running from the west to the north of the main hills.

Major Intrusions

The order of intrusion of the major rock units ([Figure 1](#)) is:

1. Gabbro; 2. Main oversaturated ring, i.e., inner quartz syenite, outer quartz syenite, microgranite ring dykes; 3. Porphyritic quartz syenite ring dyke and plug; 4. Nepheline monzonite, nepheline-bearing syenite, foyaite and microfoyaite cone sheets; 5. Leucomalignite core. Units 4 and 5 are composed mainly of nepheline-bearing, undersaturated rock types and IUGS names are used here except for samples showing trachytic textures with aligned alkali feldspar phenocrysts; for such rocks the term foyaite is retained here.

1. The equigranular gabbro consists essentially of plagioclase and pyroxene with lesser amounts of olivine and biotite ([Figure 3\(a\)](#)). Many samples contain small amounts of alkali feldspar (<5 vol. %) although these varieties and the “normal” gabbros do not show any recognisable geographic distribution.

2. Gabbros are intruded by the main oversaturated ring. The contacts between the latter and the basement are not exposed. The outer quartz syenites have variable quartz contents and the inner quartz syenites, in the northern part of the ring, are cut by offshoots from the outer quartz syenite ring.

3. The porphyritic quartz syenite ([Figure 3\(h\)](#)) occurs as two separate units: a discontinuous ring, and a single body in the undersaturated units.

4. Nepheline monzonite and nepheline syenite cone sheets intrude the oversaturated rocks and the gabbros, their centres of intrusion being to the N.W. of the main oversaturated ring centre. The contacts between the gabbro and the outer margins of the undersaturated intrusive units are often complex. The nepheline-bearing syenite (mapped as “white syenite”) consists of two crescents cut by the complex nepheline monzonite and foyaite “ring”. Typical nepheline-bearing syenites are equigranular and consist of alkali feldspar and amphibole with variable amounts of diopside pyroxene, plagioclase and nepheline (<5 vol. %) ([Figure 3\(c\)](#)). Some varieties are richer in nepheline and amphibole ([Figure 3\(d\)](#)).

The contact between the monzonitic rocks and the foyaite sheets is difficult to locate in the field. Foyaites studied are dominantly porphyritic types with alkali feldspar phenocrysts in a finer-grained groundmass (mapped as “grey syenite”). The foyaites consist of alkali feldspar, amphibole, nepheline (>5 vol. %), sometimes with pseudoleucites (~5 cm diameter). Feldspar phenocrysts and microphe-nocrysts show alignment, giving the rocks a typically foyaitic texture ([Figure 3\(e\)](#) and [Figure 3\(g\)](#)).

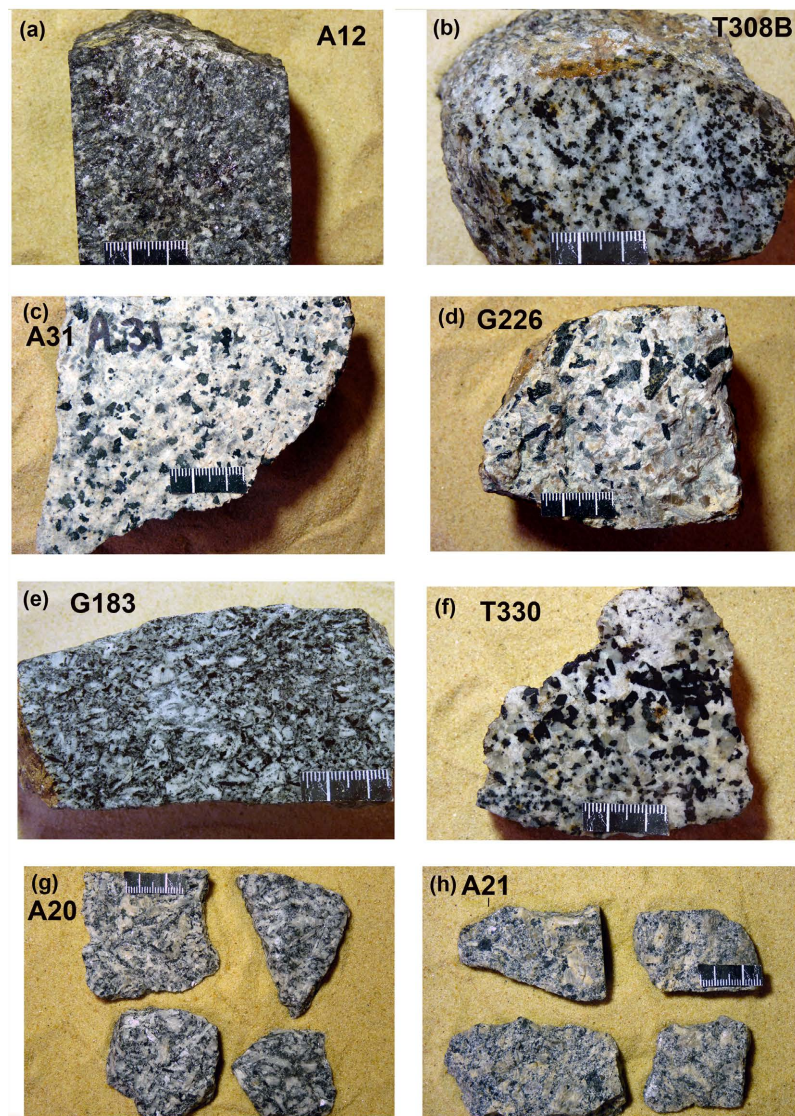


Figure 3. Representative Marangudzi hand specimens. (a) Orthocumulate gabbro A12, larger white and medium grey grains are cumulus calcic plagioclase and augite, respectively, small bright white spots are reflections from 2 - 3 mm biotite cleavage flakes; (b) Nepheline monzonite T308B, large white grains are mainly calcic plagioclase with some alkali feldspar, large dark grey/brown grains are Ti-rich biotites and hastingsites, medium grey augite, pale grey groundmass includes nepheline; (c) Nepheline-bearing syenite ("white syenite") A31, large white grains are plagioclase, pale grey alkali feldspar, dark grey/green grains are amphibole; (d) "White syenite" G226, plagioclase-free, nepheline-rich "pegmatitic" sample, large dark grey/green grains hastingsite, white grains alkali feldspar, pale grey nepheline; (e) Foyaite ("grey syenite") G183, large white grains aligned alkali feldspar (foyaitic texture), grey finer grained groundmass amphibole, alkali feldspar and nepheline; (f) Leucomalignite ("white syenite") T330, dark grey elongate amphiboles, medium grey calcic pyroxene, white grains alkali feldspar, pale grey (greasy lustre) nepheline; (g) Foyaite A20, large elongate phenocrystic alkali feldspars in finer grained matrix of amphibole, alkali feldspar and feldspathoid; note similarity to G183 (**Figure 3(e)**); (h) Porphyritic quartz syenite A21, large phenocrysts of alkali feldspar with some xenocrystic plagioclase in finer-grained groundmass of amphibole, alkali feldspar and minor quartz, see white on black (cm + mm) scale bar on each image.

A series of more basic undersaturated rocks (mainly nepheline monzonites) occurs at the eastern margin between the foyaite and nepheline-bearing syenite “rings” (Figure 1). The nepheline monzonite unit varies from basic rocks rich in calcic plagioclase and pyroxene (Figure 3(b)) to those richer in alkali feldspar and amphibole; most are rich in biotite. This unit seems to be contemporaneous with the foyaite ring. The microfoyaite (“grey syenites”) intrude the nepheline-bearing syenite and main oversaturated ring. Overall, the age relations between the silica-undersaturated intrusive units are not clear and there is considerable overlap in the modal mineralogy between the different units. However, the textural relations and geochemical features, for each unit identified, are generally characteristic; indeed, different varieties could have developed in-situ within a single ring unit (see later).

5. The leucomalignite unit (“white syenite”) forms the core of the undersaturated rings. The rocks are heterogeneous nepheline-rich rocks including a coarse-grained pseudoleucite (up to 10 cm diameter)-bearing rock, and a variety free of pseudoleucites (Figure 3(f)). The leucomalignite unit appears to be the last intruded of the major units.

3. Petrography

Table 1 lists the samples studied for the main intrusive rock units with *italic sample names* showing samples analysed both by mineral EMP methods and bulk composition analyses for major, minor and trace elements, while **bold-named** samples were analysed only for bulk rock compositions. Representative modal analyses are given in Table 2. Note that the numbers of samples studied in detail in this work vary from 1/3 (e.g., mesocumulate gabbros) to 3/4 (nepheline monzonites) of those studied petrographically and mineralogically by Rees (1960) and Gifford (1961) in their original work for each rock type; thus, this analytical database is considered to be representative of the Marangudzi complex differentiation series. Rock types collected as large specimens for laboratory studies have prefix A; samples chosen for later study by CMBH have prefixes G (Graham Rees; western Marangudzi) or T (Tony Gifford; eastern Marangudzi). The most significant mineralogical features are summarised here with details given in Supplement file S.2.

Table 1. Marangudzi samples studied at Manchester laboratories: *Italic sample numbers* studied using mineral EMP methods and bulk composition analyses, and **bold sample numbers** only by bulk composition analyses.

<i>Gabbro sheet unit:</i>		
<i>Orthocumulates</i>	<i>A8, A12, T168, T203</i>	
<i>Mesocumulates</i>	<i>Coarse grained 100, 100A, T123, G205, 75, A4</i>	T398
	<i>Medium grained G265, G266</i>	T130, T146
<i>Microgabbros</i>	<i>T101</i>	T234, T237, T247
<i>Basanite dyke</i>	<i>T178</i>	
<i>Silica-undersaturated Intrusive-ring-units:</i>		

Continued

<i>Nepheline monzonites</i>	<i>A19, T308, T303, T310, T174</i>	T296, T308B
<i>Nepheline-bearing syenites</i>	<i>A26, A31, T175, T301, G226</i>	76
<i>Foyaites</i>	<i>A1, A2, A3, A17, A20, G304</i>	G183, T153, G131
<i>Microfoyaite</i>	<i>A14, G133</i>	A15
<i>Leuco-malignites</i>	<i>A27, A28, G260, G276, T330, 730</i>	A30
<i>Silica-oversaturated Intrusive-ring-units:</i>		
<i>Porphyritic quartz syenites (PQS)</i>	<i>A21, A16, T36, G439</i>	
<i>Inner quartz syenites (IQS)</i>	<i>A6, T5, T17, T33, T49</i>	89, 103, 143, G405
<i>Outer quartz syenites (OQS)</i>	<i>A7, G118, G141, G161, G177, G63 (granite)</i>	G130, T214 (granite)

1. Gabbro sheet. The gabbros which exhibit orthocumulate and mesocumulate textures are composed of plagioclase, augite, olivine, red-brown biotite, and an Fe-Ti oxide phase (**Figure 3(a)** and **Figure 4(a)**). The augite has exsolution lamellae of orthopyroxene, which also may occur as discrete grains and rims on olivine. Biotite mainly forms discrete grains and opaque minerals are mostly titaniferous magnetites. Alkali feldspars (~0.5 mm grains, interstitial to plagioclase laths) and apatite are common accessory minerals.

(i) Plagioclase-pyroxene-olivine orthocumulates.

Rocks A8, A12, T168 and T203 are inequigranular orthocumulates with cumulus plagioclase, colourless olivine and pale grey augite. Plagioclase can be zoned with the larger grains having cores of An₉₀₋₇₅, with thick sodic-rims of An₅₀₋₄₀. The cores typically occupy about 80% of the larger grains (primocrysts). Cumulus olivine and pyroxene are comparatively unzoned. Rims on primocrysts, together with the small irregular olivine, pyroxene, and small strongly zoned sodic plagioclases, occur entirely as intercumulus phases. A12 is particularly rich in biotite (**Figure 3(a)** and **Figure 4(a)**), which occurs as deformed, large (~8 mm) poikilitic crystals, reflecting either localised slumping or longer-range transport of magma/mush from deeper source levels (see below). See Supplementary file S.2 for further details for each of the rocks. The orthocumulates show substantial variations in the proportions of cumulus and intercumulus phases (**Table 2**).

Table 2. Modal data for representative rock units in the Marangudzi alkaline ring complex (IUGS name below adopted name).

	Mesogabbro							Orthogabbro			Micro-gabbro	Nepheline monzonite				Nepheline-bearing syenite											
	Gabbros										Neph. gabbro	Neph monzo-diorite	Neph monzo	Neph monzo	Neph syen	Neph syen	Nepheline syenite										
	100	100A	G205	T130	G266	75	A4	A8	A12	T168	T101	T308	A19	T296	T303	T174	A26	A31	G226	T301	G76						
Source	Hossain (1970)																					Gifford Rees					
Olivine	14.2	10.8	6.1	12.5	7.4	2.1		4.0	15.7	7.1			-			-											
Cpx (Opx < 5%)	61.1	46.2	27.7	42.1	38.4	21.5	9.9	18.4	19.2	15.1	37.4	17.5	14.0	7.7	10.7	3.8	1.1	1.7		0.8	4.7						

Continued

Amphi- bole												0.3	2.9	14.3	19.9	7.9	21.1	12.8	6.7	22.1	17.1	
Biotite	1.2	0.3	1.7	0.1	1.5	3.8	4.1	5.1	9.5	2.5	10.8	7.7	14.2	6.1	5.3	3.0	Tr.	Tr.				
Plagio- clase	23.0	42.5	63.0	44.9	51.2	70.5	82.6	70.9	53.8	71.4	38.9	54.0	28.1	32.2	15.4	15.3	17.9	7.6	14.4	5.9		
Alkali feldspar	Tr.	-						Tr	0.1	0.2	1.8	2.8	13.4	32.4	20.2	40.8	65.6	54.2	72.0	65.6	48.0	59.2
Nepheline	0.1		-									0.6	4.2	4.7	0.5	4.5	3.4	4.8	4.5	27.7	12.6	7.3
Sodalite																					2.8	
Oxide	0.4	0.1	1.4	0.4	0.4	1.7	0.7	1.2	0.5	1.7	7.8	1.9	1.0	0.8	2.2	0.7	0.7	0.9	0.1	1.4	2.0	
Apatite (others)	Tr.	Tr	0.1	Tr	0.1	0.8		0.4	1.1	0.4	1.7	0.7	1.6	?	1.1	0.3	0.7	0.5	0.7	1.0		
Foyaite				Microfoyaite				Leucomalignite		Porph. qtz. syenite			Inner coarse syenite			Outer quartz syenite						
Nepheline syenites				Neph syen.		Neph monzo syenite		Syenite	Qtz syenite		Syenite	Qtz syenite	Syenite	Qtz syenite	Syenite	Qtz syenite	Granite					
A2	A3	A17	A20	T153	A15	G133	A28	G260	A21	A16	G439	89	T5	T49	A6	A7	G141	G177	G63	T214		
Source					Gifford (1961)				Rees (1960)						Gifford (1961)		Gifford (1961)		Rees (1960)		Gifford (1961)	
Olivine	-											0.8		0.8								
Cpx (Opx < 5%)	0.5				9.4		14.0		12.1		8.2				2.7							
Amphi- bole	19.3	15.0	25.6	17.8	10.2		~10		4.9	16.0	17.6	10.7	2.0	7.6	9.6	3.0	13.4	11.1	11.3	3.6	5.5	
Biotite								~3	~2	0.3	1.3	0.6										Tr.
Plagio- clase	-		8.3		3.5		~2		17.6		12.1	7.4		-								
Alkali feldspar	60.0	64.5	55.7	62.8	60.2	70.8	73.2	~45	32	64.6	50.6	73.4	86.5	84.3	79.6	93.5	80.0	81.7	79.2	60.0	66.1	
Nepheline	15.6	19.1	7.1	13.1	29.1	18.0	8.7	~40	45													
Sodalite	4.4		1.6		5.5																	
Oxide	1.0	1.4	0.7	0.3	0.5	2.0	0.9	-	1.7	1.5	1.2	3.8	1.9	0.8	1.4	0.5		0.3	0.4	0.4	0.8	
Apatite (others)	Tr		0.5		Tr		0.5		Tr.	Tr.	Tr	0.3				0.5						
Quartz										Tr.	17.2	3.6	0.6	7.3	9.8	~1.0	6.1	6.8	8.6	35.9	27.6	

(ii) Plagioclase-pyroxene-olivine mesocumulates.

Samples 100, 100A, T123, T398, G205, 75 and A4 include both melanocratic and leucocratic varieties (Table 1 and Table 2). In general, each of these rocks is composed modally of >80% cumulus grains; large plagioclases are comparatively homogeneous (An₈₃₋₇₉). Mesocumulates T130, T146, G265 and G266 have very similar modal compositions (Table 2).

(iii) Microgabbros. T101, T234, T237 and T247 have cumulus plagioclase and pyroxene in a finer-grained matrix but olivine is normally absent. Plagioclase is zoned with cores ~An₇₀₋₆₅ and microgabbros are more evolved than other gabbros.

Biotite is the first “hydrous” mafic mineral to appear as a liquidus phase in gab-

bro, reflecting the relatively potassic nature of the primary basaltic magma at Marangudzi, with amphibole only appearing as a subordinate mineral forming mainly by deuteric alteration.

2. Ring intrusions: silica-undersaturated units. The contact relationships between the separate units are not clear but they are all intruded later than the main gabbro sheet (**Figure 1**).

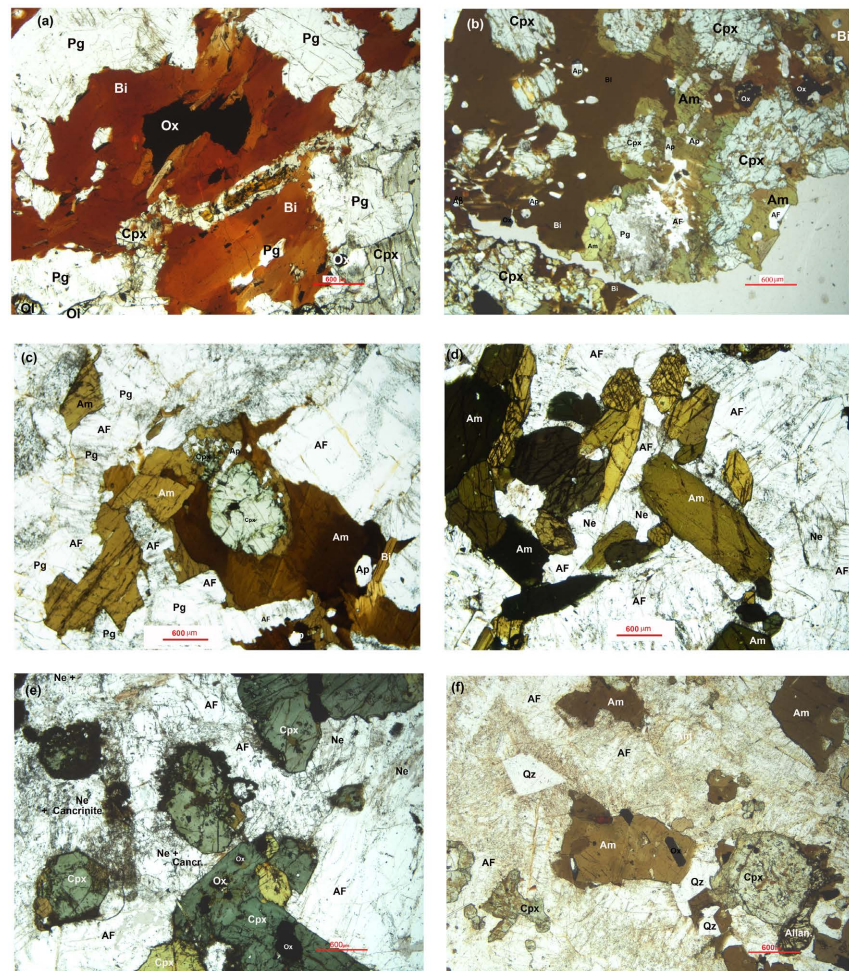


Figure 4. Thin section images for typical main Marangudzi rock types (all plain polarized light): (a) Orthocumulate gabbro A12 showing large red-brown primary biotite (Bi) surrounding Fe-Ti oxide (Ox) with smaller plagioclase (Pg), pale green augite (cpx) and olivine (Ol); (b) Nepheline monzonite A19 showing pale green primary diopside pyroxenes with reaction rims of green-brown hastingsite (Am) and large poikilitic biotite plus small apatite inclusions (Ap); (c) Nepheline-bearing syenite T175 with large alkali feldspar (AF), smaller plagioclase and pale green pyroxene with thick rims of brown hastingsitic amphibole; (d) Foyaite A17 with euhedral prismatic green-brown amphibole, cryptoperthite alkali feldspar and nepheline (Ne); (e) Leucomalignite A27, showing mid-blue-green euhedral clinopyroxene with thin rim of dark green amphibole, alkali feldspar cryptoperthite and nepheline altering to cancrinite; (f) Inner quartz syenite T33 with euhedral pale green clinopyroxene altering to pale brown amphibole, a separate euhedral grain of Am is present, matrix is alkali feldspar clouded with fine alteration products, and interstitial clear quartz (Qz). See scale bar in red (600 micron) at base of each image.

2a. Nepheline monzonite. These rocks are texturally and mineralogically variable with different proportions of plagioclase, alkali feldspar, pale grey-green clinopyroxene, deep red-brown “strained” biotite, and pleochroic, commonly poikilitic, hastingsitic amphibole [Figure 3(b) and Figure 4(b)]. Table 2 also shows the current IUGS classification for individual members of this unit. Larger tabular pyroxene and plagioclase with unzoned centres represent cumulus minerals which can show reaction rims of biotite or amphibole (Figure 4(b)) and the cumulus plagioclases can have either zoned sodic plagioclase margins or rims of micro- or crypto-perthitic alkali feldspar. The interstices between the feldspars contain small amounts of nepheline (partly altered to cancrinite) and sodalite. Accessory minerals include opaque Fe-oxides and apatite. Samples studied are: T296, T308, T303, T308B, T310, A19, and T174 (alkali-feldspar-rich). T174 contains cumulus apatite grains up to 1mm across. See Supplementary file S.2 for further details for individual samples.

2b. Nepheline-bearing syenite unit (“white syenite”). Typical samples are coarse-medium-grained with cryptoperthitic alkali feldspars (average modal amount ~65 vol. %) and smaller, abundant subhedral brown-green hastingsitic amphibole (~15 vol. %) [Figure 3(c)]; subordinate plagioclase and nepheline are present (both average ~6 vol. %) with ~2 vol. % pale green diopsidic pyroxene, which can be enclosed by poikilitic amphibole [Figure 4(c)] Biotite is only present in trace quantities while iron oxide and apatite are commonly enclosed in mafic minerals. No preferential orientation is shown by the large alkali feldspars. Analysed samples are A26, T175, T301, and A31 while G226 is a nepheline-rich pegmatitic “white syenite” (Figure 3(d)) lacking plagioclase (Table 2).

2c. Foyaite unit (“grey syenite”). The samples studied have elongate cryptoperthitic alkali feldspars (up to 1 cm) and prismatic hastingsitic amphiboles (average ~18 vol. %) set in a finer-grained matrix of cryptoperthite, feldspathoid (average ~20 vol. %, mainly nepheline) and amphibole [Figures 3(e)-(g), Figure 4(d)]; biotite is generally absent and plagioclase is only present in one sample (A17). Accessory minerals are opaque Fe-oxides and apatite. Analysed samples A1, A2, A3, A17, A20, G183 and G304 are all porphyritic types (Figure 3(e) and Figure 3(g)). Alkali feldspar phenocrysts show spectacular trachytic orientation (hence the name foyaite), as does the prismatic amphibole.

The *microfoyaite*s are mineralogically similar to the foyaite)s but the aligned cryptoperthitic alkali feldspar phenocrysts are smaller (up to 2 mm). A14, A15 and G133 are analysed microfoyaite)s.

2d. Leucomalignite unit (“white syenite”). Typical samples are heterogeneous, coarse-grained rocks with variable proportions of cryptoperthitic alkali feldspars and nepheline [Figure 3(f), Figure 4(e)]; no plagioclase is present, although some varieties contain large pseudoleucites (up to 10 cm). Mafic minerals typically are pale- to medium- green diopsidic pyroxene and hastingsitic amphibole (generally lacking magmatic biotite), with mafic mineral, modal totals varying (15 - 30 vol.%), however, pyroxene/amphibole proportions are generally similar. Analysed rocks

are A27, A28, A30, G260, G276, T330 and 730. A27 and 730 are fairly homogeneous, even-grained rocks (**Figure 4(d)**) while G260 and T330 are more coarse-grained with clusters of large mafic grains next to more felsic-rich regions, which might be nepheline and alkali feldspar disaggregated from large pseudoleucites. Some leucomalignites lack pseudoleucites and contain euhedral nepheline (A27, 730), while pyroxene and amphibole appear to be cumulus phases enclosed by large grains of interstitial alkali feldspars. **Table 2** shows modes estimated from hand specimens. See Supplementary file S.2 for details on individual samples.

Note that the nepheline syenite classification (pulaskite, foyaite, juvite) adopted by Rees (1960) and Gifford (1961) has been used by CMBH and other authors in papers published on Marangudzi samples (see Supplementary file S.3, see the section after Conclusions for details for access to remote files). However, following IUGS (in Le Maitre et al., 2002) and Mitchell and Platt (1979), this classification is changed to Pulaskite = “Nepheline-bearing syenite” and Juvite = “Leucomalignite”. Foyaite has been retained here because all samples studied have well-aligned alkali feldspar phenocrysts with medium to fine mafic-mineral-rich matrices (i.e., foyaitic texture). The principal intrusive units shown by Gifford (1961) are adopted with the western limb of the foyaite ring cutting the pulaskite as shown here in **Figure 1**.

Diagnostic mineralogical and textural features for the three main, newly-named, silica-undersaturated, felsic intrusive units are as follows:

(i) *Nepheline-bearing syenite* (original pulaskite and “white syenite”). Typical samples are coarse-grained with large cryptoperthites (~65 vol. %) and finer-grained abundant subhedral hastingsitic amphibole (~15 vol. %); subordinate plagioclase and nepheline are present (both average ~6 vol. %) with ~2 vol. % pale green diopside pyroxene. Biotite is only present in trace quantities and no preferential orientation is shown by the large alkali feldspars.

(ii) *Foyaite* (original “grey syenite”). The samples studied have elongate cryptoperthitic alkali feldspars (up to 1 cm) and prismatic hastingsitic amphiboles (average ~18 vol. %) set in a finer-grained matrix of cryptoperthite, feldspathoid (average ~20 vol. %, mainly nepheline) and hastingsite. Plagioclase is only present in one sample but pyroxene and biotite are generally absent in this rock type. Alkali feldspar phenocrysts show spectacular trachytic orientation (hence the name foyaite), as does the prismatic amphibole.

(iii) *Leuco-malignite* (original juvite and “white syenite”). Typical samples are heterogeneous, coarse-grained rocks with variable proportions of cryptoperthites and nepheline, with little or no plagioclase, while some varieties contain large pseudoleucites. Mafic minerals typically are pale- to medium- green diopside pyroxene and hastingsite amphibole (generally lacking magmatic biotite), with mafic mineral modal totals varying (15 - 30 vol.%) but the pyroxene/amphibole proportions are generally similar.

3. Ring intrusion: silica-oversaturated units.

3a. Porphyritic quartz syenite unit. These rocks are characterized by the presence of phenocrysts of tabular micropertthitic alkali feldspars (**Figure 4(f)**) and some have plagioclase xenocrysts which are strongly zoned (andesine-oligoclase) with

alkali feldspar reaction rims. The groundmass consists of intergrowths of microp-
erthitic alkali feldspar, occasional plagioclase (albite-oligoclase), prismatic and
“ragged” hastingsitic (brown-green) amphibole, and variable amounts of intersti-
tial quartz (0 - 20 vol.%); accessory minerals are opaque Fe-oxides, apatite (asso-
ciated with amphiboles) and allanite. Analysed samples are A21 (trace quartz), A16
(quartz-rich) and T36 (plagioclase-free). G439 is from the small central plug and
has similar mineralogy and textures to the other samples.

3b. Inner quartz syenite ring unit. These inequigranular rocks have large tabular
perthitic alkali feldspars, smaller microperthitic alkali feldspars, subhedral mafics
and sometimes plagioclase (andesine-oligoclase); small grains of altered olivine
(presumably original fayalite) and interstitial quartz (0% - 10%) are also present.
Pale green diopsidic pyroxene shows alteration to brown-green hastingsite, which
also forms separate grains. Accessory minerals are allanite and zircon. Analysed
samples are 89, 103, 143, A6 (plagioclase bearing), T5 (pyroxene free), T17, T33,
and T49 (minor pyroxene); T17 has fayalite pseudomorphs.

3c. Outer quartz syenite ring unit. These inequigranular rocks have subhedral
grains of microperthitic alkali feldspar, while some have cores of sodic plagioclase.
The larger feldspars are twinned and occur in a matrix of subhedral microperthite,
anhedral brown-green hastingsite, and quartz (usually <10% but locally >30%).
The amphiboles have inclusions of Fe-oxide, allanite and zircon. Analysed sam-
ples are A7, G118, G141, G177, G161 and G63; these are similar texturally and
mineralogically and mainly have <10% quartz although G63 has 35 vol. % (Rees,
1960).

4. Mineral Chemistry: Results and Principal Observations of Fractionation Trends and Conditions

Over the years, a very large database of electron microprobe analyses on the gab-
broic and felsic rocks units of the Marangudzi complex has been obtained at Man-
chester, initially using Cambridge Instruments GeoScan 5 or Cameca Camebax
microprobes, both fitted with LINK 860-500 or AN1000 energy-dispersive detec-
tors. Subsequently, combined ED/WD analyses were obtained with a Cameca
Camebax system and most recently with full WD analyses using a Cameca SX100
five-spectrometer system with PDP analysis software. In all cases, the standard set
was the same: wollastonite (Si, Ca), corundum (Al), fayalite (Fe), periclase (Mg),
jadeite (Na), sanidine (K), rutile (Ti), tephroite (Mn), apatite (P), fluorite or fluoro-
apatite (F), halite (Cl), barite (Ba), celestine or synthetic glass Srgl with 9.0 wt.%
Sr (Sr), Ni, and Cr₂O₃. Detection limits for minor/trace elements in: olivine (CaO
0.04, NiO 0.08 wt%); pyroxene (Na₂O 0.08, K₂O 0.03, Cr₂O₃ 0.05 wt.%); biotite,
amphibole (Cr₂O₃, MnO 0.02, BaO 0.03, Cl 0.1, F, 0.1 wt%); felsics (BaO 0.02, SrO
0.03 wt.%). A focused beam was used for the mafic minerals (1 - 2 µm) and for the
felsic phases, defocused spots were used (feldspars ~3 µm, feldspathoids ~5 - 10
µm, specimen current 3nA). In this paper, the compositions of the major minerals
and the main accessory phases are reported for 12 gabbroic rocks, 5 nepheline

monzonites, 5 nepheline-bearing syenites, 6 foyaites, 2 microfoyaies, 6 leuco-malignites, 4 porphyritic quartz syenites, 5 inner quartz syenites, and 6 outer quartz syenites; each of these named rock units forms distinct mapped regions making up the sub-volcanic “ring-complex”. Microprobe analyses of minerals in a microgabbro “plug” and a basanite dyke are also reported here. For mafic mineral separates (e.g., amphiboles and micas), FeO was determined by chemical analysis using the ammonium metavanadate method (Wilson, 1955).

The main compositional features of minerals from each intrusive unit are outlined below in order to assess the evolution between different key units. Supplementary file S.3 gives further analytical information and Supplementary Excel file S.5 has the full analytical database (see the section after Conclusions for details for access to remote files).

4.1. Olivine

Magnesian olivine only occurs in the gabbro sheet and fayalite (or its pseudomorph) occurs in a few quartz syenites. Compositional relations (Table 3 and Supplementary file S.5) show very little Fe/Mg core/rim variation. CaO and NiO are uniformly low and show little change with changing Fo. For olivines from the different rocks, Fo ranges from 71.4 for the least evolved gabbro mesocumulates to 45.8 mol.% for the rim in the most evolved orthocumulate (T168). The most primitive average composition for the cumulus olivines is ~Fo₇₁ and three gabbros (100, 100A, G265) define the most primitive olivine composition (Figure 5). The olivines show only limited effects of magmatic fractionation with the most Fe-rich compositions shown by core/rim values for the most evolved orthocumulate T168 (points labelled c and r; Figure 5).

Table 3. Olivine electron microprobe (11 samples) and bulk chemical analysis (2 samples) from Marangudzi gabbros.

	100A	100	G265	T203	G266	A8	A12	G205	T123	A4	T168	T168
	Mesogabb	Mesogabb	Mesogabb	Orthogabb	Mesogabb	Orthogabb	Orthogabb	Mesogabb	Mesogabb	Mesogabb	Orthogabbro	
	Core/centre											Rim
	Av. of 13	Av. of 9	Av. of 9	Chem.	Av. of 12	Av. of 9	Av. of 17	Av. of 10	Av. of 5	Av. of 5	Av. of 4	Av. of 2
Oxide w/w %												
SiO ₂	37.6 (5)	37.3 (3)	37.6 (6)	36.5	36.4 (4)	36.4 (4)	36.767 (3)	36.3 (6)	35.4 (2)	35.4 (4)	35.3 (1.1)	34.4 (2)
MgO	36.3 (1.1)	35.3 (2)	35.0 (5)	32.2	31.8 (5)	30.1 (4)	28.8 (4)	28.4 (1.2)	27.7 (1)	25.2 (5)	22.8 (2)	21.0 (8)
CaO	0.09 (5)	0.06 (5)	n.d.	0.39	0.08 (4)	n.d.	n.d.	n.d.	0.07 (4)	0.09 (5)	n.d.	n.d.
MnO	0.26 (11)	0.40 (13)	0.37 (9)	0.67	0.49 (9)	0.58 (8)	0.55 (8)	0.65 (9)	0.62 (9)	0.93 (10)	0.70 (9)	0.79 (4)
FeO	25.6 (1.5)	26.2 (5)	27.0 (5)	29.9	30.3 (8)	33.0 (5)	34.36 (7)	34.9 (1.4)	35.7 (3)	39.5 (1.1)	41.7 (6)	43.5 (6)
NiO	n.a.	n.d.	n.a.	n.d.	0.23 (17)	n.a.	n.d.	n.a.	0.13 (2)	0.12 (2)	n.d.	n.d.
Total	99.9	99.4	100.0	99.6	99.3	100.2	100.5	100.3	99.5	101.3	100.6	99.7
Atoms per 4 O												
Si	0.994 (6)	0.995 (4)	1.001 (7)	0.991	0.994 (11)	0.998 (6)	1.013 (8)	1.004 (14)	0.990 (5)	0.993 (9)	1.011 (26)	1.0044 (11)

Continued

Mg	1.434 (32)	1.406 (4)	1.390 (10)	1.303	1.296 (16)	1.231 (7)	1.182 (14)	1.173 (43)	1.157 (2)	1.054 (19)	0.972 (11)	0.913 (30)
Ca	-	0.002 (1)		0.011	-	-	-	-	0.002 (1)	0.003 (1)	-	-
Mn	0.006 (2)	0.009 (3)	0.008 (2)	0.015	0.011 (2)	0.014 (2)	0.012 (2)	0.015 (2)	0.015 (2)	0.022 (2)	0.017 (2)	0.019 (1)
Fe	0.566 (33)	0.586 (10)	0.601 (7)	0.679	0.694 (17)	0.757 (11)	0.792 (13)	0.808 (36)	0.835 (5)	0.926 (24)	1.000 (17)	1.063 (20)
Ni	-	-			-	-	-	-	-	0.002 (1)	-	-
Total	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
mol% Fo probe	71.4 (1.7)	70.2 (4)	69.6 (4)		64.7 (8)	61.5 (5)	59.5 (6)	58.8 (1.9)	57.6 (2)	52.6 (1.1)	48.9 (4)	45.8 (1.3)
Maximum <i>mg#</i>	73.0	70.8	70.0		65.7	62.0	60.0	60.5	57.8	53.6	49.2	
mol% Fo chem.	71.9		69.1	65.2			57.6	58.2		56.1	48.5	

Note: n.a., not analysed; n.d., not detected; detection limit CaO ~0.04 wt%; NiO ~0.08 wt%; standard deviations for last places in brackets.

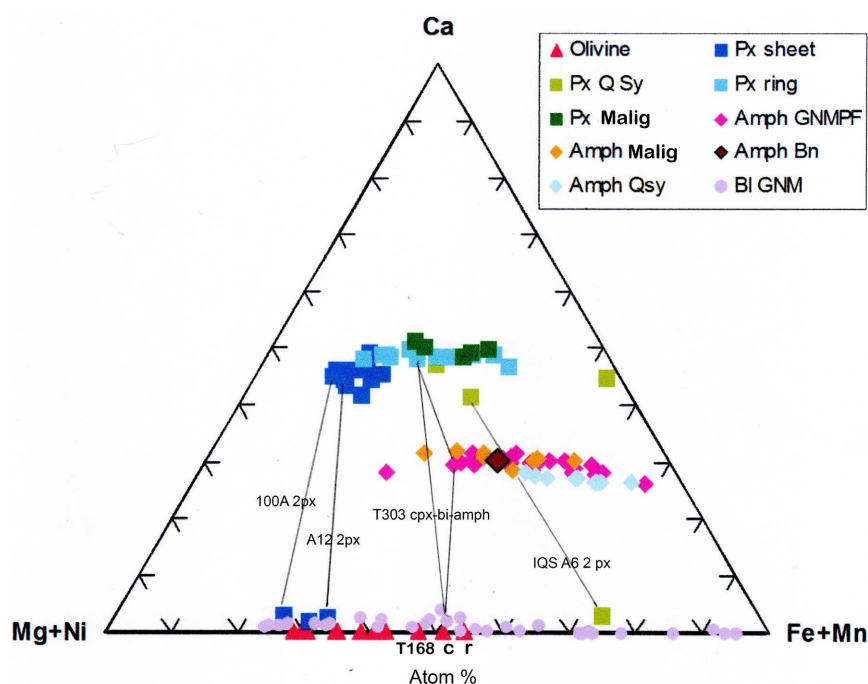


Figure 5. Compositions of mafic minerals (olivine, clinopyroxene, orthopyroxene, amphibole and biotite) are plotted in the Ca (+ Sr, Ba)-Mg-(Fe + Mn) variation diagram as atomic %. The “Ca” component for the biotites mainly reflects their elevated Ba concentrations. Representative “tie-lines” for two-pyroxene pairs are shown for mesocumulate gabbro 100A and orthogabbro A12 and for the coexisting clinopyroxene-biotite-hastingsitic amphibole trio for nepheline monzonite T303. Note that orthopyroxene compositions are more Fe-rich than coexisting clinopyroxene and also that coexisting amphiboles are always more Fe-enriched than the coexisting biotites. Symbol labelled GNMPF is for the series Gabbro-Nepheline Monzonite-Nepheline-bearing syenite-Foyaite (see GNM), Bn = basanite T178. To preserve clarity, biotite from all the Marangudzi rock types has the same symbol.

4.2. Pyroxenes

Table 4 gives average clinopyroxene compositions for each of the major pyrox-

ene-bearing units. The tholeiitic affinities of the main olivine-gabbro are reflected in the coexisting clino- and ortho-pyroxene (100A, G266 and A12). Clinopyroxene is comparatively homogeneous from core to rim for the gabbros and quartz syenites but is more variable in the silica-undersaturated units (deviation for wt.% MgO generally within 1% - 4% relative for the gabbro pyroxenes, 2% - 5% for silica-oversaturated “ring units”, and much higher values of 6% - 19% for the silica-undersaturated rings) (Supplementary file S.5).

Table 4. Representative Marangudzi pyroxene compositions for the main intrusive units.

Oxide wt. %	A12 Orthocu Av 10 Opx	A12 Ortho Av 13 Cpx	Mesocum gabbro Av 8 Cpx	Ortho cum gb Av 4 Cpx	Neph. Monzon. Av 5 Cpx	Neph- bearing Syenite Av 4 Cpx	Foyaite Av 3 Cpx	Malignite Av 5 Cpx	PQS A21 Av 2 Cpx	IQS A6 Av 2 Opx	IQS A6 Av 2 Cpx	OQS T17 Av 7 Cpx
SiO ₂	54.21	52.17	50.74	50.98	50.37	50.26	47.96	47.62	49.77	48.44	48.05	47.69
TiO ₂		0.54	0.50	0.50	0.48	0.49	0.35	0.85	0.32	0.11	1.33	0.02
Al ₂ O ₃	0.34	2.41	2.88	3.17	3.79	2.85	3.18	4.88	1.02	0.13	0.70	0.27
Cr ₂ O ₃		0.38	0.19	0.12		0.09						
Fe ₂ O ₃ *		1.38	2.75	2.23	3.59	3.80	6.36	5.82	3.67	0.78	4.92	2.42
FeO*	20.38	7.17	6.11	7.19	7.73	10.97	13.02	10.10	12.01	40.58	16.23	27.52
MnO	0.45	0.23	0.19	0.27	0.39	0.70	0.89	0.66	0.81	1.83	0.75	0.83
MgO	23.44	14.78	14.00	14.03	11.14	8.56	5.71	7.47	9.17	7.75	8.46	0.64
CaO	1.26	21.84	21.87	21.73	22.88	22.56	21.74	22.66	22.45	1.29	19.97	19.99
Na ₂ O	n.d.	0.23	0.41	0.25	0.73	1.02	1.22	0.99	0.40	0.03	0.22	0.45
K ₂ O	n.d.	0.02	0.04	0.02								
Total	100.08	101.15	99.66	100.47	101.04	101.21	100.44	101.05	99.62	100.94	100.63	99.86
Std.dev. MgO (relative)	0.39	0.55	0.41	0.36	0.71	0.95	1.13	0.45	0.49	0.12	0.26	0.03
Atoms 6 O, 4 cation (apfu)												
I.E.	0.325	0.24	0.255	0.267	0.351	0.474	0.628	0.533	0.471	0.725	0.566	0.938
Si	1.998	1.917	1.894	1.895	1.879	1.905	1.870	1.819	1.929	1.983	1.881	1.968
Al	0.015	0.104	0.127	0.128	0.166	0.127	0.146	0.219	0.047	0.006	0.032	0.013
Ti	0	0.015	0.014	0.014	0.014	0.014	0.010	0.024	0.009	0.003	0.039	0.006
Cr	0	0.011	0.006	0.003	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000
Fe ³⁺	0	0.038	0.083	0.075	0.101	0.108	0.187	0.167	0.107	0.024	0.145	0.075
Fe ²⁺	0.628	0.22	0.186	0.211	0.241	0.348	0.425	0.343	0.389	1.389	0.531	0.950
Mn	0.014	0.007	0.007	0.009	0.012		0.030	0.022	0.027	0.063	0.025	0.029
Mg	1.29	0.81	0.779	0.777	0.619	0.484	0.332	0.425	0.529	0.473	0.493	0.039
Ca	0.05	0.86	0.875	0.865	0.924	0.916	0.908	0.927	0.932	0.057	0.838	0.884
Na	0	0.016	0.030	0.023	0.053	0.075	0.092	0.073	0.030	0.002	0.016	0.036

Continued

K	0	0.001	0.001	0.001								
Fe ³⁺ /ΣFe ⁺ %	0	14.78	30.880	26.730	30.280	24.300	30.500	34.920	21.600	1.690	21.400	7.320
<i>mg#</i> max	67.4	78.2	69.680	55.500	63.580	50.300	34.100	45.500	50.300	24.200	41.300	3.570
<i>mg#</i> mean probe	66.73	75.29	73.922	53.938								
<i>mg#</i> chem.anal	63.7	74.1	73.32	54.325								
CaTi (Al ₂ O ₆) (molar)	0	0.78	0.751	0.738	0.732	0.760	0.577	1.382	0.490	0.170	2.050	0.310
CaAl (AlSiO ₆)	0.37	2.23	2.774	2.763	3.790	2.720	3.510	4.846	0.740	-0.020	-1.210	0.030
CaFe ³⁺ (Fe ³⁺ SiO ₆)	-0.45	0.57	1.412	1.403	1.308	0.925	2.640	2.672	2.010	0.550	3.370	1.020
NaFe ³⁺ (Si ₂ O ₆)	0	0.86	1.577	1.210	2.866	4.058	5.190	4.122	1.590	0.100	0.860	1.840
CaSiO ₃	2.14	41.36	41.714	41.018	43.892	45.288	44.060	43.510	45.620	2.160	39.790	44.230
MgSiO ₃	65.05	42.31	41.516	41.260	33.656	26.225	18.547	24.026	27.750	23.820	25.920	2.020
Fe ²⁺ SiO ₃	32.43	11.89	10.256	11.613	13.770	20.028	25.480	19.444	21.800	73.220	29.210	50.550
Putirka (2008)												
Two-px Temp		903/7.3									650/4.3	
°C/Press kbar												

Note: Based on Fe³⁺ calculated. I.E. Iron enrichment = Fe_{tot}/(Mg + Fe_{tot} + Mn); *mg#* = Mg/(Mg + Fe_{tot} + Mn); Fe³⁺ fixed to use all Na (acmite), then combined with Ca to make Ti tschermaks calcic ferripyroxene; all Ti combined with 2Al to make Tschermaks Al calcic px; remaining Ca makes Wo, all Mg makes En and all Fe²⁺ makes ferrosilite (formulae as in above table). Wo-En-Fs defines the pyroxene chemical system. *Oxide proportions calculated stoichiometrically.

Gabbro meso- and ortho-cumulate clinopyroxenes show lower Ca contents (~0.86 apfu) than those for the nepheline monzonite, nepheline-bearing syenite, foyaite and leucomalignite intrusive units (0.91 - 0.93 apfu) (**Figure 6**); the higher Ca relationship reflects the alkaline affinities of the latter units. Small clinopyroxene “fragmented” inclusions in nepheline-bearing syenite amphibole T301 are particularly Mg-rich and are locally altered to Mg-rich biotite, whereas larger separate pale green clinopyroxenes are less Mg-rich. T301 clinopyroxene has an average composition with Fe-enrichment factor lower than that for some of the nepheline monzonite biotites. Thus, the clinopyroxene in individual samples for each of the nepheline monzonite to nepheline-bearing syenite to foyaite sample series shows a scattered trend around Ca = 0.92 apfu, but average compositions for each intrusive unit (large symbols in **Figure 6(a)**) show a slightly decreasing Ca trend with evolution (ranging 0.3 - 0.7). The last intruded leucomalignite samples (**Figure 6**) have clinopyroxene compositions with similar higher Ca with Fe-enrichment factor ranging 0.4 - 0.65. In addition, the average clinopyroxene in the interior quartz syenite has a much lower Ca value than those for the porphyritic and outer quartz syenites, reflecting the presence of a coexisting orthopyroxene phase in the interior quartz syenite. Individual clinopyroxenes from the gabbros to nepheline-bearing rocks show scattered increasing Na and Mn (**Figure 6(b)** and **Figure 6(d)**); the averages for each of these units define clear evolutionary trends. Ti (**Figure 6(c)**) and Al (Suppl. file S.5) show similar scattered horizontal trends from gabbros to “foyaite” samples with increasing Fe-enrichment factor,

with the leucomalignites plotting above that trend. The average compositions for each confirm the clear horizontal trends for the gabbro to foyaitic rock series, with the average leucomalignite displaced to a slightly higher Ti (**Figure 6(c)**). **Figure 6** also shows that each of the average quartz syenite compositions shows distinct positions for Na, Ti and Mn, with the average outer quartz syenite having the most evolved I.E. value.

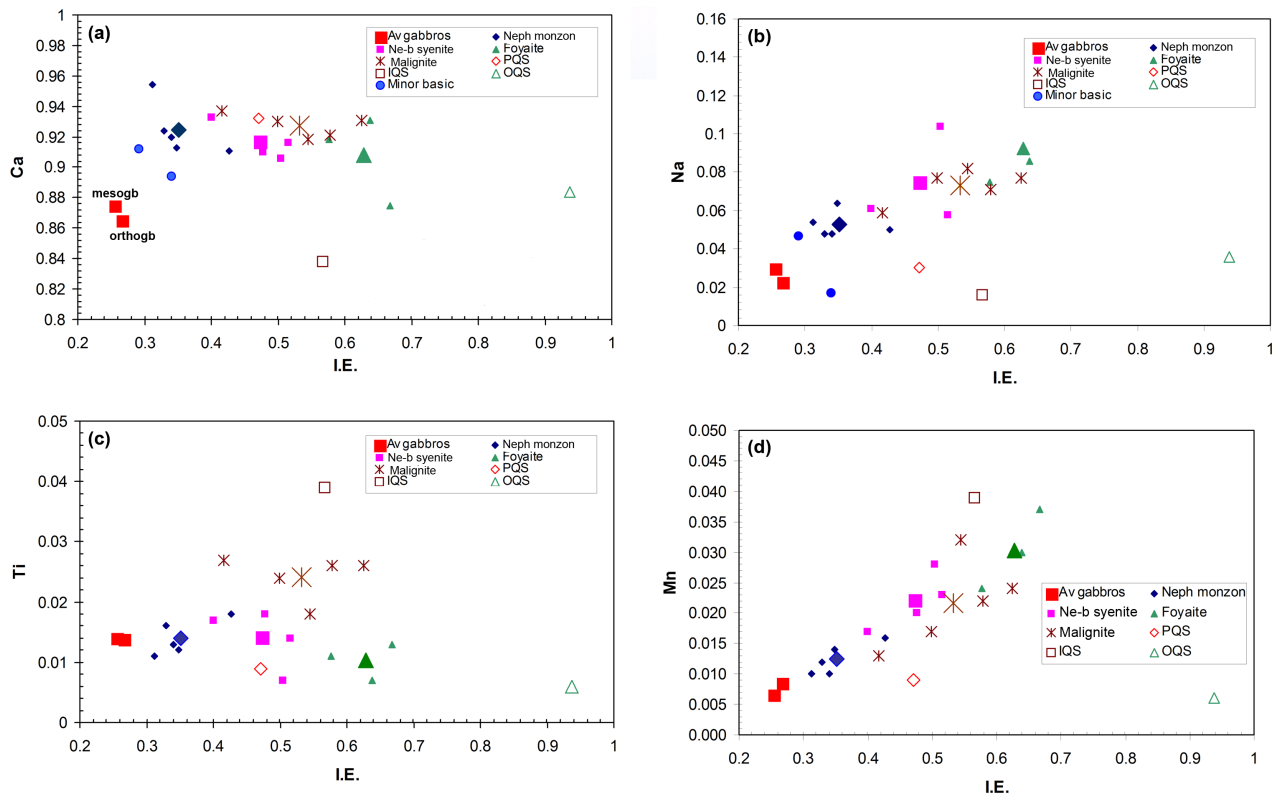


Figure 6. Clinopyroxene atomic proportions (apfu) for Ca (6a), Na (6b), Ti (6c) and Mn (6d) *versus* the iron variation index I.E. $(\text{Fe} + \text{Mn})/(\text{Mg} + \text{Fe} + \text{Mn})$ atomic). Individual rock samples are shown with small symbols and the average value for separate intrusive units is shown with a large symbol having the same colour as for the individual parent rock samples. See text for explanation.

The calculated molecular proportions of the clinopyroxenes have very small proportions of the CaTi - and CaFe^{3+} -end members (<1 mole %), slightly larger CaAl (AlSiO_6) (1 - 4 mol.%), and low acmite ($\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ 1 - 2 mol.%), reflecting their miaskitic nature (Mitchell, 1990). Clinopyroxenes from the gabbro classify as “augites” [also see Table 4 in Deer et al. (1978)] and have a mean $mg\#$ value of 78, which represents the mean composition of the cumulus clinopyroxenes. Clinopyroxenes from other units have higher Ca contents and are diopside-hedenbergite. The main compositional variations for the pyroxenes from each of the units are shown in **Figure 5**. Gabbro clinopyroxenes cluster with orthopyroxenes for three gabbros next to the En-Fs join. In **Figure 5**, lines of constant atomic $\text{Fe}/(\text{Fe} + \text{Mg})$ fan out from the Ca apex but for sample 100A the clinopyroxene has a slightly higher $mg\#$ than the coexisting orthopyroxene

and the tie-line shown in **Figure 5** diverges slightly from a line of constant *mg#*. The coexisting pyroxenes in gabbros G266 and A12 show a similar relationship, with *mg#* values for clinopyroxene being 5% - 10% more magnesian than for the coexisting orthopyroxene (Suppl. file S.5; tie-line for G266 not shown in **Figure 5**).

Compositions of the clinopyroxenes in the rocks forming the ring-type and plug intrusive units are also shown in **Figure 5**. The nepheline monzonite ring unit clinopyroxenes continue the trend of Fe enrichment (*mg#* 68-56) and have CaAl- and CaFe³⁺ end-member values similar to those for the orthocumulate clinopyroxene (**Table 4** and Suppl. file S.5). Although some clinopyroxenes plot above the diopside-hedenbergite join, the recalculated Wo, En and Fs end-members have Wo < 50 (**Table 4**) and plot just inside the diopside-hedenbergite field (Deer et al., 1978). Note that the maximum *mg#* for clinopyroxene single spot analyses in nepheline monzonites average 63.6 (**Table 4**), which is significantly less than the mean value of *mg#* = 83 for the three most primitive cumulus clinopyroxenes in the gabbros (see above). The NaFe³⁺-component is significantly higher than for the gabbro clinopyroxenes, which explains the green colour of the more-evolved, alkali-rich character of the nepheline monzonite pyroxenes. The nepheline-bearing syenites containing plagioclase have pale green clinopyroxenes that continue these relationships (*mg#* 58-46), as do the foyaite unit pyroxenes (*mg#* 40-30), which are slightly richer in acmite; the nepheline-bearing syenite clinopyroxenes are diopsides and those in the foyaite are hedenbergites. The last-intruded nepheline syenite unit (leucomalignites) has more-primitive, magnesian pale-green clinopyroxenes in some rocks (overall range *mg#* 57-35; diopside to hedenbergite) with slightly elevated CaAl- and NaFe³⁺-clinopyroxene components (Suppl. file S.5).

Pyroxenes in the quartz syenite units are much less abundant than the associated amphiboles and some inner quartz syenites contain coexisting clino- and ortho-pyroxenes with the former being much more magnesian than the coexisting orthopyroxene, as shown by the tie-line orientation (e.g., A6, **Table 4**; **Figure 5**). The clinopyroxenes in this unit are less aluminous than those in the gabbros and the silica-undersaturated ring units, and have very variable Mg and Fe contents with *mg#* varying from 50 (porphyritic quartz syenite A21, salite) to 41.3 (inner quartz syenite A6, ferroaugite) to 3.6 (inner quartz syenite T17, ferrohedenbergite). The very Fe-rich clinopyroxene in T17 is accompanied by a Fe-rich silicate (~Fe_{1.86}Si_{1.1}O₄) that might be a fayalite pseudomorph.

Calculated temperatures and pressures for clino-orthopyroxene pairs (Putirka, 2008) from three gabbros and one inner quartz syenite are presented in **Table 4** and Suppl. file S.5. The gabbros fall at the lower end of the acceptable equilibrium test and the quartz syenite temperature is lower than those provided by the gabbro samples. However, the temperatures are plausible (gabbro average 925°C ± 30°C; quartz syenite 770°C); see below for further discussion (Section 6).

Table 5. Average compositions of biotites from Marangudzi main intrusive units.

	Meso-cumulate	Ortho-cumulate	Nepheline monzonite	Neph-bearing syenite	Micro-foyaite	Leuco-malignite	Qtz syenite	Minor basics
	Av of 6	Av of 3	Av of 4	Av of 4	Av of 2	Av of 3	Av of 4	Av of 3
SiO ₂	36.99	36.79	34.25	35.42	33.13	32.07	35.80	36.11
TiO ₂	4.19	5.74	4.35	3.71	1.65	1.25	3.52	4.75
Al ₂ O ₃	14.29	14.51	15.44	13.96	15.09	20.83	12.13	14.56
Cr ₂ O ₃	0.17	0.00		0.06	0.06			
MgO	16.76	14.71	10.13	10.09	6.00	4.45	7.04	10.87
MnO	0.07	0.03	0.28	0.46	0.97	0.79	0.30	n.d.
FeO*	12.20	14.37	21.01	22.53	28.27	27.34	27.68	20.56
CaO	0.14	0.24	0.02	0.10	0.08	0.01	0.03	0.18
BaO	0.55	0.88	2.01	1.20	0.40	0.02	0.02	0.40
Na ₂ O	0.50	0.30	0.23	0.40	0.27	0.09	0.12	0.45
K ₂ O	9.37	9.45	8.88	8.86	8.89	9.51	9.01	9.27
Cl	0.32	0.22	0.10			0.02		0.29
F	1.04	0.56				0.03		0.76
Total (-O = Cl, F)	95.94	97.43	96.55	96.51	96.73	97.14	95.93	98.27
Std. dev. MgO %	0.90	0.82	0.54	0.53	0.39	0.86	0.14	0.83
Si	5.646	5.584	5.418	5.595	5.509	5.126	5.786	5.585
Al tet	2.392	2.416	2.572	2.405	2.492	2.874	2.214	2.415
Sum Z	8.038	8.000	7.990	8.000	8.000	8.000	8.000	8.000
Al oct	0.161	0.178	0.296	0.194	0.304	0.983	0.109	0.243
Ti	0.477	0.657	0.518	0.441	0.343	0.151	0.431	0.551
Cr	0.009	0.000	0.000	0.000	0.000	0.000		
Mg	3.784	3.324	2.386	2.366	1.431	1.056	1.705	2.505
Mn	0.009	0.004	0.037	0.062	0.135	0.107	0.041	0.021
Fe ³⁺	0.097	0.150	0.195	0.261	0.139	0.068	0.250	0.090
Fe ²⁺	1.452	1.676	2.580	2.726	3.712	3.315	3.517	2.573
Sum Y	5.989	5.989	6.012	6.049	6.063	5.680	6.052	5.983
Ca	0.022	0.039	0.000	0.008	0.008	0.000	0.002	0.030
Ba	0.033	0.052	0.125	0.037	0.009	0.000	0.001	0.024
Na	0.146	0.089	0.071	0.123	0.084	0.027	0.039	0.134
K	1.812	1.830	1.792	1.786	1.839	1.940	1.870	1.829
Sum X	2.013	2.011	1.988	1.954	1.939	1.968	1.912	2.017
Cl	0.081	0.056	0.026	0.059	0.042	0.003		0.076
I.E.	0.290	0.355	0.539	0.559	0.730	0.769	0.688	0.516
Total Al	2.553	2.594	2.868	2.599	2.795	3.858	2.323	2.657

Continued

Total cats	16.040	16.000	15.990	16.003	16.002	15.648	15.963	15.972
$^w\text{O}^{2-}$	0.881	1.304	1.079	1.028		0.267	0.887	0.940
<i>mg#</i> %	71.08	64.47	45.78	43.65	26.54	20.63	30.97	48.233
16 cat $\text{Fe}^{3+}/\text{totFe}$ %	5.0	8.8	7.2	9.6	4.2	2.1	6.8	3.133
14 cat $\text{Fe}^{3+}/\text{totFe}$ %	4.0	7.8	10.7	14.7	9.5	3.2	6.8	1.267
Initial cats	16.087	16.053	16.070	16.094	16.050	16.221	15.989	15.990
Annite ($^w\text{O}^{2-}$)	0.280	0.337	0.526	0.540	0.728	0.767	0.690	0.523
Temperature °C								
Henry et al. (2005, HGT)	772	795	730	710	690	662	687	741
Luhr et al. (1984)	1014	1030	753	717		604	670	791
Pressure Mb, Uchida et al. (2007)	120	133	216	134	194	516	51	152

4.3. Biotites

Red-brown biotite is the last-formed primary magmatic mineral in the Marangudzi gabbros and less-evolved silica-undersaturated rocks. Wones (1981) related the higher stability of micas compared with amphiboles to lower silica activity, lower water fugacity, and moderately high K_2O of such magmas (Huntington, 1979). Mica compositions for each individual rock are given in Supplementary file S.5 together with average compositions for each intrusive unit; Table 5 gives the averages for each unit with petrologically significant parameters. Zoning is limited, as reflected by the MgO standard deviation (~5% - 6% relative), which is only slightly larger than found for primary clinopyroxene. Biotites from alkaline basaltic/ultramafic rocks are commonly enriched in Ba and Ti, leading to multivalent cation, multi-site cation exchange, combined with the presence of extra-oxygen replacing OH, F, Cl anions in the *W* site (denoted $^w\text{O}^{2-}$) (Henderson & Foland, 1996; Chukanov et al., 2011; Ventruti et al., 2020; Henderson, 2025).

Hossain (1970) provided partial compositions for a Ti-rich biotite separate from Marangudzi alkali gabbro A12 (atomic $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.136$). It is probable that ~30% oxybiotite molecule ($^w\text{O}^{2-}$) is present (Henderson, 2025); thus, the Li et al. (2020a, 2020b) spreadsheet for biotite is used to estimate the $^w\text{O}^{2-}$ values for the average Marangudzi biotite compositions. Cell formulae data given for Marangudzi EMP analyses (all Fe as FeO) were calculated for $[22+(^w\text{O}^{2-})/2]$ oxygens and 16 cations (Henderson, 2025) to obtain Fe^{3+} and Fe^{2+} values (Table 5). Molar proportions of annite (Fe^{2+} end-member) confirm that annite contents increase with evolution. No tetrahedral Fe^{3+} or Ti^{4+} is present and all samples contain octahedral Al. The biotites in gabbros have excess O ($^w\text{O}^{2-}$) ranging from ~0.9 for the most magnesian sample to ~1.5 in the most evolved orthocumulate (T168); thus, for most of the Marangudzi biotites, the average oxy mica proportion is 45% - 50%. However, the most evolved microfoyaite (A14) has 20% while a leucomalignite with a deuterite mica (A28) has 0% oxybiotite (Table 5); the samples show a coupled relation-

ship between Ti and $^{w}O^{2-}$ (Henderson, 2025).

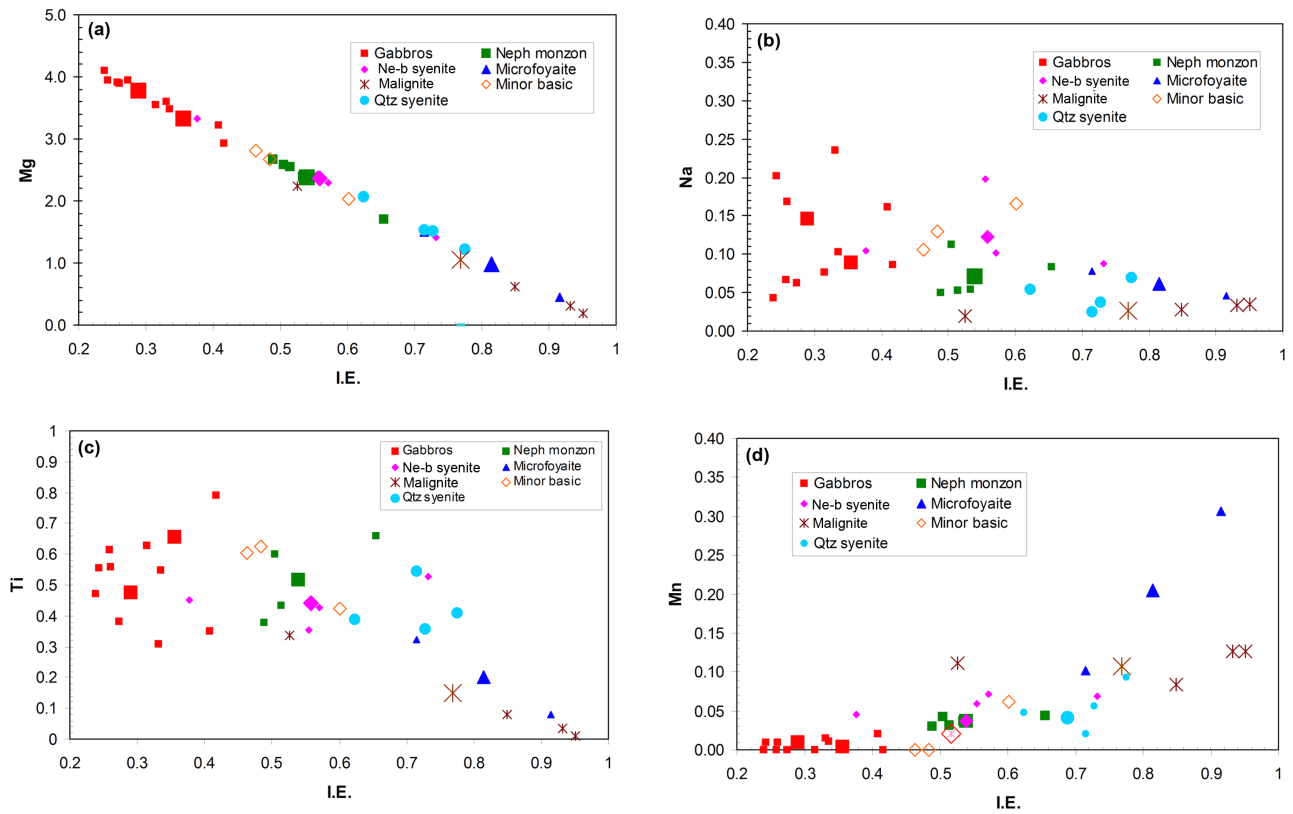


Figure 7. Biotite atomic proportions (apfu) for Mg (7a), Na (7b), Ti (7c) and Mn (7d) *versus* iron variation index I.E. Symbol types are identified as in **Figure 6**. See text for explanation.

Figure 7(a) shows the plot of Mg *vs* I.E. to assess individual biotite compositions from different intrusive units. Thus, biotites from two nepheline-bearing syenites show that one is very primitive (T301 with I.E. 0.38 and 2.2% Ba) and the other is evolved (T175 with I.E. 0.73 and BaO < 0.05%). The former is present as small inclusions in amphibole and the latter occurs as small laths at amphibole rims. Sample T301 has lower I.E. than any of Ba-rich nepheline monzonite biotites and is more primitive than biotites in two of the evolved gabbros. One leucomalignite has a primary magmatic biotite (G260) with an I.E. matching that of the average nepheline monzonite while those for the deuteric biotite in A28 match that of an evolved microfoyaite biotite (A14). Nevertheless, the average biotites for an orthocumulus gabbro-to-microfoyaite series show a clear trend of decreasing Mg with increasing I.E. In **Figures 7(b)-(d)**, the individual samples show little clear trend for the gabbros, while nepheline monzonite and nepheline-bearing syenite follow with a decrease for Ti (**Figure 7(c)**), and an increase for Mn (**Figure 7(d)**). For the intrusive unit averages, Na may show a small decrease with increasing I.E, Ti, a clear decrease, and Mn a clear increase.

Figure 5 shows that the biotite compositions define a continuous trend from gabbro through to nepheline-bearing syenites host rocks (*mg#* range 76% - 26%;

Suppl. file S.5; **Table 5**). The mica compositions in the last-intruded leucomalignite unit are different in the two samples studied; G260 is definitely a primary magmatic biotite phase ($mg\# = 40.4\%$) but the siderophyllite in A28 is a hydrothermal phase ($mg\# 14.9$). Crystallization of biotite as a major magmatic phase ended before formation of the foyaites, with plagioclase-bearing foyaitite A17 lacking modal biotite even though clinopyroxene is present. Oversaturated rock biotites have $mg\#$ ranging 62% - 78% but their plotted symbol is not differentiated from that for the other biotites to avoid unnecessary complexity. The parameters given in **Table 5** show low model $Fe^{3+}/\Sigma Fe$ values for biotites, with no clear difference for the silica-undersaturated and over-oversaturated rock series.

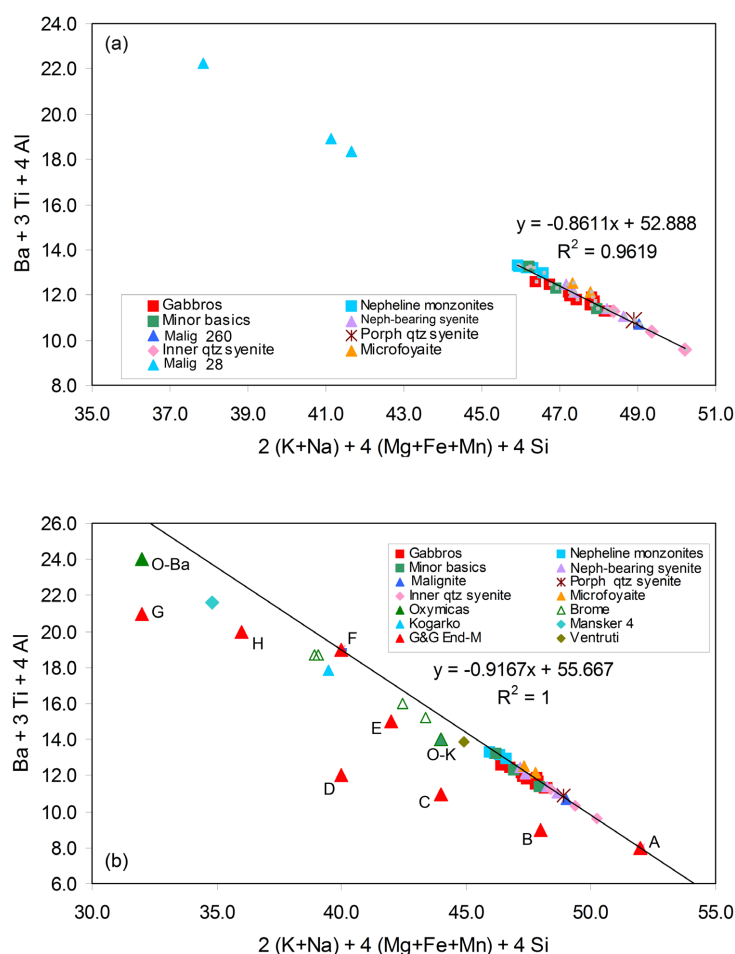


Figure 8. (a) Modified Guo and Green (1990) variation diagram for average biotite compositions for each of the main Marangudzi rock units to define how the intersite-intervallence evolutionary trend is critically dependent on the presence of the oxybiotite molecule (Henderson, 2025). The large dark green triangles mark the positions of hypothetical mica end-members, phlogopite (Ph, $K_2Mg_6[Si_6Al_2O_{20}](OH)_4$) and oxymica Al-Ti-kinoshitalite ($BaMg_4Ti_2[Si_4Al_4O_{20}]O_4$, Kogarko et al., 2005; Henderson, 2025). (b) Relationship shown between the oxy-mica function ($^{w}O^{2-}$, apfu) and deduced temperature for each of the rock types. The linear fit shown is for the average biotite compositions for the whole Marangudzi complex. See text for the explanation of the compositional variations.

Henderson (2025) showed how high-temperature magmatic biotites might have Ti and Ba entry controlled by complex vacancy-free, multivalent cation interchanges. The Guo and Green's (1990) exchange mechanism: $2(\text{K} + \text{Na}) + 4\text{M}^{2+} + 4\text{Si} \leftrightarrow \text{Ba} + 3\text{Ti} + 4\text{Al}$ is used here to model that interaction; M^{2+} includes all Fe as Fe^{2+} , with Mg and Mn. The plotted position of each sample is not affected by varying Fe/Mg ratios and variations mainly reflect variable Al and/or Ti. Most of the Marangudzi samples plot in the same tight group with mica in leucomalignite G260 at the bottom (Figure 8(a)); all are primary micas. Micas from leucomalignite A28 are displaced upwards from that group and are hydrothermally-formed Al-rich siderophyllites. Biotites from the gabbros, minor basics, and nepheline-bearing syenites plot over similar ranges of composition to the nepheline monzonites plotting at the top of the group, reflecting their higher Al, Ti and Ba contents. The dark green triangles mark the positions of Guo and Green's (1990) end-member phlogopite ($\text{K}_2\text{Mg}_6[\text{Al}_2\text{Si}_6]\text{O}_{22}(\text{OH})_4$, see annite) and an Al-rich K-Ti-kinoshitalite ($\text{K}_2\text{Mg}_6[\text{Al}_4\text{Si}_4]\text{O}_{22}(\text{OH})_4$). Neither has vacancies and the compositional trend passes through the Marangudzi magmatic mica compositions and is only slightly lower than the A28 hydrothermal micas; thus, the magmatic biotites are clearly stoichiometric with full cation sites (Henderson & Foland, 1996; Henderson, 2025). Biotites from gabbros and nepheline-bearing syenites plot over similar ranges of composition, with nepheline monzonites (blue-green squares) plotting at the top of the compositional series reflecting their higher Al, Ti and Ba contents.

The final rows of data given in Table 5 (and Suppl. file S.5) give tentative estimates for the crystallization temperatures of Marangudzi micas; both sets of estimates provide possible temperature ranges rather than absolute values. The top temperature values are obtained using biotite atomic parameters for Ti and $mg\#$ $[\text{Mg}/(\text{Mg} + \text{Mn} + \Sigma\text{Fe})]$ (Henry et al., 2005); see Suppl. file S.5, biotite folder. The temperature estimates given below those values are based on Ti/ Fe^{2+} of magmatic Ti-rich micas calibrated with Fe-Ti-oxide equilibrium (Luhr et al., 1984). Also given in Table 5 are estimates of the pressure of formation of Marangudzi biotites based on the total Al content (Uchida et al., 2007). Later work has shown that the Henry et al. (2005) method can be widely applied, including to differentiated mafic igneous complexes, provided that a Ti-rich phase (ilmenite, rutile, or titanite) is present (e.g., Namur et al., 2009; Keevil et al., 2020; Shagalov et al., 2021; Brenan et al., 2023). Using the Luhr et al. calibration, biotites from 8 gabbros provide an average temperature of $1070^\circ\text{C} \pm 130^\circ\text{C}$, considerably higher than the Henry et al.'s average of $795^\circ\text{C} \pm 20^\circ\text{C}$; by contrast, the biotites from two altered gabbros (A4 and T123) have lower values of 705°C and 709°C , respectively. The more fractionated rocks all show closer temperature estimates for average biotites in each of the intrusive units (Table 5). Figure 8(b) shows the average of the two estimated temperatures for biotites versus the extra-O factor ($^{\text{w}}\text{O}^{2-}$); the latter is strongly dependent on Ti content. The linear fit is for the full dataset but individual intrusive unit plots show displaced sub-parallel trends; nepheline monzonites have average formation temperatures about 50°C below the gabbro trend, with more-evolved

nepheline-bearing syenites (lower $mg\#$), least evolved microfoyaite and leucomalignite samples (higher $mg\#$) about 40°C lower still, reflecting the order of formation in the silica-undersaturated differentiation sequence.

Alkali basalt differentiation from liquidus to solidus conditions at $P_{H_2O} = 1 - 2$ kbar (5.5 - 7 km) is ~1170°C to 870°C (Yoder & Tilley, 1962; Richter & Carmichael, 1996) with equivalent temperatures for nepheline syenites and quartz syenites of ~900°C to 750°C (McDowell & Wyllie, 1971; Millhollen, 1971; Moussallam et al., 2013; Martel et al., 2013). Thus, biotites in the orthocumulate gabbros and nepheline monzonites precipitated as primary phases with nepheline-bearing syenite biotites forming closer to the solidus, and biotite re-equilibration probably continued subsolidus (see Section 6).

4.4. Amphiboles

Primary, green- or green-brown calcic amphiboles are common in all Marangudzi ring-type units but also are present as minor phases which have re-equilibrated subsolidus in gabbros. Borley and Frost (1963) and Henderson (1968) reported chemical compositions for Marangudzi amphibole separates with formulae calculated to 24 anions without considering an oxy-amphibole component.

With regard to possible cation vacancies and the presence of oxyamphibole (Hawthorne et al., 2012) components, formula calculation for Marangudzi amphiboles was addressed by Henderson and Mitchell (2026). For analyses lacking water data, anhydrous, stoichiometric cell proportions are usually calculated on a 23 oxygen basis; this assumes the presence of exactly $2(OH, F, Cl)^-$ anions. In his consideration of the cell formulae for biotite, Henderson (2025) stressed the requirement that, for calculating mica formulae, each site vacancy must be considered as a real component. The same approach is used here for amphiboles lacking water and Fe valence analyses (Henderson & Mitchell, 2026), with formulae calculated for $(23 + {}^wO^{2-}/2)$ oxygens and 16 or 13 cation cells. Based on this approach, the total cation values ($\Sigma cats^{16}$) range 16.11 - 16.54 (average 16.26) for silica-undersaturated rocks and 15.96 - 16.09 (average 16.05) for quartz syenites. The very low 16 cation total for the latter indicates the presence of significant vacancies in the (Na + K) component; thus, the equivalent Σ^{13} value [i.e., $\Sigma cats^{16} - (Ca + Na + K)$] ranges 13.23 - 13.38 (average 13.31). However, for the apparent silica-undersaturated average amphibole cation total of 16.26 apfu with all Fe as FeO, the equivalent T + C cation total is 13.21 apfu; thus calculated 16-cation and 13-cation model Fe^{3+} contents agree within error, indicating that those amphiboles are stoichiometric [i.e., 24 anion T + C cation totals close to 13.000 ($\Delta C = 0.0$), Henderson & Mitchell (2026)].

The full Marangudzi EMP amphibole dataset is attached as Supplementary file S.5 but Table 6 gives average amphibole compositions for each of the Marangudzi major intrusive units with wt.% EMP spot analyses for each individual Marangudzi sample entered with all Fe as FeO. Most samples show only limited compositional zoning, as is demonstrated by the standard deviations for the analysed MgO val-

ues. The atomic proportions calculated for all elements, as well as the model Fe^{3+} and Fe^{2+} based on a stoichiometric cell with $(23 + {}^{\text{W}}\text{O}^{2-}/2)$ oxygens and 16 cations (i.e., $\Delta\text{C} = 0$) are given in **Table 6** (see Supplementary file S.5 for individual samples). The rows below the cell formulae data give the ${}^{\text{W}}\text{O}^{2-}$ factor for each sample obtained using the Li et al. (2020c) spreadsheet, together with calculated values for I.E., *mg#* and $\text{Mg}/(\text{Mg} + \text{Fe})$. Amphibole names given in Suppl. file S.5 are mainly taken from those suggested in the Li et al. spreadsheet and are based on the IMA scheme (Hawthorne et al., 2012; Oberti et al., 2007). The least evolved amphiboles in nepheline monzonites and silica-undersaturated rock syenites are magnesio-hastingsites with some having slightly higher Ti, giving an additional Ti-rich prefix, however, most of the amphiboles are hastingsites.

Table 6. Average amphibole for each Marangudzi major intrusive unit.

	Average gabbro 2	Aver neph monz 5	Ave. neph- bearing syenite 5	Average foyaite 5	Average microfoy 3	Average malignite 5	Average PQS 4	Average IQS 3	Average OQS 5
Oxide wt.%									
SiO ₂	39.73	38.53	38.26	38.11	36.94	37.91	41.35	41.12	40.51
TiO ₂	0.37	2.09	1.89	1.46	0.94	2.32	1.74	2.01	1.79
Al ₂ O ₃	11.16	13.60	12.17	12.22	11.31	13.09	8.16	8.04	7.76
FeO	22.50	20.12	23.66	24.83	28.94	20.61	26.13	28.79	30.47
MnO	0.31	0.38	0.97	0.80	1.44	0.66	0.68	0.72	0.79
MgO	7.70	7.38	5.47	4.95	2.44	6.93	5.42	3.81	2.81
CaO	11.32	11.55	11.30	11.06	10.17	11.59	10.75	10.40	10.13
BaO	0.12	0.18	0.02	0.02		0.40	0.00	0.00	0.06
Na ₂ O	2.08	2.04	2.27	2.43	2.84	1.93	2.16	1.94	2.14
K ₂ O	1.64	2.27	2.03	2.00	1.93	2.35	1.31	1.30	1.35
Cl	1.78	0.18	0.09	0.10	0.06	0.20	0.33	0.00	0.65
F	1.15	0.80	1.00	0.91	1.53	1.15	1.30	1.00	0.85
Total (less H ₂ O, F, Cl)	96.89	98.14	98.03	97.88	96.95	97.98	97.75	98.12	97.81
Std dev Mg	0.36	0.47	0.48	0.66	0.59	0.44	0.36	0.25	0.50
I.E. index	0.632	0.609	0.716	0.742	0.876	0.636	0.724	0.813	0.854
(23 + ${}^{\text{W}}\text{O}^{2-}/2$) formula Atoms per formula unit	16 cats	16 cats	16 cats	16 cats	16 cats	16 cats	13, $\Delta\text{C} = 0$	13, $\Delta\text{C} = 0$	13, $\Delta\text{C} = 0$
Si	6.226	5.951	6.007	6.002	5.976	5.910	6.490	6.481	6.453
Al tet	1.775	2.049	1.993	1.998	2.024	2.090	1.508	1.493	1.457
Ti tet	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.006	0.090
Total T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000

Continued

Al oct	0.299	0.421	0.260	0.272	0.156	0.314	0	0	0.000
Ti oct	0.043	0.244	0.224	0.172	0.089	0.272	0.213	0.210	0.124
Fe ³⁺	0.387	0.579	0.736	0.817	1.181	0.701	0.873	1.104	1.179
Fe ²⁺	2.616	2.022	2.371	2.458	2.734	2.017	2.557	2.696	2.883
Mn	0.041	0.049	0.130	0.105	0.198	0.087	0.090	0.097	0.106
Mg	1.751	1.708	1.280	1.174	0.586	1.610	1.270	0.890	0.711
Total C	5.135	5.023	5.006	4.996	4.950	4.996	5.065	5.002	5.021
Ca	1.906	1.910	1.901	1.868	1.762	1.935	1.808	1.756	1.728
Ba	0.007	0.009	0.001	0.001	0.000	0.019	0.000	0.000	0.001
Na	0.620	0.611	0.690	0.736	0.891	0.581	0.657	0.593	0.662
K	0.332	0.448	0.406	0.402	0.399	0.468	0.262	0.262	0.274
Total B + A + ΔC	3.000	3.001	3.004	3.002	3.002	3.000	2.743	2.612	2.671
Total cats	16.00	16.00	16.00	16.00	16.00	16.00	15.74	15.61	15.68
Cl	0.482	0.048	0.025	0.028	0.016	0.053	0.175		0.176
F	0.496	0.394	0.504	0.461	0.783	0.566	0.641	0.497	0.426
Total Al	2.073	2.470	2.256	2.270	2.180	2.404	1.549	1.493	1.475
^W O ²⁻	0.048	0.386	0.357	0.299	0.229	0.419	0.319	0.403	0.364
Range ^W O ²⁻	0.47 - 0.49	0.45 - 0.31	0.48 - 0.27	0.3 - 0.24	0.26 - 0.19	0.53 - 0.27	0.44 - 0.27	0.45 - 0.37	0.44 - 0.3
Fe ³⁺ /ΣFe	0.149	0.224	0.237	0.248	0.262	0.258	0.254	0.291	0.292
<i>mg</i> [#] [⊗]	0.368	0.391	0.284	0.258	0.127	0.367	0.265	0.187	0.146
Range <i>mg</i> [#]	0.60, 0.13	0.51 - 0.30	0.50 - 0.15	0.42 - 0.2	0.22 - 0.07	0.53 - 0.17	0.31 - 0.21	0.3 - 0.1	0.18 - 0.1
Mg/(Mg + Fe ²⁺)	0.400	0.427	0.310	0.320	0.160	0.396	0.320	0.217	0.170
Temperature °C									
Ridolfi and Renzulli (2012) Eqn 2	706	825	916	890	1048	893	856	784	797
Temp Putirka	848	986	907	892	860	946	800	772	762
Temp Helz	593	796	773	721	660	824	774	793	765
Pressur Ridolfi and Renzulli (2012), Eqn 1b Mbar	161	427	357	327	343	447	378	389	297
ΔNNO (log units) Ridolfi and Renzulli (2012) Eqn 3	0.5	3.1	3.2	3.2	4.4	3.6	-0.6	-2.3	-2.1
H ₂ O imagma wt % Ridolfi and Renzulli (2012) Eqn 4	8.7	5.1	3.4	4.0	2.1	3.6	4.5	4.8	4.7

Note: *mg*[#][⊗] = Mg/(Mg + Mn + Fe).

The full dataset includes separate analyses for core and rim of larger grains together with compositions for smaller grains in the matrix of porphyritic samples; thus, individual samples show significant ranges of I.E. but that does not necessarily lead to significant changes in Al, Na and Ca (see below and full dataset in Supplementary file S.5). **Figure 9** shows plots for Si, Ca, Na, K, Ti and Mn vs I.E. for the average intrusive unit compositions. **Figures 9(b)-(c)** show data for Ca

and Na variation in each individual sample with rim compositions marked with large open symbols (some joined to core compositions with labelled tie lines); thus, the plotted points are scattered, making it difficult to deduce clear trends. **Figure 9(b)** shows that the nepheline syenite and leucomalignite members show little clear trend but rims for nepheline-bearing syenites and foyaites occasionally show lower Ca contents. For **Figure 9(c)**, Na shows no clear trends for nepheline monzonite and leucomalignite amphiboles (see Al not shown); with some rims in nepheline-bearing syenite and foyaites having higher Na. The limited changes in Na and K contents in the less evolved ring units are probably controlled by coexisting alkali feldspar and nepheline buffering the alkali contents.

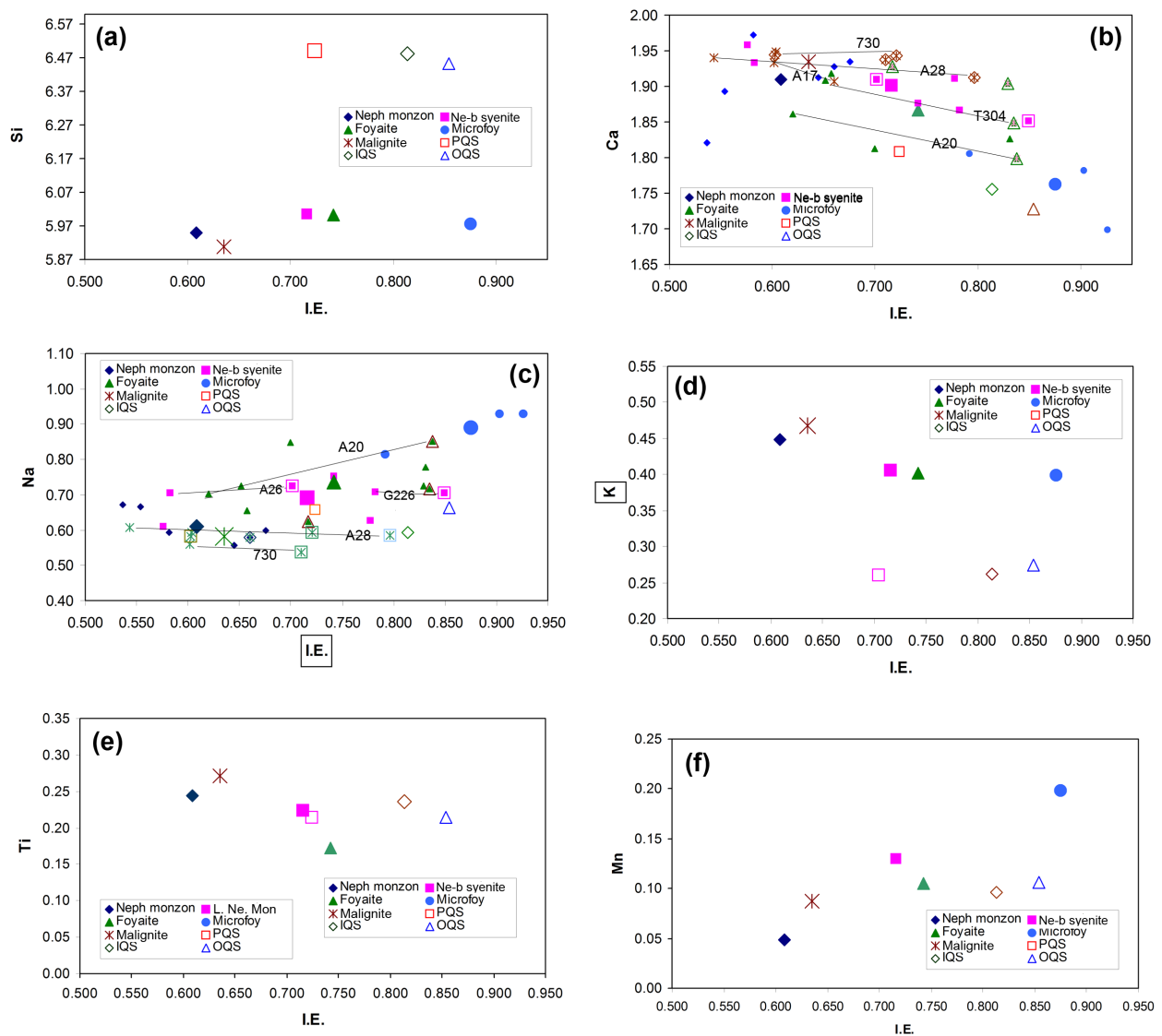


Figure 9. Amphibole atomic proportions (apfu) for Si (9a), Ca (9b), Na (9c), K (9d), Ti (9e) and Mn (9f) *versus* the iron variation index I.E. Individual rock data are shown with small symbols for Ca and Na to show the compositional within each intrusive unit and the average values for separate intrusive units are shown with a large symbol having the same colour as for the individual parent rock samples. Only average values are shown for Si, K, Ti and Mn to clarify trends within the silica-undersaturated rock types and to emphasise differences for the silica-oversaturated rock amphiboles. See text for explanation.

Each Marangudzi intrusive unit tends to have amphiboles with distinct mineralogical, chemical and textural features. In particular, the nepheline monzonite, nepheline-bearing syenite and foyaite units show overlapping extents of differentiation (**Figure 5**), perhaps related to local concentration of volatile components developing local pegmatite-like segregations similar to those shown by differentiated minor alkaline intrusions (e.g., Nash & Wilkinson, 1970; Carman, 1994; Marsh, 1996; Gibb & Henderson, 1996). This concept is tested by calculating average mineral compositions for each Marangudzi intrusive unit. Thus, in **Figure 9**, the average amphibole composition for each rock type is shown with a large coloured symbol, showing clear evolutionary trends of decreasing Ca and Ti (**Figure 9(b)** and **Figure 9(e)**) and increasing Na and Mn (**Figure 9(c)** and **Figure 9(f)**), coupled to increasing I.E. for the series nepheline monzonite-nepheline-bearing syenite-foyaite-microfoyaite. By contrast, the last intruded leucomalignite unit has amphibole compositions overlapping with those of the earlier intruded nepheline monzonites (also see **Figure 5**; Supplementary file S.5). The other panels in **Figure 9** show average intrusive rock unit values with Si and K showing little variation (**Figure 9(a)** and **Figure 9(d)**) (see Al not shown) with increasing I.E. Each of the panels in **Figure 9** shows the average composition for the different quartz syenite units (large open symbols) compared to those for the silica undersaturated rock types having similar I.E. values. Thus, quartz syenites have amphiboles with much higher Si and lower K (see Al, not shown) and slightly lower Ca, Na and Mn than the amphiboles in nepheline-bearing rock types, reflecting the critical compositional differences between the distinct parental magmatic compositions (see Henderson, 1968).

The bottom rows in **Table 6** show the estimated crystallization temperature, pressure, oxygen fugacities and magma water content based on experimental studies; the different petrogenetic approaches are based on: (i) amphibole Ti contents (Helz, 1973, 1982); (ii) statistical analyses of amphibole bulk chemical compositions (Ridolfi & Renzulli, 2012); (iii) amphibole Si, Ti, total Fe and Na (equation 5, Putirka, 2016) [Suppl. file S.5, amphibole folder]. The Putirka calculation consistently provides temperatures significantly higher than Helz values and an average of these is rather similar to the Ridolfi and Renzulli values (Ridolfi & Renzulli, 2012). The data will be fully considered below (Section 6) but some difficulties are summarised here for average data. In particular, note that the Ridolfi and Renzulli (2012) model pressure, temperature, oxygen partial pressure and silicate melt water content values obtained from their equations are based on analysed amphibole compositions obtained using published experimental work, mainly on intermediate and silica-saturated parent rocks at controlled physical conditions. Only two of the 21 experimental datasets were on silica-undersaturated alkali-rich basaltic parents and none were alkali-rich syenites. The average amphibole in Marangudzi nepheline monzonites and syenites is 5.5 ± 0.7 kbar and $895^\circ\text{C} \pm 50^\circ\text{C}$ and for the average amphibole in quartz syenites is 1.4 ± 0.7 kbar and $795^\circ\text{C} \pm 20^\circ\text{C}$. While both sets of data for temperature estimates are plausible, the pressures for the sil-

ica-undersaturated rock units are higher than would normally be expected for sub-volcanic ring intrusion and, as discussed above, may be 2 - 3 kbar too high unless nucleation and early growth occurred in the lower crust with rapid transfer upwards of magma to ring-dyke intrusion at higher levels. The lower pressure estimates for the quartz syenites at ~1 kbar are consistent with the probable intrusion depth. In addition, the unexpectedly high (Ridolfi & Renzulli, 2012) oxygen fugacity estimates for amphiboles also may reflect the lack of nepheline-rich samples in the experimental database; thus, the model data for the Marangudzi nepheline syenite amphiboles (average $\Delta\text{NNO} +3.4 \pm 1$) are probably 2 - 3 orders of magnitude too oxidising, while the data for quartz syenite amphiboles (average -2.0 ± 0.5) are, as expected, closer to the QFM buffer (Andersen, 1984). In addition, the range of calculated ΔNNO for the Marangudzi silica-oversaturated and undersaturated syenites covers 5 orders of magnitude; experimental work for basalt glasses on the FMQ buffer at the same temperature might have $\text{Fe}^{3+}/\Sigma\text{Fe}$ values varying from 0.2 to 0.7 (e.g., Fudali, 1965; Matzen et al., 2022) but averages for analysed Marangudzi amphiboles show similar $\text{Fe}^{3+}/\Sigma\text{Fe}$ for nepheline syenite amphiboles of ~0.23 and ~0.16 for quartz syenite amphiboles (Henderson, 1968) consistent with both amphibole species having formed with similar QFM properties. In sum, it seems that only qualitative estimates for oxygen fugacity should be made for evolved potassic, silica-undersaturated alkaline igneous rocks using the method of Ridolfi and Renzulli (2012).

For all of the physical and chemical formation conditions estimated here, it is assumed that the contrasting values for the different rock types are more reliable than the absolute values. Thus, the Cl-rich ferropargasite in altered gabbro A4 is clearly a hydrothermal, subsolidus phase with a crystallization temperature of ~600°C at an oxygen fugacity slightly more oxidising than the QFM buffer; however, Ridolfi and Putirka temperatures for the amphibole in gabbro T123 suggest that it is a late magmatic phase at ~850°C. All amphiboles in the nepheline monzonites, nepheline-bearing syenites, foyaites and leucomalignites give similar temperatures for each of the geothermometers quoted here, with an average of ~850°C - 900°C; ΔNNO oxidation estimates are probably 2 orders of magnitude too high, see earlier. The temperature for the nepheline monzonites is late-stage magmatic but for the nepheline syenites an early- to mid-magmatic crystallization temperature is indicated. The silica-oversaturated rock amphiboles all suggest a significantly lower temperature of 750°C - 800°C under oxygen fugacities similar to those for the nepheline syenites. As expected, where compositional data are available for both amphibole cores and rims, the latter temperatures are 20°C - 30°C lower.

4.5. Feldspars

Full compositional data are given for plagioclase and alkali feldspar in Supplementary file S.5. Average analyses for each intrusive unit are given here in Table 7. The feldspar An and Or proportions are displayed in Figure 10 as a function of I.E. for coexisting primary biotite in gabbros, nepheline monzonites and neph-

eline-bearing syenites and amphibole for foyaites, leucomalignites and quartz syenites, allowing assessment of how well-coupled the feldspars and mafic minerals are between the fractionated intrusive rock units. Standard deviations for CaO in plagioclase and K₂O in alkali feldspar reflect the zoning within each phase and, in the case of plagioclase, the most calcic compositions are usually very similar for cores in cumulus grains and for the central parts of matrix plagioclases. The bottom rows of **Table 7** give the extreme variations for plagioclase (An variation) and alkali feldspar [Or and Ba-feldspar (celsian molecule Cn)].

Table 7. Average feldspar compositions in main Marangudzi intrusive units.

	Mesocumulus gabbro		Orthocumulus gabbro		Minor basics		Nepheline monzonite		Nepheline-bearing syenites			Foyaites		
	Av 9 Plag F	Av 2 Alk F	Av 2 Plag F	Av 2 Alk F	Av 2 Plag F	Av 2 Alk F	Av 5 Plag	Av 5 Alk F	Av 4 Plag	Av 4 Alk F	G226 Alk F	A17 Plag F	A17 Alk F	Av 4 Alk F
wt. %														
SiO ₂	48.26	63.13	53.08	63.23	50.83	62.04	52.14	61.35	57.83	63.64	64.82	58.17	63.53	63.55
Al ₂ O ₃	32.23	18.86	29.67	19.11	31.49	20.41	29.39	19.57	25.43	18.95	18.38	25.47	19.25	18.32
Fe ₂ O ₃	0.49	0.16	0.36	0.11	0.34	0.12	0.15	0.08	0.14	0.07	0.12	0.2	0.11	0.08
CaO	15.87	0.54	12.65	0.73	14.37	0.98	12.34	0.42	8.02	0.44	0.28	7.56	0.4	0.23
SrO	0.09	0.00	0.17	0.00	0.00	0.00	0.35	0.26	0.15	0.07		0.28	0.14	0.06
BaO	0.08	1.18	0.10	1.73	0.03	3.55	0.10	3.32	0.07	1.04	0.01	0.13	1.46	0.33
Na ₂ O	2.49	1.03	4.15	1.39	3.40	2.69	4.39	1.69	7.00	3.56	4.58	7.24	3.5	4.04
K ₂ O	0.11	14.24	0.31	13.42	0.15	10.85	0.25	12.52	0.30	10.88	10.08	0.26	10.76	10.66
Total	99.61	99.11	100.47	99.70	100.61	100.63	99.11	99.17	99.27	98.66	98.27	99.31	99.15	97.30
Stdev Ca	0.67	0.00	2.45	0.00	1.45	0.00	1.88	0.00	0.73	0.00		0.34		0.00
Stdev K	0.00	0.50	0.00	0.35	0.00	0.90	0.00	0.46	0.00	0.43	0.8		0.7	0.58
Si	8.89	11.82	9.60	11.79	9.21	11.52	9.45	11.62	10.47	11.83	11.96	10.555	11.781	11.91
Al	7.01	4.16	6.33	4.20	6.73	4.47	6.37	4.38	5.46	4.15	3.996	5.377	4.208	4.05
Fe ³⁺	0.07	0.06	0.05	0.01	0.05	0.01	0.02	0.01	0.02	0.01	0.016	0.027	0.015	0.01
Ca	3.13	0.07	2.46	0.15	2.79	0.20	2.40	0.09	1.55	0.09	0.055	1.424	0.079	0.05
Sr	0.01	0.00	0.01	0.00	0.00	0.00	0.04	0.03	0.02	0.01	0	0.029	0.015	0.01
Ba	0.00	0.09	0.00	0.13	0.00	0.26	0.01	0.25	0.00	0.08	0.001	0.009	0.106	0.02
Na	0.89	0.37	1.45	0.50	1.19	0.97	1.56	0.62	2.48	1.28	1.638	2.584	1.258	1.47
K	0.02	3.40	0.07	3.19	0.03	2.57	0.06	3.03	0.07	2.58	2.374	0.055	2.546	2.55
An	77.16	2.73	61.52	3.65	70.16	4.88	59.38	2.12	37.57	2.14	1.35	34.72	1.98	1.10
Ab	21.93	9.43	36.42	12.57	28.97	24.20	38.10	15.39	60.17	31.76	40.27	62.99	31.42	30.88
Or	0.64	85.66	1.78	80.61	0.85	64.39	1.42	75.61	1.75	64.01	58.36	1.35	63.58	62.28

Continued

Sl	0.19	0.00	0.21	0.00	0.00	0.00	0.93	0.71	0.40	0.20	0	0.71	0.38	0.15
Cn	0.12	2.19	0.09	3.18	0.05	6.54	0.18	6.17	0.12	1.90	0.01	0.23	2.64	0.59
An c/r	87/62		88.48				87/32		52/27			37/29		
Or c/r		94/79		85/72				92/55		72/56	92/78		59/67	
Cn c/r														
Sl c/r														
Temp °C														
Putirka (2008)			968		905		900			845		825		
	Microfoyaite				Malignite		PQS		IQS		OQS			
	G133 Plag	G133 Alk F	A14 Ab Per	A14 Or Per	AF Av 5	Av 2 Pg F	Av 3 Alk F	Av 2 Pg F	Av 4 Alk F	G63 Plag F		G63 Alk F		
wt. %														
SiO ₂	61.55	65.44	61.28	64.26	60.12	60.36	64.05	61.35	64.28	67.93		66.29		
Al ₂ O ₃	24.07	19.19	17.14	18.56	19.32	24.87	18.20	23.52	18.41	21.58		19.12		
Fe ₂ O ₃	0.09	0.09	0.15	0.1	0.12	0.18	0.11	0.17	0.18	0.13		0.07		
CaO	4.96	0.19	0.01	0.4	0.22	6.74	0.28	5.56	0.37	1.55		0.07		
SrO	0.1	0.24			0.88	0.05	0.00	0.03	0.00	n.d.		n.d.		
BaO	0.01	0.13	0.01	0	4.07	0.03	0.37	0.01	0.57	0.01		0.02		
Na ₂ O	8.87	3.59	1.45	11.7	1.16	7.88	4.00	8.50	5.08	10.92		2.13		
K ₂ O	0.42	11.23	14.62	0.16	12.83	0.30	10.74	0.38	9.02	0.24		13.72		
Total	99.99	100.09	94.65	95.17	98.57	100.39	97.80	99.51	98.01	102.37		101.48		
Stdev Ca	0.2													
Stdev K		0.25	1.1		0.61									
Si	10.942	11.903	11.973	11.865	11.57	10.73	11.94	10.97	11.91	11.65		11.96		
Al	5.043	4.114	3.948	4.038	4.40	5.22	4.00	4.96	4.02	4.36		4.07		
Fe ³⁺	0.012	0.009	0.021	0.014	0.02	0.02	0.02	0.02	0.02	0.02		0.01		
Ca	0.945	0.037	0.002	0.078	0.04	1.29	0.06	1.07	0.07	0.28		0.01		
Sr	0.01	0.025	0	0	0.09	0.01	0.00	0.00	0.01	0.00		0.00		
Ba	0.001	0.009	0.001	0	0.32	0.00	0.03	0.00	0.04	0.00		0.00		
Na	3.057	1.267	0.546	4.19	0.44	2.71	1.44	2.95	1.81	3.63		0.74		
K	0.095	2.608	3.646	0.038	3.13	0.07	2.56	0.09	2.15	0.05		3.16		
An	24.62	0.94	0.05	1.82	0.99	31.62	1.34	25.99	1.74	7.15		0.36		
Ab	74.12	32.06	13.04	97.3	10.84	66.55	35.19	71.82	43.75	91.53		18.98		
Or	2.46	66.13	86.89	0.87	78.21	1.67	62.68	2.12	53.12	1.30		80.61		

Continued

Sl	0.31	0.63	0	0	2.17	0.13	0.11	0.06	0.31	0.00	0.00
Cn	0.03	0.24	0.02	0	7.79	0.05	0.67	0.02	1.07	0.02	0.04
An c/r	24/22									105	
Or c/r		63/72									90/71
Cn c/r		0.2									
Sl c/r		0.7/0.6									
Temp °C											
Putirka (2008)	766		418				807		A6 816, T49 666		552

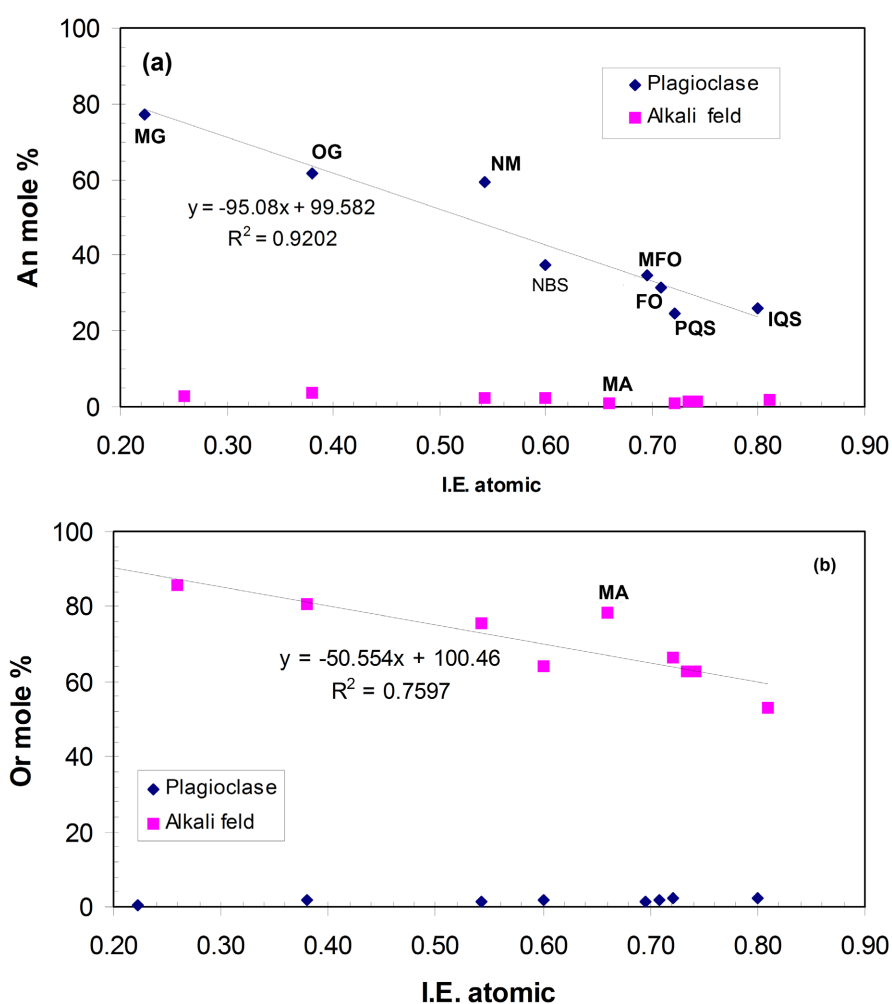


Figure 10. Plagioclase and alkali feldspar mole % An (10a) and Or (10b) values for the average feldspar compositions in each of the different intrusive units in the Marangudzi complex. Linear fits are shown for average An in plagioclase and average Or in alkali feldspar. See text for explanation.

Five mesocumulates define the most calcic plagioclases overall with An averag-

ing 80.3 ± 1.6 (100, 100A, G265, A4, T398) followed by three mesocumulates with 75.2 ± 2.2 (T123, T205, G266); four orthocumulates, as expected, have a more evolved An of 66.8 ± 7.3 (A8, A12, T168, T203) [Suppl. file S.5 and **Table 7**]. Orthocumulate A12 plagioclase has thick sodic rims (**Figure 10**). **Table 7** also gives averaged analyses of plagioclase phenocrysts in minor basic intrusions ($\sim\text{An}_{54}$ for microgabbro, T101 and basanite dyke, T178), both slightly more evolved than for the orthocumulate gabbros. However, the basanite has large, very calcic plagioclase cores (An_{93}) which are probably antecrystic. The average plagioclase compositions for the basaltic composition rocks are displayed in the feldspar ternary variation diagram (**Figure 11**), in which Ba and Sr are added to the Ca end-member; the most An-rich point in **Figure 11** is for mesocumulate T123 while the orthocumulates A12 and T168 have An_{63} and An_{61} , respectively.

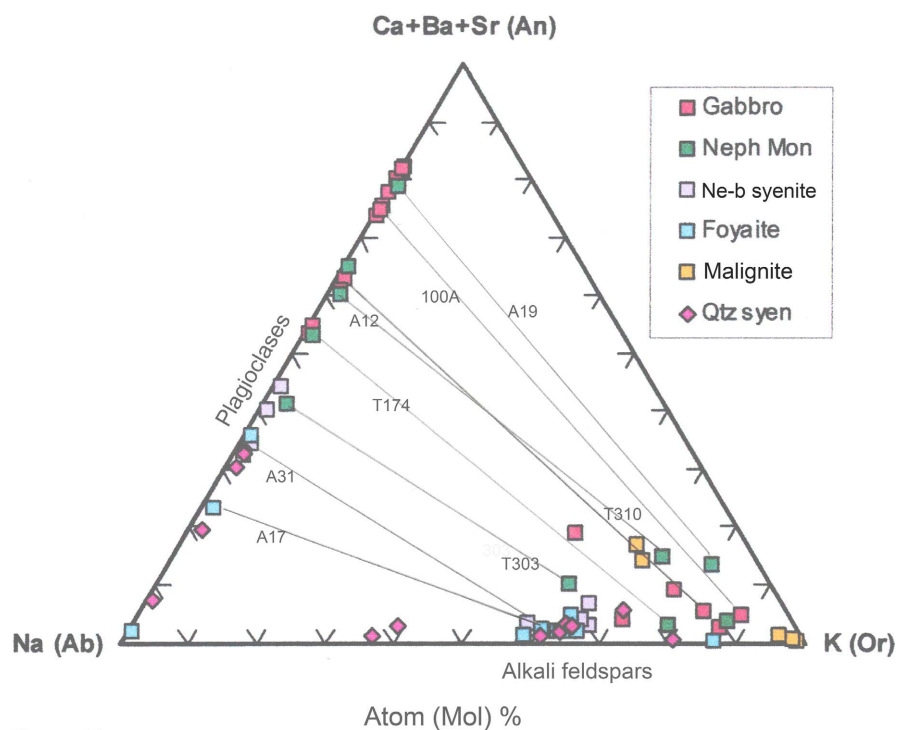


Figure 11. Compositions for average plagioclase and alkali feldspars for the different Marangudzi units plotted in the variation diagram for Ca (+ Ba + Sr) (An)-Na (Ab)-K (Or) as mole %. Coexisting plagioclase-alkali feldspar tie lines are shown for gabbros (100A, A12), nepheline monzonites (A19, T310, T303, T174) and nepheline syenites (A31, A17). The high “An” parameters for some nepheline monzonite and leucomalignite alkali feldspars mainly mark their enrichment in Ba and Sr, rather than Ca (see text).

Alkali feldspar compositions are available for four gabbros (100A, G266, A12 and T168) (**Table 7**, **Figure 10**), a microgabbro and a basanite. All are late-crystallized phases located in the interstices of plagioclase subhedral grains and are potassic, varying from $\text{Or}_{88.5}$ for sample 100A, which coexists with calcic plagioclase (An_{81}), to $\text{Or}_{76.5}$ for T168, which coexists with evolved plagioclase ($\text{An}_{60.3}$). Sr composition estimates are available for bulk alkali feldspar separates from Ne-

bearing syenites A26 (1600 ppm) and A31 (590 ppm); foyaites A1 (660 ppm), A20 (720 ppm), microfoyaite A14 (30 ppm); and leucomalignite A28 (800 ppm) [<0.3 Sr feldspar]. However, BaO (wt.%) values of 1.00 (100A), 1.29 (G266), 1.18 (R12) and 2.36 (T168) confirm the enrichment of Ba at this stage of the magmatic evolution (Cn in mol. %, 1.83, 2.54, 2.05 and 4.31 respectively) [Suppl. file S.5, **Table 7**].

The nepheline monzonite and nepheline-bearing syenites units both contain plagioclase (usually cumulus) and alkali feldspar (interstitial) (**Table 7**). Plagioclase only occurs in one foyaitite (A17) but also occurs in microfoyaite G133 (**Table 7** and **Figure 10**). In nepheline monzonites, the most calcic plagioclases (An₈₇, T308 and A19) match that for the gabbro; the most evolved sample (T174) has an average plagioclase An₄₄, slightly less calcic than that for orthocumulate A12. The plagioclase in the nepheline-bearing syenites analysed extends this trend to An₃₂ (A31). Both the Sr and Ba contents of the plagioclase in the nepheline monzonites and nepheline-bearing syenites show some fluctuation but the most evolved rocks have Sr and Ba at the detection limit. The average compositions of interstitial alkali feldspars in the nepheline monzonites vary from Or₈₇ (T308) to Or₆₁ (T303) but the variable Ba and Sr contents show BaO up to 5.5% (T310) and SrO up to 0.59% (T174). The nepheline-bearing syenite alkali feldspars have less variable compositions (Or₆₇₋₅₈) with maximum SrO of 0.17% and BaO of 2.3% (**Table 7**). **Figure 11** shows a substantial scatter of points for K-rich alkali feldspars in microgabbro T101 and nepheline monzonites A19 and T310, mainly reflecting their variable and exceptional Ba enrichments (Suppl. file S.5, **Table 7**). **Figure 10(a)** shows that the Marangudzi plagioclase feldspars from the gabbros, nepheline-bearing syenite and foyaitic rocks fall close to a trend of decreasing An (and increasing Ab, not shown here) with evolution. However, the nepheline monzonites are displaced upwards from that trend, reflecting that the “An” content for some rocks is strongly enriched with Ba (and Sr), which are included in that component.

Alkali feldspar in foyaitite A17 and microfoyaite G133 show the typical alkali feldspar alignment. The compositions of both the plagioclase and the alkali feldspar for A17 overlap with those for the evolved nepheline-bearing syenites for most of the end-member components but the plagioclase in G133 is less calcic with much lower Sr and Ba contents (**Table 7**). All the foyaites show that the alkali feldspar compositional trend continues with low An and then high Ab and Or showing relatively little change through the series from A1 to T304. Sr and Ba components decrease to very low concentrations for the most evolved foyaites. Microfoyaite A14 has a coarsely perthitic alkali feldspar allowing analyses of the Or and Ab-rich components for two-phase Ab-Or phases (**Table 7**); these analyses confirm that the Or-rich solvus flank is shallower than that for the Ab-rich flank. **Figure 11** shows how the foyaitic plagioclases extend the trend from the nepheline-bearing syenites towards more Na-rich compositions; the Or content remains low throughout the plagioclase fractionation series. The alkali feldspars in the foyaites mainly plot close to the Na-K (Ab-Or) sideline, reflecting their low contents of Ca, Sr and Ba (**Fig-**

ure 11).

The magnesian compositions of the mafic minerals in the leucomalignites have shown that they do not fit into the same evolutionary pattern as the other silica-undersaturated rocks and the same is true for the alkali feldspars. Their compositions (Suppl. file S.5) show that the pseudoleucite-free rocks A27 and 730 have strongly zoned alkali feldspars with the compositions for A27 and sample 730 averaging Or₆₇ and Or₇₀, respectively. Both are very rich in Sr and Ba with low Ca and the elevated “An” contents shown for those alkali feldspars clearly reflect the high Ba and Sr content rather than for Ca. The feldspars in both rocks enclose euhedral nephelines and mafic phases; the zoning trend is exceptionally well developed in A27 with SrO 2.0 - 0.5 wt.% and BaO 12.6 - 2.5 wt.%. The CaO content is uniformly low and Na shows a small decrease. There is an inverse relationship between orthoclase content, which ranges from Or₄₉ to Or₇₉ in order of decreasing Ba; the combined Or + Sl + Cn is effectively constant at 82 ± 2 mol.%. In **Figure 11**, the two leucomalignites with Sr- and Ba-rich alkali feldspars plot well away from the Na-K side line.

Figure 11 shows that leucomalignite alkali feldspars are very close to being Or end-members. These relationships are consistent with the feldspar in A28 mainly being derived from pseudoleucite which, in turn, is likely to have formed from primary leucite which typically has very low Na, Ca and crystal/liquid *D* values for both Ba and Sr (Henderson, 1965; Henderson et al., 2012). Leucomalignite feldspars in G260 and T330 have intermediate features, with some compositions having very low Sr (<0.1%) and Ba (<0.2%) and others with much higher concentrations (0.4% and 1.0%, respectively). Thus, it is probable that some feldspar (and nepheline) grains with high K and low Sr and Ba might be derived from pseudoleucite disaggregation [leucomalignites A28, G260 and T330 (average Or₉₈)]. **Figure 10(b)** shows a clear trend of decreasing Or with evolution ranging from gabbros to nepheline monzonite to nepheline-bearing syenites, foyaitic rocks and also includes the quartz syenites (as did the An trend in **Figure 10(a)**); this reflects a genetic relationship between different silica-undersaturated Marangudzi rock units. The leucomalignite is undoubtedly part of that same genetic complex but the displacement of the average sample from the general trend is probably related to the exceptionally K-rich feldspars forming from breakdown of earlier-formed leucite.

Quartz syenites mainly have microperthitic alkali feldspars but in some perthites are coarser while others are cryptoperthites. The compositions available (Suppl. file S.5, **Table 7**) are mainly for unaltered plagioclase cores and separate grains, and for cryptoperthitic alkali feldspars, but separate exsolved phases were analysed in some coarsely exsolved syenites. The average plagioclase in porphyritic quartz syenite A21 is An₃₂ but the most Ca-rich centres are up to An₅₀ with rims as sodic as An₁₉. Alkali feldspars average Or₆₃ with core/rim ranges of Or₇₂ to Or₅₃ and Ba-feldspar (Cn) from 1.8 to 0.3 mole %. The separate plagioclase grains in the inner quartz syenite and outer porphyritic quartz syenite units are less calcic

than those in the porphyritic quartz syenite (An_{26} and An_{75} , respectively). Cryptoperthite in plagioclase-free inner quartz syenite ranges Or_{52-29} and the coarsely alkali feldspar in porphyritic quartz syenite T17 has compositions Or_{93} and Ab_{98} for the separate components. Ba (and Sr) contents for all the feldspars in the quartz syenite units are much lower than those of the silica-undersaturated rocks.

Tie-lines for averaged plagioclase-alkali feldspar compositions for each parent rock are shown in **Figure 11** for gabbros and the silica-undersaturated differentiated rock series. Thus, tie-lines for mesocumulate gabbro 100A and orthocumulate gabbro A12 show that the latter rock is more evolved with a lower An content but with similar alkali feldspar compositions; this leads to a slightly “flatter” tie line for A12. The two feldspar pairs for nepheline monzonites A19, T310, T174, and T303 show similar evolutionary shifts to lower An plagioclases but also show a trend towards lower Or contents; the slopes of the tie lines decrease with differentiation as would be expected for coexisting equilibrium plagioclase and alkali feldspar (e.g., Carmichael, 1965; Berlin & Henderson, 1969). Nepheline-bearing syenite A31 has a 2-feldspar tie-line reflecting a more evolved composition, as does that for foyaite A17. Tie lines are not shown for Marangudzi quartz syenites but the compositions summarised above would plot in the same general regions as those for nepheline-bearing syenite A31 and foyaite A17.

Suppl. file S.5 and **Table 7** give data for the temperatures provided by geothermometry calculations for all of the two-phase assemblages (including those for coarse-grained perthites) [Putirka, 2008; Equation 27a, “global regression calculation”]. The least evolved gabbro (100A) has an estimated temperature of $\sim 1000^{\circ}\text{C}$ (average mesocumulate value 968°C) but the orthocumulates (A12 and T168) are more evolved and are lower with $\sim 900^{\circ}\text{C}$. Average equilibration temperature for feldspar pairs in the nepheline monzonites is also 900°C (**Table 7**). The more evolved feldspar pairs in nepheline-bearing syenites show averages of 845°C and only foyaite and microfoyaite, with coexisting separate feldspars having lower estimates of 825°C (foyaite A17) and $\sim 770^{\circ}\text{C}$ (microfoyaite G133). In contrast, the coarsely exsolved alkali feldspar in microfoyaite R14 suggests a temperature of $\sim 420^{\circ}\text{C}$ consistent with its formation by post-magmatic hydrothermal recrystallization (see earlier). The feldspar pairs in the least-altered quartz syenites (porphyritic quartz syenites A21, A16 and inner quartz syenite A6) suggest equilibration close to the solidus ($\sim 800^{\circ}\text{C}$) but inner quartz syenite and porphyritic quartz syenite have lower temperatures of $\sim 640^{\circ}\text{C}$ and 550°C , respectively, indicative of post-magmatic processes. The variation in temperature reflects the trend of changing tie-line slopes displayed in **Figure 11**. Feldspar data will be assessed further below (Section 6).

4.6. Nepheline

Nepheline occurs in some gabbros as small interstitial grains and then increases in amount as the rock types become more silica-undersaturated. The full nephe-

line dataset is given in Suppl file S.5 and **Table 8** gives averages for the silica-undersaturated intrusive units. Nepheline in orthocumulate T203 is the most Ca-rich nepheline found (CaO 3.3 wt.%) with less in nepheline monzonites ~2.5%. Nepheline-bearing syenite to foyaite averages range 1.9% - 1.2% with evolved microfoyaite (A14) having <0.5% CaO. The heterogeneous leucomalignite nephelines have CaO varying from 0.5 to 1.5 wt.% CaO. The basanite dyke (T178, 2.4% CaO) is similar to that in the nepheline monzonites. Sr and Ba were always below the detection limit of ~0.015%.

Atomic formulae for nephelines were calculated to 32 oxygens (**Table 8**) with end-member formulae determined for a stuffed tridymite model (Barth, 1963; Henderson, 2020). Thus, Ca is calculated as the tridymite-structured Ca-nepheline molecule rather than as anorthite, which most authors use. The Ca-Ne molecule has a value double that of An with an excess SiO₂ (denoted Q' here), half of that reported for an An-calculation.

Table 8. Nepheline compositions in Marangudzi mafic rocks and silica-undersaturated syenites.

	Gabbro		Nepheline monzonites				Neph.-bearing syenites				Foyaite				
	T203	T303	T308	T308	T310	A19	T301	A26	A17	A1	A2	A3	A20	G226	T304
	One anal.	Av 3	Av 6	Av 6	Av 3	Av 3	Av of 4	Av 10	Av of 10	Av 3	Av 3	Av 3	Av 5	Av 15	Av 13
	Ne-plag intergrowth														
SiO ₂	42.52	43.92	43.34	42.18	42.82	42.42	43.56	43.65	44.06	41.51	44.00	44.07	41.89	43.44	43.40
Al ₂ O ₃	32.77	34.04	33.69	32.38	34.82	34.12	34.14	33.96	33.89	31.00	33.53	34.27	31.32	32.77	32.60
Fe ₂ O ₃	0.25	0.00	0.38	0.28	0.33	0.19	0.29	0.27	0.29	0.40	0.00	0.00	0.20	0.29	0.29
CaO	3.14	2.14	2.55	2.73	2.53	2.23	2.12	2.13	1.76	1.06	0.94	1.48	1.05	1.50	1.55
Na ₂ O	14.62	15.63	15.01	15.06	15.24	14.19	15.75	14.93	15.98	16.20	15.37	15.20	15.93	15.37	15.82
K ₂ O	4.01	4.21	4.78	4.88	4.51	5.06	4.40	4.66	4.43	5.31	5.10	4.99	5.32	5.05	5.08
Total	97.07	99.95	99.38	97.24	99.91	98.03	99.98	99.54	100.1	95.07	98.94	100.01	95.51	98.14	98.46
Si	8.329	8.358	8.304	8.303	8.159	8.239	8.289	8.245	8.365	8.380	8.459	8.383	8.413	8.431	8.417
Al	7.566	7.635	7.608	7.512	7.821	7.810	7.657	7.652	7.583	7.377	7.598	7.682	7.414	7.497	7.452
Fe ³⁺	0.037	0.000	0.054	0.042	0.047	0.028	0.042	0.039	0.041	0.060	0.000	0.000	0.029	0.042	0.043
Ca	0.659	0.437	0.523	0.576	0.516	0.465	0.433	0.436	0.357	0.229	0.194	0.302	0.225	0.312	0.322
Na	5.553	5.765	5.578	5.747	5.630	5.343	5.812	5.536	5.881	6.340	5.728	5.606	6.203	5.786	5.947
K	1.002	1.023	1.169	1.225	1.096	1.255	1.067	1.135	1.073	1.367	1.251	1.212	1.363	1.250	1.256
Sum cats	23.51	23.22	23.22	23.41	23.27	23.14	23.30	23.14	23.30	23.75	23.23	23.18	23.65	23.33	23.44
Sum T	15.93	15.99	15.97	15.86	16.03	16.08	15.99	16.05	15.99	15.82	16.06	16.06	15.86	15.97	15.91
ΔAl	-0.272	-0.027	-0.133	-0.573	0.111	0.309	-0.045	0.146	-0.047	-0.728	0.231	0.260	-0.574	-0.122	-0.355
ΔT	-0.240	-0.024	-0.117	-0.504	0.098	0.271	-0.040	0.129	-0.041	-0.642	0.203	0.229	-0.506	-0.107	-0.313

Continued

$\Delta\text{Al}/\Delta\text{T}$	1.135	1.125	1.137	1.137	1.133	1.140	1.125	1.136	1.146	1.134	1.138	1.135	1.134	1.134	1.134
AlNe	68.95	72.07	69.04	71.32	69.78	66.44	72.13	68.70	73.01	78.50	71.60	70.08	77.17	71.80	73.80
FeNe	0.46	0.00	0.68	0.52	0.59	0.35	0.53	0.49	0.51	0.75	0.00	0.00	0.37	0.52	0.53
Ks	12.53	12.78	14.61	15.32	13.69	15.68	13.34	14.19	13.42	17.08	15.64	15.15	17.03	15.62	15.70
CaNe	16.50	10.93	13.11	14.42	12.90	11.64	10.81	10.93	8.95	5.73	4.86	7.56	5.65	7.81	8.08
Q^{xs}	1.56	4.22	2.55	−1.58	3.04	5.88	3.19	5.69	4.12	−2.07	7.91	7.22	−0.22	4.24	1.88
	100.00	100.00	100.00		100.0	100.0	100.00	100.00	100.00	100.00	100.00	100.00		100.00	100.00
$Q^{(\text{Si-Al})}$	4.54	4.52	4.01	4.68	1.82	2.51	3.69	4.09	4.63	5.89	5.38	4.38	6.05	5.58	5.76
Ne	80.26	80.64	78.92	78.22	81.94	78.60	81.01	79.10	80.29	77.53	77.31	78.21	77.06	77.33	77.59
Ks	14.49	14.30	16.54	16.68	15.95	18.45	14.87	16.22	14.65	16.71	16.88	16.90	16.93	16.70	16.39
$Q^{(\text{Si-Al})}$	5.25	5.06	4.54	5.10	2.12	2.95	4.11	4.68	5.06	5.76	5.81	4.88	6.02	5.97	6.01
	Microfoyaaites				Leuco malignites						Basanite dyke				
	G133		A14	A28	730		G260		A27	T330			T178		
	Av 2		Av 15	Av 5	Av 9		Av 12		Av 23	Av 6			Av 2		
wt. %															
SiO ₂	42.85		42.28	42.87	42.16		42.13		42.23	41.26			44.07		
Al ₂ O ₃	32.95		30.93	35.14	32.05		33.66		33.02	32.85			34.39		
Fe ₂ O ₃	0.00		0.34	0.28	0.47		0.53		0.46	0.20			0.22		
CaO	1.43		0.43	0.89	1.28		0.55		1.55	0.51			2.37		
Na ₂ O	15.20		16.34	15.57	15.56		15.86		15.50	15.75			15.56		
K ₂ O	5.12		5.62	6.70	5.46		6.86		5.73	7.16			4.48		
Total	97.55		95.95	101.19	96.59		99.07		98.05	97.14			100.86		
Cations per 32 O															
Si	8.388		8.481	8.141	8.354		8.185		8.255	8.151			8.312		
Al	7.602		7.313	7.865	7.485		7.708		7.607	7.724			7.646		
Fe ³⁺	0.000		0.051	0.040	0.070		0.078		0.067	0.030			0.031		
Ca	0.299		0.093	0.181	0.272		0.114		0.325	0.109			0.478		
Na	5.769		6.358	5.731	5.978		5.975		5.876	6.090			5.689		
K	1.278		1.438	1.624	1.379		1.701		1.429	1.822			1.078		
Sum cats	23.33		23.73	23.58	23.55		23.76		23.56	23.93			23.23		
Sum T	15.99		15.85	16.05	15.91		15.97		15.93	15.91			15.99		
Del Al	−0.043		−0.618	0.187	−0.364		−0.120		−0.283	−0.377			−0.047		
Del T	−0.038		−0.546	0.164	−0.321		−0.105		−0.249	−0.331			−0.041		
$\Delta\text{Al}/\Delta\text{T}$	1.135		1.131	1.140	1.135		1.139		1.137	1.139			1.136		
AlNe	72.11		78.83	71.14	73.86		73.72		72.61	75.74			70.73		
FeNe	0.00		0.64	0.50	0.87		0.97		0.84	0.38			0.38		
Ks	15.98		17.97	20.30	17.24		21.26		17.87	22.77			13.48		

Continued

CaNe	7.47	2.33	4.54	7.02	2.86	8.15	2.75	11.95
Q ^{2s}	4.44	0.22	3.52	1.00	1.19	0.54	-1.64	3.46
	100	100	100	100	100	100	100	100
Q ^(Si-Al)	4.91	6.98	1.47	4.99	2.50	3.63	2.48	3.98
Ne	77.53	76.11	76.69	77.07	75.87	77.36	75.09	80.30
Ks	17.18	17.21	21.73	17.78	21.59	18.82	22.46	15.22
Q ^(Si-Al)	5.28	6.68	1.58	5.15	2.54	3.83	2.45	4.49

The proportions of the end-members in the Marangudzi nephelines were calculated using Henderson and de Oliveira (2022). Stoichiometry parameters $\Delta\text{Al}^{\text{cc}}$ and $\Delta\text{T}^{\text{ch}}$, the $\Delta\text{Al}^{\text{cc}}/\Delta\text{T}^{\text{ch}}$ ratio, and the mol. % values for the various nepheline end-members are given in Table 8. Ks contents increase rather irregularly from $\text{Ks}_{12.5}$ for nepheline in the least-evolved basic rock to Ks_{18} in the most-evolved microfoyaite; alkali feldspars in the same rocks range Ks_{80-60} but note that lower Ks contents are present in nephelines which coexist with alkali feldspars enriched in Ba coupled with lower K. Leucomalignite nephelines are slightly more potassic ranging Ks_{17} to Ks_{23} but these nephelines are still less K-rich than the ideal nepheline formulae (Ks_{25}), even though the alkali feldspars in the leucomalignites are almost K-end-members ($\sim\text{Or}_{96-99}$) in leucomalignites A28, G260 and T330 (Suppl. file S.5).

Henderson (2020) and Henderson and de Oliveira (2022) recommended that the excess SiO_2 parameter $Q^{(\text{Si-Al})}$ is the most reliable, as its calculation does not depend on Na, which is vulnerable to loss in the electron microprobe beam. This recommendation is followed here. The stoichiometry parameters $\Delta\text{Al}^{\text{cc}}$ and $\Delta\text{T}^{\text{ch}}$ values are mostly <0.6 , which Henderson (2020) suggested is the limit for considering acceptable analyses. The coupled $\Delta\text{Al}/\Delta\text{T}$ ratios (Table 8) are close to 1.135, which is the ideal value for stoichiometric stuffed-tridymite structure nephelines (Henderson, 2020). The Ca-Ne end-member in Marangudzi nephelines varies from 16.5 mol.% in gabbro T203 to ~5% in evolved foyaites; these represent late-magmatic minerals. Microfoyaite A14 has exsolved perthitic alkali feldspars, pointing to sub-solidus hydrothermal reactions and the nepheline in that rock has the lowest Ca-Ne contents, reflecting this post-magmatic stage. In addition, magmatic nephelines showing negative $\Delta\text{Al}/\Delta\text{T}$ ratios close to 0.5 might have small amounts of a primary cancrinite molecule in solid solution (Henderson, 2020). The high delta values for the nepheline in some foyaites (A1, A20, A14) suggest the presence of primary cancrinite in solid solution. On that basis, calculation of these compositions using Spreadsheet 2 (Henderson, 2020; Henderson & de Oliveira, 2022) provides estimates of 4 - 6 mol.% vishnevite molecules (ideal Na-cancrinite). In addition, the magmatic-textured nepheline in nepheline monzonite T308 shows lower delta values of ~0.1 (Table 8) as well as a low model vishnevite content of 1 mol.%; however, the associated intergrowth

between early plagioclase and nepheline in this sample has delta values of over 0.5 (vishnevite ~5 mol.%), perhaps consistent with a very-late stage, localised alkali-exchange/recrystallization of primary plagioclase to form such a texture (see Henderson & Gibb, 1972; Mitchell & Platt, 1979). The coexisting alkali feldspar and nepheline compositions show typical magmatic tie lines when plotted in the Ne-Ks-Qz residua system (see Suppl. file S.5; Tilley, 1954 and Henderson et al., 2014).

Finally, excess $Q^{(Si-Al)}$ values (Henderson, 2020) do not show clear variation with rock type; indeed, apart from two of the more evolved nepheline monzonites, the whole series from gabbro through to evolved foyaites have $Q^{(Si-Al)}$ falling within the range 4.5 to 6 mol.%. The nepheline in all of rocks is the last main phase to crystallize under magmatic conditions, which, in turn, suggests similar solidus temperatures and similar compositions for each fractionated residual melt. However, leucomalignite rock types show more variation (Suppl. file S.5). Thus, the least evolved leucomalignite R730 has $Q^{(Si-Al)} = 5.2$ mol.%, followed by the similar textured rock A27 with a value of 3.8 mol.%; neither of these rocks contains pseudoleucites. Leucomalignite A28 has abundant large pseudoleucites with some having the coarse-grained K-rich alkali feldspar and nepheline grains disaggregated to define large felsic patches; this sample has the lowest $Q^{(Si-Al)}$ of 1.6 mol.%, reflecting a source from the pseudoleucite rather than direct crystallization from the magma. Leucomalignites G260 and T330 have white patches of disaggregated pseudoleucites, and the nephelines have intermediate $Q^{(Si-Al)}$ values of 2.5 mol.% reflecting the mixed source of mineral components.

4.7. Sodalite

Sodalite and associated nepheline occur interstitially between larger alkali-feldspar laths. Coarser, more-even-grained nepheline-rich rocks in the foyaitite ring-unit have larger rounded grains of sodalite (1 - 2 mm across) with “trains” of fluid inclusions. Compositions for sodalite are given in Suppl. file S.5 and averages for each intrusive unit in Table 9. The most reliable analyses obtained with a larger beam (3 - 5 μ m) have close to 8 atoms Na pfu with only very small concentrations of K and Ca. The presence of Ca and low analytical totals could be explained by the presence of some Ca-cancrinite (Henderson, 2020). Indeed, separate grains of Ca-bearing cancrinite (9.3 wt.% CaO) have been analysed in microfoyaite A14 and similar composition phases have also been found in leucomalignites A27 and sample 730.

Other hydrated aluminosilicates formed during deuteric alteration processes are analcime and phillipsite (nepheline monzonite T308) (Table 10); Henderson et al., (2014) showed that at 1 kbar $P(H_2O)$ analcime formed stably and rapidly at temperatures below 500°C, well below the magmatic solidus, Ca-rich analcime is unstable above ~400°C (Henderson & Gibb, 1977), while many other zeolites form at even lower temperatures (e.g., phillipsite, natrolite, <200°C, Deer et al., 2004).

Table 9. Microprobe analyses (ED) of sodalites in Marangudzi silica-undersaturated syenites.

	Leuco neph. monzonites				Foyaite				Microfof	Leuco malignites	
	T175	T301	A1	A2	A17	A20	G226	T304	A14	A27	730
	Av. 3	One anal.	One anal.	Av. 2	One anal.	Av. 2	Av. 6	Av. 5	Av. 7	One anal.	One anal.
SiO ₂	37.20	37.27	34.86	37.40	37.78	36.77	37.35	37.33	35.39	36.78	36.67
Al ₂ O ₃	31.06	34.03	32.91	32.40	33.67	30.72	32.46	31.10	30.17	31.46	31.21
Fe ₂ O ₃	0.10	0.22	0.32	0.00	0.29	0.10	0.08	0.15	0.18	0.01	0.02
CaO	0.03	0.09	0.66	0.25	0.17	0.13	0.05	0.17	0.07	0.00	0.05
Na ₂ O	25.62	24.35	23.25	24.35	23.78	24.38	24.69	25.37	25.37	25.67	24.48
K ₂ O	0.02	0.02	0.06	0.11	0.06	0.18	0.06	0.09	0.04	0.02	0.03
Cl	7.36	7.36	6.45	6.88	7.46	7.01	7.34	7.21	7.21	7.51	7.53
Total (with O-Cl)	99.74	101.67	97.06	99.83	101.54	97.71	100.38	99.79	96.82	99.75	98.29
Atoms per 12(Si + Al + Fe)											
Si	6.042	5.767	5.661	5.937	5.835	6.039	5.923	6.045	5.974	5.975	5.989
Al	5.946	6.207	6.300	6.063	6.131	5.949	6.067	5.937	6.003	6.024	6.008
Fe ³⁺	0.012	0.025	0.039	0.000	0.034	0.012	0.010	0.018	0.023	0.001	0.003
Ca	0.004	0.014	0.115	0.042	0.028	0.023	0.008	0.030	0.013	0.000	0.009
Na	8.069	7.307	7.322	7.495	7.121	7.765	7.591	7.966	8.303	8.085	7.750
K	0.003	0.003	0.013	0.021	0.012	0.037	0.011	0.019	0.009	0.003	0.005
Cl	2.027	1.931	1.775	1.851	1.953	1.953	1.974	1.979	2.064	2.067	2.084
Sum X	8.076	7.324	7.470	7.558	7.161	7.825	7.610	8.015	8.355	8.088	7.764

Table 10. Marangudzi oxide average analyses for magnetite and ilmenite in each intrusive unit.

	Gabbro		Neph monzonite		Neph.- bearing syenites	Foyaite		Microfoyaite		Leuco malignite		All SiO ₂ oversaturated units	
	MT	IL	MT	IL	MT	MT	IL	MT	MT	MT	IL	MT	IL
SiO ₂	0.21	0.12	0.15	0.01	0.06	0.07	0	0.02	0.08	0.03	0.06	0.12	0.06
TiO ₂	5.43	50.96	5.28	50.62	6.17	3.42	51.05	0.96	4.08	4.51	49.63	5.04	50.90
Al ₂ O ₃	2.91	0.07	1.94	0.01	1.06	0.67	0	0.16	0.88	1.057	0.01	1.76	0.04
V ₂ O ₃	0.44	0.25	0.06	0.21	0.01	0.01	0.17	n.a.	n.a.	0		0.16	0.22
Cr ₂ O ₃	0.79	0.00	0.03		0.05	0.01		n.d.	n.d.	0	n.a.	0.28	0.00
MgO	0.55	1.10	0.11	0.07	0.04	0.01	0.05	0.01	0.03	0.047	0.03	0.22	0.58
MnO	0.29	1.11	0.50	3.84	0.83	0.88	7.31	1.03	1.09	0.693	8.13	0.58	3.34

Continued

SiO ₂	0.30	0.01	0.08	0.01	0.03	0.00	0.03	0.00	0.51
TiO ₂	2.20	49.15	4.86	50.42	6.03	48.51	6.03	48.51	8.58
Al ₂ O ₃	0.43	0.00	0.40	0.00	0.35	0.00	0.35	0.00	2.56
V ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0
Cr ₂ O ₃	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.50
MgO	0.01	0.03	0.01	0.04	0.00	0.02	0.00	0.02	0.46
MnO	0.21	2.31	0.32	1.64	0.43	2.44	0.43	2.44	0.53
Fe ₂ O ₃	61.69	6.14	58.09	3.45	58.01	6.63	58.01	6.63	46.09
FeO	32.49	40.38	35.02	42.85	36.82	41.11	36.82	41.11	38.06
NiO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0
Total	97.39	98.02	98.79	98.40	101.69	98.72	101.69	98.72	99.30
Atoms/ox/cat	32/24	24/16	32/24	24/16	32/24	24/16	32/24	24/16	32/24
Si	0.097	0.001	0.025	0.001	0.009	0.000	0.009	0.000	0.156
Ti	0.520	7.641	1.130	7.799	1.369	7.488	1.369	7.488	1.985
Al	0.157	0.000	0.147	0.000	0.126	0.000	0.126	0.000	0.911
V	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0
Cr	0.013	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.122
Mg	0.005	0.010	0.003	0.010	0.002	0.005	0.002	0.005	0.209
Mn	0.054	0.405	0.083	0.285	0.110	0.424	0.110	0.424	0.139
Fe ³⁺	14.596	0.956	13.542	0.532	13.120	1.024	13.120	1.024	10.67
Fe ²⁺	8.544	6.980	9.069	7.370	9.265	7.058	9.265	7.058	9.794
Ni	8.603	7.395	6.200	5.013	0.000	0.000	0.000	0.000	0
Sum M ²⁺	0.000	0.000	2.957	2.653	9.373	7.490	9.373	7.490	10.141
Total cats	24.000	16.000	24.000	16.000	24.000	16.000	24.000	16.000	24
Spinel									
M ²⁺ Al ₂ O ₄	0.987	0.000	0.920	0.000	0.787	0.000	0.787	0.000	5.81
M ²⁺ V ₂ O ₄	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0
M ²⁺ Cr ₂ O ₄	0.083	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.18
M ²⁺ Fe ³⁺ ₂ O ₄	92.363	0.000	84.917	0.000	82.090	0.000	82.090	0.000	68.09
M ²⁺ ₂ TiO ₄	6.563	0.000	14.160	0.000	17.120	0.000	17.120	0.000	25.32
Ilmenite									
M ²⁺ TiO ₃	0.000	94.100	0.000	97.167	0.000	93.600	0.000	93.600	
Fe ³⁺ ₂ O ₃	0.000	5.900	0.000	2.833	0.000	6.400	0.000	6.400	
Lepage (2003)									
Temp		592		521		614		609	
-log O ₂		-20		-26		-18		-20	

4.8. Oxides

Titaniferous magnetites are the main oxide minerals in the gabbroic and syenitic rocks. These can show fine exsolution lamellae of ilmenite and electron microprobe analyses of the Fe-oxides were obtained using a defocused beam (3 - 5 μm) or a rastered beam. Separate grains of magnetite and ilmenite occur in mesocumulate gabbro G205, evolved orthocumulate T168, and in nepheline monzonites, foyaites, leucomalignites, and quartz syenites (Suppl. file S.5). Multiple ilmenite spot analyses are only available for orthogabbro T168, nepheline monzonite T.174 and some quartz syenites. Magnetite and ilmenite compositions are given in **Table 11** together with averages for each of the intrusive units. Atomic formulae are recalculated to 32 oxygen, 24 cations (magnetite) and 24 O, 16 cations (ilmenite) to obtain Fe valence data based on strict stoichiometry (Droop, 1987). The mol.% proportions of the end member molecules were calculated as follows: Spinel phase: Magnetite ($M^{2+}X^{3+}_2O_4$, $M^{2+} = \text{Fe}^{2+} + \text{Mg} + \text{Mn} + \text{Ni} + \text{Zn}$; $X^{3+} = \text{Al}, \text{Fe}^{3+}, \text{V}, \text{Cr}$); ilvospinel ($M^{2+}_2\text{TiO}_4$); rhombohedral phase ilmenite ($M^{2+}\text{TiO}_3$); and hematite X_2O_3 . In coexisting mineral pairs, spinel concentrates Al and ilmenite concentrates Mn.

In the gabbro to foyaite series, titano-magnetites tend to show a steady decrease in Al-spinel contents with little systematic change in the model $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio; V- and Cr-spinels decrease rapidly from the gabbros to the nepheline monzonites and are uniformly lower in silica-undersaturated rocks. The ilvospinel contents peak in the nepheline-bearing syenites and have extremely low values in the foyaites (**Table 11**). The Fe^{3+} -spinel end-member (magnetite) is significantly higher in the foyaites than in the other nepheline syenites, reflecting a more-oxidised Fe valence. Overall, the coexisting ilmenite shows very limited variation except for Mn.

Table 11. Microprobe analyses of deuteritic aluminosilicates.

	T308	T308	A14	A27	730
	Analcime	Phillipsite		Cancrinite	
	Ne mon	Ne mon	Microfoy	Leuco-malignite	Leuco-malignite
wt. %					
SiO ₂	50.31	49.51	34.02	37.21	34.64
Al ₂ O ₃	23.76	24.51	29.33	31.25	30.65
Fe ₂ O ₃	0.18	0.02	0.04	0.06	0.01
CaO	1.12	5.97	9.28	9.17	9.52
SrO	0.01	0.12	n.d.	0.06	0.06
BaO	n.d.	0.04	n.d.	n.d.	0.04
Na ₂ O	11.78	4.08	15.16	13.95	15.19
K ₂ O	0.80	5.91	0.02	0.04	0.02

Continued

Total	87.95	90.15	87.84	91.73	90.14
Atoms per fixed cations or fixed oxygens					
	12Si		32O		
Si	7.70	10.12	5.95	6.03	5.87
Al	4.28	5.90	6.05	5.96	6.12
Fe ³⁺	0.02	-	0.01	0.06	0.01
Ca	0.18	1.31	1.74	1.59	1.73
Sr	-	0.014	-	0.006	0.006
Ba	-	0.003	-	-	0.003
Na	3.50	1.61	5.19	4.38	4.99
K	0.16	1.54	-	0.01	-

Note: n.d., not detected; detection limit ~0.03wt.%.

The compositions of coexisting spinel and ilmenite are used to estimate “equilibration” temperature and oxygen fugacity (e.g., [Lepage, 2003](#)); values are reported in [Table 11](#) and Suppl. file S.5. For the silica-undersaturated series, an average ilmenite composition is used for each of the individual intrusive units. Average temperatures for the Fe-oxide pairs in the different rock types are mainly ~600°C with log oxygen fugacities (log f_{O_2}) of ~-22 bar, showing that re-equilibration of the Fe valence has occurred below the magmatic solidus. Coexisting ilmenite-magnetite pairs in the nepheline monzonite, silica-undersaturated “syenites” and quartz syenites generally plot close to the low temperature extension of the quartz-fayalite-magnetite (QFM) buffer curve.

4.9. Apatite and Titanite

Apatite is the main accessory mineral in the basic rocks and compositions are given in [Table 12\(a\)](#) and Suppl. file S.5. Apatite in the gabbros is likely to be a cumulus phase but most have similar compositions except for Cl and F. Unfortunately, Cl was not determined in apatite from plagioclase mesocumulate A4, although its halogen/hydroxyl site is full with 2.06 atoms pfu of fluorine. All the other compositions available have both F and Cl present (F > Cl), with halogens totalling 1.4 - 2.1 atoms pfu. Titanite is present as an accessory mineral and compositions are given in [Table 12\(b\)](#) for a nepheline monzonite (T178), two leucomalignites (G260, T330) and a porphyritic quartz syenite (T36). For each analysis, sufficient Al and Fe are present to combine with Ti to fill the corner-sharing octahedral sites.

Table 12. (a) Apatite analyses; (b) Microprobe analyses (ED) of titanite.

(a)									
	A4	A8	A12 Av	G265	G205	G266	T168	T26B	T101
wt.%	One anal.	Av 3	Av 7	Av 2	Av 4	Av 2	Av 5	Av 7	Av 6

Continued

CaO	55.95	54.84	54.38	55.17	54.44	55.07	54.88	54.67	55.14
FeO	n.d.	n.d.	n.d.	n.d.	0.58	0.31	n.d.	0.32	0.38
P ₂ O ₅	40.38	40.38	40.31	40.14	39.93	40.37	40.95	41.25	40.67
Cl	n.a.	1.52	1.22	1.35	1.41	1.92	1.21	0.53	0.79
F	3.80	1.94	1.92	2.42	1.84	3.01	2.06	2.89	2.33
Total	98.53	97.53	96.75	97.75	96.66	99.11	97.96	98.10	98.07
Atoms per 25 oxygens									
Ca	10.306	10.185	10.145	10.258	10.187	10.193	10.105	10.018	10.153
Fe	-	-	-	-	0.084	-	-	0.046	0.054
P	5.877	5.926	5.942	5.897	5.896	5.905	5.958	5.973	5.917
Cl	-	0.447	0.359	0.396	0.415	0.561	0.352	0.154	0.229
F	2.063	1.061	1.050	1.329	1.016	1.646	1.119	1.561	1.258

Note: n.d., not detected; detection limit Fe ~0.03 wt.%.

(b)

wt. %	T178	G260	T330	T36
	Nepheline monzonite	Leuco malignite	Porphyritic quartz syenite	
SiO ₂	30.61	30.14	30.82	30.28
TiO ₂	37.36	31.86	36.96	32.08
Al ₂ O ₃	1.66	2.85	2.33	3.01
FeO	1.37	2.60	1.76	2.53
CaO	28.83	28.60	28.66	27.49
MnO	n.d.	0.06	n.d.	0.12
MgO	0.06	0.08	n.d.	0.11
Total	99.89	96.19	100.53	95.62
Cats/4Si				
Si	4Si	4Si	4Si	4Si
Ti	3.672	3.180	3.608	3.187
Al	0.256	0.446	0.357	0.468
Fe ²⁺	0.150	0.289	0.191	0.279
Ca	4.037	4.067	3.986	3.890
Mn	-	0.007	-	0.137
Mg	0.012	0.015	-	0.022

Note: Detection limit Fe ~0.03 wt.%.

5. Geothermometry and Geobarometry of the Marangudzi Ring Complex

In this section, the calculated temperatures and pressures of formation for the Ma-

rangudzi mineral suite are integrated and discussed; information gleaned from a review of published high temperature/high pressure experimental petrology results on relevant composition systems (Supp. file S.4) is key here (see Data Availability section after the Conclusions for all remote file access). As discussed earlier (Section 4.3), an alkali basalt parental magma at $P_{H_2O} = 1 - 2$ kbar (5.5 - 7 km) would differentiate from a liquidus at $\sim 1170^\circ\text{C}$ to a solidus at $\sim 870^\circ\text{C}$ (Yoder & Tilley, 1962; Righter & Carmichael, 1996). Equivalent temperatures for nepheline syenite and quartz syenite composition magmas would be $\sim 900^\circ\text{C}$ to 750°C (McDowell & Wyllie, 1971; Millhollen, 1971; Moussallam et al., 2013; Martel et al., 2013). A parental intermediate alkaline olivine-tholeiite magma would have a water-saturated liquidus at 1 kbar of about 1170°C with a dry liquidus about 100°C higher, with olivine on the liquidus. More evolved alkaline basaltic rocks provide similar phase equilibrium conditions (see Suppl. file S.4). Thus, an intrusion model temperature of about 1150°C for the parental magma for the Marangudzi complex will be assumed here.

The model geothermometer data for the Marangudzi mineral assemblages are combined in Table 13 with footnotes identifying the source references for calculations; published Excel spreadsheets have aided some of these. The oxygen geobarometer data discussed earlier for amphibole (Section 4.4) showed that qualitative estimates obtained with the Ridolfi and Renzulli (2012) method gave $f(\text{O}_2)$ estimates for Marangudzi nepheline syenite amphiboles ~ 2 orders of magnitude too oxidising; in addition, estimated $\text{Fe}^{3+}/\Sigma\text{Fe}$ values for amphiboles from both the over- and undersaturated rock types were not consistent with the Fe valence values obtained chemically. Other estimates for the amphiboles were much more consistent with the complex having differentiated close to the QFM buffer, which appears to be usual for wide-ranging igneous rock series (e.g., Fudali, 1965; Carmichael & Nicholls, 1967; Nash & Wilkinson, 1970; Henderson et al., 1989; Cottrell & Kelley, 2011; Berry et al., 2018).

Table 13. Geo-thermometer/barometer model data for Marangudzi magmatic fractionation.

	1	2	3	4	5	6	7	8
	Olivine-Cpx	Opx-Cpx Table 4	Plag.-Alk. Feldspar Table 7	Amphib. Suppl. S.5	Plag.-Amphib. Suppl. S.5	Biotite Table 5	Magnet.- Ilmenite Table 10	10Biotite- Orthocl.- Magnet.
	T °C	T °C	T °C	T °C	T °C	T °C	T °C/ $f\text{O}_2$	T °C/ $f\text{O}_2$ (log units)/ $f\text{H}_2\text{O}$ bars
Mesocumulate gabbros								
R100A	1008	954	998			1034		980/-12/
R100	1008					1011		
G265	1006					907		
T203	1010							
G266	1008	901	938			968		980/-12.2/675
T398	991							

Continued

G205	1003				803	586/–22.2		
Orthocumulate gabbros								
A8	1006				942			
A12	960	913	926		861		960/–12.3/1150	
T168 c	984		884		934			
T168 r	978					604/–21.4	930/–13.6/1050	
Evolved minor intrusions								
T101			822		801		822/–14.3/1730	
T178			824	848	700		824/–15.8/1200	
Altered cumulate gabbros								
T123	1007			796	1007	722		
A4	999			590	959	712		
Porph Quartz syenites		Opx-Cpx	Plag.-Alk. Feldspar	Amphib.	Plag.-Amphib.	Biotite	Magnet- Ilmenite	T °C/ fO_2 (log units)/ fH_2O bar
A21			800	825	797	675		
A16			814	793	794		542/–21.4	
T36				778		651	631/–17.8	
G439				749				
Inner Qtz Syen								
A6		771	816	807	810	710	596/–21	790/–16.8/165
T5				771		666	608/–20	
T49			666	768				
T17							381/–38	
Outer Qtz Syen.	Pg-AF	Amph.	Pg-Am		Mgt-Ilm			
G161 c		801			607/–18.3			
G161 r		766						
G63	552	744	620					
G118		779						
R141		780						
R177		770						
	3	4	5	6	7		8	
	Plag.-Alk. Feld	Amph. Supp. S.5	Plag.-Amph. Suppl. S.5	Biot. Table 5	Mgt-Ilm Table 10		Biotite-Ortho.-Magnetite	
	T °C	T °C	T °C	T °C	T °C, fO_2		T °C, fO_2 (logs), fH_2O bars	
Neph. monzon.								
T308	900	825	887	717			825/–15/700	
R19	1007	862	911	746				

Continued

T310	885	824	899	702	
T303	831	862	849	781	
T174	870	881	838	762	551/–21.4
Ne-bearing Syenite					
T175	870	847	841	706	
T301	830	856	806	774	856/–15/220
R26 c	817	904	900	700	900/–14.5/1130
R26 r		882	862		
R31	861	918	955	674	920/–14.3/1180
Foyaite		T °C			
R1		836			
R2 c		855			
R2 r		831			
R20		825			490/–25.5
R226		820			
R304 c		877			
R304 r		844			
Plag. Foy. + Microfof					
R17 c	725	845	835		
R17 r		828	809		
G133	766	849	816	642	850/–15.5/1060
A14	836	840		608	840/–15.6/1500
Leuco-malignites					
R27 c		878			
R27 r		845			
R260		898			825/–15.8/300
R730		890			585/22
R330		905			
A28 c		930			
A28 r		860			

Note: 1. Powell and Powell (1974), Mg, Fe, Al = 2Ti in cpx T ; 2. Putirka (2008), Eqn 36; 3. Putirka (2016), Eqn 27a global fit; 4. Av of Ridolfi and Renzulli (2012), Eqn. 2, Putirka (2016), Eqn 5, Helz (1982), Ti fit; 5. Anderson (1995), Anderson et al. (2008); Holland and Blundy (1994) fit with $P = 1 - 2$ kb; 6. Av. of Henry et al. (2005) and Luhr et al. (1984), Mg, Fe, Ti; 7. Lepage (2003); 8. Wones (1981), Nash and Wilkinson (1970), Speer (1984).

Wones defined how the fugacity of water can be estimated from the physical variables for the biotite (annite), sanidine and magnetite assemblage as:

$$\log f(\text{H}_2\text{O}) = 4818/T + 6.69 + 3\log x_{\text{annite}} + 1/2\log(\text{O}_2) - \log a_{\text{sanidine}} - \log a_{\text{magnetite}} - 0.011(P-1)/T \quad (1)$$

where T is absolute temperature, P is total pressure in bars, x is most simply defined by the mole fraction of Fe^{2+} [i.e. $\text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$] in the biotite octahedral site, and a is the activity of sanidine and magnetite. [Czamanske and Wones \(1973\)](#) revised this equation to include a term for the annite (OH) content being lower than the ideal amount 2 (per 12 anions pfu), due to replacement of (OH) by F and Cl, to give the relationship:

$$\log f(\text{H}_2\text{O}) = 4818/T + 6.69 + 3\log x_{\text{annite}} + 2\log x(\text{OH})_{\text{bio}} + 0.5\log f(\text{O}_2) - \log a_{(\text{KAlSi}_3\text{O}_8)} - \log a_{(\text{Fe}_3\text{O}_4)} \quad (2)$$

The presence of $f(\text{O}_2)$ reduces the (OH) activity and thus the estimated water fugacity, and this approach was followed by other petrologists (e.g., [Parsons, 1981](#)). [Fabbrizio et al. \(2006\)](#) also increased the rigour of the treatment by modifying the annite activity by introducing exchange terms for Al and Si, but apparently no account was taken in that work of the possibility of oxy-mica substitution further changing the thermodynamic properties of the (OH) structural site. The approach followed here is to simplify the exchange model so that trends are emphasised for the Marangudzi complex as a whole rather than absolute values for temperature and pressure. In any case, the presence of F is likely to increase the thermal stability of phlogopite-biotite by as much as 100°C ([Sun et al., 2022](#)); the presence of oxymica stabilising entry of Ti and Ba into micas, also seems to be a high- T effect. Thus, assuming that the (OH) site is full with $(\text{OH} + \text{F} + \text{Cl} + \text{O}) = 2.0$ apfu, the Wones equation will serve to give an indication of the relationship between temperatures and water fugacity for the Marangudzi complex, with the possibility that temperatures may be slightly higher than those adopted.

Table 13 and Suppl. file S.5 summarise the magmatic-stage temperatures deduced for the main Marangudzi minerals using the different geothermometers referred to above. The mesocumulate gabbros show good agreement for temperatures based on olivine-clinopyroxene (7), clino-orthopyroxene (2), plagioclase-alkali feldspar (2) pairs and primary biotite (5) averages; the overall average is $972^\circ\text{C} \pm 57^\circ\text{C}$. The orthocumulate gabbros also show good agreement for temperatures based on olivine-clinopyroxene (4), clino-orthopyroxene (1), plagioclase-alkali feldspar (2) pairs and primary biotite (3) averages, with an overall average of $939^\circ\text{C} \pm 43^\circ\text{C}$. Thus, the gabbro unit mineral assemblages are consistent with formation within $\sim 150^\circ\text{C}$ of the intrusion temperature. The high temperature for the primary biotite in the Marangudzi gabbros is consistent with it being an early crystallizing phase, reflecting the K-rich character of the parental magma. The two gabbros that contain amphibole (T123 and A4) confirm these magmatic temperatures for olivine-clinopyroxene and plagioclase-amphibole pairs (average 990°C) but the estimated amphibole temperature of 590°C for A4 is consistent with re-equilibration of an earlier amphibole during post-magmatic hydrothermal alteration. Two alkali-basalt minor intrusions (T101 and T178) have slightly lower temperatures for plagioclase-alkali feldspar pairs and separate amphibole and biotite temperatures averaging 800°C , a late-stage magmatic temperature.

No fresh olivine was found in nepheline monzonites but their plagioclase-alkali feldspar (5), plagioclase-amphibole pairs (5), and the separate amphibole temperature (5) data in **Table 13** show mid- to late-stage magmatic formation conditions (average $875^{\circ}\text{C} \pm 44^{\circ}\text{C}$), which is only slightly lower than those of the most evolved orthocumulate gabbro (T168 rim). It is clear that amphibole is an early crystallizing phase at Marangudzi from about 900°C ; textural evidence is consistent with it being a primary magmatic phase over a considerable range of temperature. Textural relations for biotite are consistent with its initial magmatic crystallization but it appears to be more liable to sub-solidus equilibration than amphibole based on their temperatures. The clinopyroxene and plagioclase compositions for the less-evolved nepheline monzonites (e.g., T308) are very similar to those for the most fractionated orthocumulates; it is probable that any early olivine had been fully consumed by a reaction relationship with mica (see **Barton & Hamilton, 1978**). For the nepheline-bearing syenites, plagioclase-alkali feldspar (4), plagioclase-amphibole pairs (5), and the separate amphibole temperature (5) data in **Table 13** show that mid- to late-stage magmatic formation conditions (average $868^{\circ}\text{C} \pm 27^{\circ}\text{C}$), are only slightly lower than (within error) those of the most nepheline monzonite (T174). For the plagioclase containing foyaitic rocks (A17, A14, G133), plagioclase-alkali feldspar (2), plagioclase-amphibole pairs (3), and the separate amphibole temperature (3) show late-stage magmatic formation conditions (average $815^{\circ}\text{C} \pm 37^{\circ}\text{C}$) for Marangudzi, while the later-intruded leuco-malignites has a separate amphibole temperature (7) average of $880^{\circ}\text{C} \pm 26^{\circ}\text{C}$ matching that of the earlier-formed and -intruded nepheline monzonites. However, the separate biotite temperatures recorded for Marangudzi nepheline-monzonites and syenites (range $781^{\circ}\text{C} - 608^{\circ}\text{C}$) suggest that even if it started crystallizing from the magma, its re-equilibration continued well into the sub-solidus stage.

To widen the Marangudzi petrogenesis model, analyses of coexisting olivine, alkali feldspar, magnetite and magmatic biotite in Marangudzi gabbros were used to obtain estimates of equilibration temperature and oxygen fugacity using the approach developed by **Nash and Wilkinson (1970)** for the Shonkin-Sag sill. Thus, their nested annite composition and cross-cutting fayalite contours as a function of temperature and $f\text{O}_2$ (**Nash & Wilkinson, 1970**, their Figure 8) allow annite and fayalite contents for four Marangudzi gabbros (100A, G266, A12 and T168) to suggest temperature and $f\text{O}_2$ estimates. The assigned temperature and oxygen fugacity values are recorded in **Table 13** together with the calculated mole fraction (activity) of Or in coexisting alkali feldspar and of the mole fraction of $M^{2+}\text{Fe}^{3+}\text{O}_4$ in the spinel phase (calculated to 32 oxygens and 24 cations); the latter value is given for Fe-oxides in **Table 11**. In effect, the Nash and Wilkinson approach was based on the fundamental properties of the FMQ buffer, so the deduced values plot in a band below the QFM buffer curve, very close to the compositions defined by the Shonkin Sag sill. However, the Fe oxidation state for the Marangudzi amphiboles has shown that the average Marangudzi oxidation state may be an order of magnitude more oxidising than the QFM buffer. The $f\text{O}_2$ deduced for the Ma-

rangudzi mineral assemblage has therefore been increased by an order of magnitude, placing the oxidation regime to be slightly higher than the Ni-NiO buffer, which is 0.72 log units higher than that of QFM.

The log fugacity of water can now be calculated from the Wones equations given above, where the annite activity is defined by the presence of 3 octahedral M^{2+} atoms in end-member annite; the results for temperature, fO_2 , and fH_2O are given in **Table 13**. For the gabbros, the water fugacities range 675 - 1150 bars and average 920 bars. In addition, for the least evolved nepheline monzonite (T308), it is assumed that a primary olivine of composition $Fe_{0.54}$ was present before it was completely consumed by a reaction relationship with biotite; thus, a model temperature of 840°C oxygen fugacity of -16.6 bar provide a water fugacity estimate of 1100 bar. The overall average water fugacity for the gabbro and nepheline monzonite units would be ~960 bars which implies that the magma is effectively saturated with water if the total pressure is assumed to be ~1000 bars (P_{H_2O} , P_{total}).

Table 13 also shows application of the same approach to rocks that do not contain olivine where a temperature for primary amphibole is used to deduce the equivalent fO_2 on a Shonkin Sag sill trend. Thus, for nepheline monzonite T308, a temperature of 825°C would have a log fO_2 of about -15 bars, which with the analysed values for the coexisting biotite, alkali feldspar and magnetite, would provide a water fugacity of ~700 bars, slightly lower than the value obtained by assuming the presence of a “virtual” olivine. Equivalent model values are also given in **Table 13** for nepheline-bearing syenites A26, T175, T301 and A31, leucomalignite G260, and quartz syenite A6, normalized to an amphibole temperature and for minor basaltic units T101 and T178 normalized to a plagioclase-alkali feldspar temperature estimate. Including those “model” estimates for nepheline-bearing syenites, leucomalignites, microfoyaite and quartz syenite would give an overall average water fugacity of 900 bars for the gabbro and ring complex and a larger value of 1450 bars for the microgabbro (T101) and basanite dyke (T178).

The temperature conditions deduced for the silicate-undersaturated ring units (nepheline monzonites, nepheline-bearing syenites, foyaite, and leucomalignites) are all consistent with a solidus temperature of ~750°C - 800°C, matching the generally assumed values for nepheline syenites and syenites (see earlier). The low magnetite-ilmenite temperatures all point to sub-solidus alteration, while the presence of any analcime or zeolitic minerals would all be restricted to lower-temperature hydrothermal alteration.

The quartz syenite units have alkali feldspar, amphibole, plagioclase and quartz forming under magmatic conditions with temperatures being defined by orthoclino-pyroxene (1), plagioclase-alkali feldspar (5), plagioclase-amphibole (4) pairs and separate amphibole (13) values of 763°C ± 66°C. Biotites in the porphyritic quartz syenite and inner quartz syenite IQS have lower temperatures ~670°C, which is also recorded by the plagioclase-alkali feldspar temperature for IQS T49 with the most quartz-rich syenite G63 having an even lower two-feldspar temperature of 552°C. Both of these temperatures and an average Marangudzi magnetite-ilmen-

ite re-equilibration value (**Table 13**) of $606^{\circ}\text{C} \pm 83^{\circ}\text{C}$ (with average $\log f\text{O}_2^- = -17.9$ bar), lower than the expected solidus of 720°C to 750°C (Tuttle & Bowen, 1958; Yoder & Tilley, 1962).

The overall petrogenetic model for the Marangudzi igneous complex will be fully developed in Paper II (in preparation) with the conclusions of the formation conditions developed above for the coexisting minerals being combined with the detailed bulk rock geochemistry described there for the sheet-like, transitional tholeiitic/alkaline gabbro intrusion; the fractionated silica-undersaturated nepheline monzonite-nepheline-bearing syenite-foyaite-leucomalignite ring-units; and the silica-oversaturated quartz syenite ring-dykes. Based on that work, it is anticipated that the sources of the primary magmas based on major-, minor-, and trace-element geochemistry will become clearer.

6. Conclusion

1. The K-rich gabbro sheet intrusion is transitional between tholeiitic and alkaline, with biotite as the first hydrated mafic mineral to crystallize as a primary phase.
2. Evolved silica-undersaturated rings show increasing undersaturation and decreasing plagioclase An , with nepheline monzonites evolving progressively to form nepheline-bearing syenite, foyaite, and leucomalignite units. Hastingsitic amphibole becomes the dominant hydrous mafic phase within the nepheline-bearing syenite stage.
3. Marangudzi differs from many alkaline complexes that have coeval silica-oversaturated and under-saturated syenites in that amphiboles in both rock types are all Ca-amphiboles rather than having some more Na-rich species, reflecting the metaluminous (see miaskitic) nature of the parental magmas.
4. Co-existing mineral analysis geothermometry/barometry data have been combined with published phase equilibrium work on natural rocks and synthetic model systems (e.g., Ne-Ks-Qz) suggesting that the complex formed by initial intrusion of a basaltic, or perhaps basanitic, parental magma at a depth of 3 - 7 kms (1 to 2 kbars) and a temperature of 1150°C - 1200°C to form the sheet-like gabbro unit followed by intrusion of ring-type units of silica oversaturated and silica undersaturated rock series. The mineral geochemistry of the main units and deduced equilibration temperatures are summarised in **Table 13**.
5. No early-crystallizing amphibole is present in the gabbros, but it does form under post-magmatic conditions in some gabbros at $<800^{\circ}\text{C}$, while biotite temperatures suggest that re-equilibration occurred during post-magmatic cooling.
6. The different nepheline-bearing ring units all show similar mineral composition ranges and crystallization temperatures consistent with tapping of slightly different composition magmas from different parts of a zoned lower level magma chamber within a short timescale. The progressive changes in rock-forming mineral solid solutions suggest that the K-rich orthocumulate gabbros, nepheline monzonite, nepheline-bearing syenite, and foyaite/microfoyaite units formed successively during fractional crystallization during lower-level magma development; however,

a less-evolved leucomalignite unit was intruded later.

7. Note that the coeval quartz syenite units formed separately from the other Karoo Marangudzi ring units, involving assimilation of significant amounts of siliceous crustal rocks as indicated by their Sr and Nd isotopic compositions (see [Folland et al., 1993](#) and unpublished M.S. and Ph.D. theses of [Landoll, 1987, 1994](#)).

Data Availability

Note that supplementary word text files S.1 to S.4 and supplementary Excel file S.5 can be accessed via Figshare at: <https://doi.org/10.6084/m9.figshare.33352674>, or at the Manchester University Figshare site at <https://doi.org/10.48420/33368707>, which has some extra information. At both sites, files S.1, S.2, S.3 and S.4 are in one source file and S.5 in another; all supplementary files of interest can be downloaded and stored on the user's computer.

Acknowledgements

I thank Roger H. Mitchell for his incisive comments and recommendations during earlier stages of preparation of this paper; Kirsten Loach (John Rylands, University of Manchester Library) and Rhian Jones (School of Earth and Environmental Sciences) helped set up and check figshare repository files.

David Plant (deceased 7th January 2020) was a trusted colleague and friend for over 3 decades and was my co-author with others on publications involving: john-smithite (Ca-arsenic apatite) and synthetic Pb, Sr and Ba arsenates; synthetic ferri-spinel “end-members” with Mg, Mn, Co, Ni, Zn and natural and synthetic magnetite; djerfisherite $K_6(Fe, Cu, Ni)_{25}S_{26}Cl$; and calzirtite $Ca_2Zr_5Ti_2O_{16}$. In that work, he developed the microprobe methods to obtain reliable data for these “difficult” samples; in addition, for my Ti- and Ba-rich biotites and amphiboles, he dealt with the serious overlaps between the Ti *K* and Ba *L* peaks with both ED and WD methods, as well as for WD analyses of F in high Fe samples. Over that time, we must have used two ED-modified Cambridge Geoscans, two ED/WD Cambridge probes and a 5 WD spectrometer, Cameca SX100 Camebax; the last was funded in 1997 on a Joint UK Research Council, Special Equipment Programme, in collaboration with the Manchester University Materials Science department.

David was involved in obtaining ALL of the Marangudzi microprobe analyses reported here and I dedicate this paper to him, in recognition of his patience and skill, and to honour him for his contributions.

Conflicts of Interest

The author has no known competing financial interest or personal relationship that could appear to have influenced the work reported in this paper; he is an Emeritus Professor and has not held any paid employment or received any specific grant from funding agencies in the public, commercial, or not-for-profit sectors to support this work.

References

- Andersen, T. (1984). Crystallization History of a Permian Composite Monzonite-Alkali Syenite Pluton in the Sande Cauldron, Oslo Rift, Southern Norway. *Lithos*, 17, 153-170. [https://doi.org/10.1016/0024-4937\(84\)90016-1](https://doi.org/10.1016/0024-4937(84)90016-1)
- Anderson, J. L. (1995). Status of Thermobarometry in Granitic Batholiths. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh*, 87, 125-138. <https://doi.org/10.1017/s0263593300006544>
- Anderson, J. L., Barth, A. P., Wooden, J. L., & Mazdab, F. (2008). 4. Thermometers and Thermobarometers in Granitic Systems. In K. D. Putirka, & F. J. Tepley III (Eds.), *Minerals, Inclusions and Volcanic Processes* (pp. 121-142). De Gruyter. <https://doi.org/10.1515/9781501508486-005>
- Barth, T. F. W. (1963). The Composition of Nepheline. *Schweizerische Mineralogische Petrographische Mitteilungen*, 43, 153-164.
- Barton, M., & Hamilton, D. L. (1978). Water-Saturated Melting Relations to 5 Kilobars of Three Leucite Hills Lavas. *Contributions to Mineralogy and Petrology*, 66, 41-49. <https://doi.org/10.1007/bf00376084>
- Berlin, R., & Henderson, C. M. B. (1969). The Distribution of Sr and Ba between the Alkali Feldspar, Plagioclase and Groundmass Phases of Porphyritic Trachytes and Phonolites. *Geochimica et Cosmochimica Acta*, 33, 247-255. [https://doi.org/10.1016/0016-7037\(69\)90141-0](https://doi.org/10.1016/0016-7037(69)90141-0)
- Berry, A. J., Stewart, G. A., O'Neill, H. S. C., Mallmann, G., & Mosselmans, J. F. W. (2018). A Re-Assessment of the Oxidation State of Iron in MORB Glasses. *Earth and Planetary Science Letters*, 483, 114-123. <https://doi.org/10.1016/j.epsl.2017.11.032>
- Borley, G., & Frost, M. T. (1963). Some Observations on Igneous Ferrohastingsites. *Mineralogical Magazine and Journal of the Mineralogical Society*, 33, 646-662. <https://doi.org/10.1180/minmag.1963.033.263.03>
- Brenan, J. M., Maciag, B. J., & Hanley, J. J. (2023). Geochemical Variation in Biotite from the Devonian South Mountain Batholith, Nova Scotia: Constraints on Emplacement Pressure, Temperature, Magma Redox State and the Development of a Magmatic Vapor Phase (MVP). *American Mineralogist*, 108, 2004-2023. <https://doi.org/10.2138/am-2022-8691>
- Carman, M. F. (1994). Mechanisms of Differentiation in Shallow Mafic Alkaline Intrusions, as Illustrated in the Big Bend Area, Western Texas. *Journal of Volcanology and Geothermal Research*, 61, 1-44. [https://doi.org/10.1016/0377-0273\(94\)00008-5](https://doi.org/10.1016/0377-0273(94)00008-5)
- Carmichael, I. S. E., & Nicholls, J. (1967). Iron-Titanium Oxides and Oxygen Fugacities in Volcanic Rocks. *Journal of Geophysical Research*, 72, 4665-4687. <https://doi.org/10.1029/jz072i018p04665>
- Carmichael, I. S. E. (1965). Trachytes and Their Feldspar Phenocrysts. *Mineralogical Magazine and Journal of the Mineralogical Society*, 34, 107-125. <https://doi.org/10.1180/minmag.1965.034.268.09>
- Chukanov, N. V., Aksenov, S. M., Kasatkin, A. V., Škoda, R., Nestola, F., Nodari, L. et al. (2011). 3T Polytype of an Iron-Rich Oxyphlogopite from the Bartoy Volcanic Field, Transbaikalia: Mössbauer, Infrared, Raman Spectroscopy, and Crystal Structure. *Physics and Chemistry of Minerals*, 46, 899-908. <https://doi.org/10.1007/s00269-019-01049-7>
- Cottrell, E., & Kelley, K. A. (2011). The Oxidation State of Fe in MORB Glasses and the Oxygen Fugacity of the Upper Mantle. *Earth and Planetary Science Letters*, 305, 270-282. <https://doi.org/10.1016/j.epsl.2011.03.014>
- Cox, K. G. (1972). The Karroo Volcanic Cycle. *Journal of the Geological Society*, 128, 311-336. <https://doi.org/10.1144/gsjgs.128.4.0311>

- Cox, K. G., Johnson, R. L., Stillman, C. J., Vail, J. R., & Wood, D. N. (1965). The Geology of the Nuanetsi Igneous Province. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 257, 71-218. <https://doi.org/10.1098/rsta.1965.0003>
- Cox, K. G., Macdonald, R., & Hornung, G. (1967). Geochemical and Petrographic Provinces in the Karoo Basalts of Southern Africa. *American Mineralogist*, 52, 1451-1474.
- Czamanske, G. K., & Wones, D. R. (1973). Oxidation during Magmatic Differentiation, Finnmarka Complex, Oslo Area, Norway: Part 2, the Mafic Silicates. *Journal of Petrology*, 14, 349-380. <https://doi.org/10.1093/petrology/14.3.349>
- Deer, W. A., Howie, R. A., & Zussman, J. (1978). *Rock-Forming Minerals, Single-Chain Silicates, Volume 2A* (2nd ed., pp. i-viii, 1-668). The Geological Society London.
- Deer, W. A., Howie, R. A., & Zussman, J. (2004). *Rock-Forming Minerals, Framework Silicates: Silica Minerals, Feldspathoids, and the Zeolites, Volume 4B* (2nd ed., pp. i-xv, 1-982). The Geological Society London.
- Droop, G. T. R. (1987). A General Equation for Estimating Fe³⁺ Concentrations in Ferromagnesian Silicates and Oxides from Microprobe Analyses, Using Stoichiometric Criteria. *Mineralogical Magazine*, 51, 431-435. <https://doi.org/10.1180/minmag.1987.051.361.10>
- Duncan, A. R., & Marsh, J. S. (2006). The Karoo Igneous Province. In M. R. Johnson, C. R. Armhaeur, & A. J. Thomas (Eds.), *The Geology of South Africa* (pp. 501-520). Geological Society of South Africa.
- Ellam, R. M., & Cox, K. G. (1991). An Interpretation of Karoo Picrite Basalts in Terms of Interaction between Asthenospheric Magmas and the Mantle Lithosphere. *Earth and Planetary Science Letters*, 105, 330-342. [https://doi.org/10.1016/0012-821x\(91\)90141-4](https://doi.org/10.1016/0012-821x(91)90141-4)
- Fabbrizio, A., Rouse, P. J., & Carroll, M. R. (2006). New Experimental Data on Biotite + Magnetite + Sanidine Saturated Phonolitic Melts and Application to the Estimation of Magmatic Water Fugacity. *American Mineralogist*, 91, 1863-1870. <https://doi.org/10.2138/am.2006.2055>
- Foland, K. A., Landoll, J. D., Henderson, C. M. B., & Chen, J. (1993). Formation of Cogenetic Quartz and Nepheline Syenites. *Geochimica et Cosmochimica Acta*, 57, 697-704. [https://doi.org/10.1016/0016-7037\(93\)90380-f](https://doi.org/10.1016/0016-7037(93)90380-f)
- Fudali, R. F. (1965). Oxygen Fugacities of Basaltic and Andesitic Magmas. *Geochimica et Cosmochimica Acta*, 29, 1063-1075. [https://doi.org/10.1016/0016-7037\(65\)90103-1](https://doi.org/10.1016/0016-7037(65)90103-1)
- Gibb, F. G. F., & Henderson, C. M. B. (1996). The Shiant Isles Main Sill: Structure and Mineral Fractionation Trends. *Mineralogical Magazine*, 60, 67-97. <https://doi.org/10.1180/minmag.1996.060.398.06>
- Gifford, A. C. (1961). *The Geology of Eastern Marangudzi Southern Rhodesia*. Ph.D. Thesis, University of London.
- Gough, D. I., Brock, A., Jones, D. L., & Opdyke, N. D. (1964). The Paleomagnetism of the Ring Complexes at Marangudzi and the Mateke Hills. *Journal of Geophysical Research*, 69, 2499-2507. <https://doi.org/10.1029/jz069i012p02499>
- Guo, J., & Green, T. H. (1990). Experimental Study of Barium Partitioning between Phlogopite and Silicate Liquid at Upper-Mantle Pressure and Temperature. *Lithos*, 24, 83-95. [https://doi.org/10.1016/0024-4937\(90\)90018-v](https://doi.org/10.1016/0024-4937(90)90018-v)
- Harris, C., Luttinen, A., & Howarth, G. H. (2026). The Karoo Large Igneous Province. *South African Journal of Geology*, 129, 63-82. <https://doi.org/10.25131/sajg.129.2741>
- Hawkesworth, C. J., Marsh, J. S., Duncan, A. R., Erlank, A. J., & Norrý, M. J. (1984). The Role of Continental Lithosphere in the Generation of the Karoo Volcanic Rocks: Evidence from Combined Nd- and Sr-Isotope Studies. In A. J. Erlank (Ed.), *Petrogenesis of*

- the Volcanic Rocks of the Karoo Province* (pp. 341-454). The Geological Society of South Africa.
- Hawthorne, F. C., Oberti, R., Harlow, G. E., Maresch, W. V., Martin, R. F., Schumacher, J. C. et al. (2012). Nomenclature of the Amphibole Supergroup. *American Mineralogist*, 97, 2031-2048. <https://doi.org/10.2138/am.2012.4276>
- Helz, R. T. (1973). Phase Relations of Basalts in Their Melting Range at $P_{H_2O} = 5$ kb as a Function of Oxygen Fugacity: Part I. Mafic Phases. *Journal of Petrology*, 14, 249-302. <https://doi.org/10.1093/petrology/14.2.249>
- Helz, R. T. (1982). Phase Relations and Compositions of Amphiboles Produced in Studies of the Melting Behaviour of Rocks. In D. R. Veblen, & P. H. Ribbe (Eds.), *Amphibole: Petrology and Experimental Phase Relations* (pp. 279-353). Mineralogical Society of America.
- Henderson, C. M. B. (1964). *The Geochemistry of the Marangudzi Complex, Southern Rhodesia*. Ph.D. Thesis, University of London.
- Henderson, C. M. B. (1965). Minor Element Chemistry of Leucite and Pseudoleucite. *Mineralogical Magazine and Journal of the Mineralogical Society*, 35, 596-603. <https://doi.org/10.1180/minmag.1965.035.272.03>
- Henderson, C. M. B. (1968). Chemistry of Hastingsitic Amphiboles from the Marangudzi Igneous Complex, Southern Rhodesia. In *I.M.A. Papers and Proceedings, Fifth General Meeting* (pp. 291-304). Mineralogical Society.
- Henderson, C. M. B. (2020). Nepheline Solid Solution Compositions: Stoichiometry Revisited, Reviewed, Clarified and Rationalised. *Mineralogical Magazine*, 84, 813-838. <https://doi.org/10.1180/mgm.2020.78>
- Henderson, C. M. B. (2025). Ti- and Ba-Rich Phlogopitic Micras in Alkaline Basic and Upper Mantle Igneous Rocks; Stoichiometry, Stability, and Fe Valence Estimation Reassessed and Rationalised. *Geochimica et Cosmochimica Acta*, 406, 57-81. <https://doi.org/10.1016/j.gca.2024.10.011>
- Henderson, C. M. B., & Foland, K. A. (1996). Ba- and Ti-Rich Primary Biotite from the Brome Alkaline Igneous Complex, Monteregian Hills, Quebec: Mechanisms of Substitution. *The Canadian Mineralogist*, 34, 1241-1252.
- Henderson, C. M. B., & Gibb, F. G. F. (1972). Plagioclase-Ca-Rich-Nepheline Intergrowths in a Syenite from the Marangudzi Complex, Rhodesia. *Mineralogical Magazine*, 38, 670-677. <https://doi.org/10.1180/minmag.1972.038.298.03>
- Henderson, C. M. B., & Gibb, F. G. F. (1977). Formation of Analcime in the Dippin Sill, Isle of Arran. *Mineralogical Magazine*, 41, 534-537. <https://doi.org/10.1180/minmag.1977.041.320.21>
- Henderson, C. M. B., & Mitchell, R. H. (2026). A Pragmatic Approach for Using Conventional Electron Microprobe Analyses to Obtain Reliable Formulae for Differentiated Alkali Igneous Rock Amphiboles by Assessing the Possible Presence of Oxy-Amphibole Components. *Journal of Geoscience and Environment Protection*, 14, 169-224. <https://doi.org/10.4236/gep.2026.146010>
- Henderson, C. M. B., & de Oliveira, Í. L. (2022). Substitution of 'Small' Divalent Cations (e.g. Mg) for Si and Al in the Nepheline Tetrahedral Framework: 1. Calculation of Atomic Formulae and Stoichiometry Parameters. *Mineralogical Magazine*, 86, 243-253. <https://doi.org/10.1180/mgm.2022.24>
- Henderson, C. M. B., Hamilton, D. L., & Waters, J. P. (2014). Phase Equilibria in $NaAlSiO_4$ - $KAlSiO_4$ - SiO_2 - H_2O at 100 MPa Pressure: Equilibrium Leucite Composition and the Enigma of Primary Analcime in Blairmorites Revisited. *Mineralogical Magazine*, 78, 171-202.

- <https://doi.org/10.1180/minmag.2014.078.1.13>
- Henderson, C. M. B., Pendlebury, K., & Foland, K. A. (1989). Mineralogy and Petrology of the Red Hill Alkaline Igneous Complex, New Hampshire, U.S.A. *Journal of Petrology*, 30, 627-666. <https://doi.org/10.1093/petrology/30.3.627>
- Henderson, C. M. B., Richardson, F. R., & Charnock, J. M. (2012). The Highwood Mountains Potassic Igneous Province, Montana: Mineral Fractionation Trends and Magmatic Processes Revisited. *Mineralogical Magazine*, 76, 1005-1051. <https://doi.org/10.1180/minmag.2012.076.4.16>
- Henry, D. J. (2005). The Ti-Saturation Surface for Low-to-Medium Pressure Metapelitic Biotites: Implications for Geothermometry and Ti-Substitution Mechanisms. *American Mineralogist*, 90, 316-328. <https://doi.org/10.2138/am.2005.1498>
- Holland, T., & Blundy, J. (1994). Non-Ideal Interactions in Calcic Amphiboles and Their Bearing on Amphibole-Plagioclase Thermometry. *Contributions to Mineralogy and Petrology*, 116, 433-447. <https://doi.org/10.1007/bf00310910>
- Hossain, M. T. (1970). *Petrology and Mineralogy of the Marangudzi Ring Complex, Rhodesia*. Ph.D. Thesis, University of Manchester.
- Howarth, G. H., Marsh, J. S., Duncan, A. R., Harris, C., Heinonen, J. S., Richardson, S. H. et al. (2023). Petrogenesis of the Tuli Basin High-Ti Picrites and Basalts, Karoo CFB, Southern Africa: Classification, Stratigraphy, Emplacement, and Mantle Source Heterogeneity. *Lithos*, 440, Article ID: 107040. <https://doi.org/10.1016/j.lithos.2023.107040>
- Huntington, H. D. (1979). Kiglapait Mineralogy I: Apatite, Biotite, and Volatiles. *Journal of Petrology*, 20, 625-652. <https://doi.org/10.1093/petrology/20.3.625>
- Keevil, H. A., Namur, O., & Holness, M. B. (2020). Microstructures and Late-Stage Magmatic Processes in Layered Mafic Intrusions: Symplectites from the Sept Îles Intrusion, Quebec, Canada. *Journal of Petrology*, 61, egaa071. <https://doi.org/10.1093/petrology/egaa071>
- Kogarko, L. N., Uvarova, Y. A., Sokolova, E., Hawthorne, F. C., Ottolini, L., & Grice, J. D. (2005). Oxykinoshitalite, A New Species of Mica from Fernando de Noronha Island, Pernambuco, Brazil: Occurrence and Crystal Structure. *The Canadian Mineralogist*, 43, 1501-1510. <https://doi.org/10.2113/gscanmin.43.5.1501>
- Landoll, J. D. (1987). *Application of Age and Isotope Data to the Petrogenesis of the Marangudzi Alkaline Igneous Complex, Southern Zimbabwe*. Master's Thesis, The Ohio State University.
- Landoll, J. D. (1994). *The Role of Crystal Interactions in the Formation of Cogenetic Silica Oversaturated Syenites: Evidence from the Alkaline Complexes of Abu Khruk (Egypt), Mt Shefford (Quebec), and Marangudzi, (Zimbabwe)*. Ph.D. Thesis, The Ohio State University.
- Landoll, J. D., Foland, K. A., & Henderson, C. M. B. (1989). Excess Argon in Amphiboles from Fluid Interaction and Short Intrusion Interval at the Epizonal Marangudzi Complex, Zimbabwe. *Journal of Geophysical Research: Solid Earth*, 94, 4053-4069. <https://doi.org/10.1029/jb094ib04p04053>
- Le Maitre, R. W., Streikesen, A., Zanettin, B., Le Bas, M. J., Bonin, B., Bateman, P. et al. (2002). *Igneous Rocks: A Classification and Glossary of Terms. Recommendations of the International Union of Geological Sciences Subcommision on the Systematics of Igneous Rocks* (p. 236). Cambridge University Press.
- Lepage, L. D. (2003). ILMAT: An Excel Worksheet for Ilmenite-Magnetite Geothermometry and Geobarometry. *Computers & Geosciences*, 29, 673-678. [https://doi.org/10.1016/s0098-3004\(03\)00042-6](https://doi.org/10.1016/s0098-3004(03)00042-6)

- Li, X., Zhang, C., Behrens, H., & Holtz, F. (2020a). Calculating Biotite Formula from Electron Microprobe Analysis Data Using a Machine Learning Method Based on Principal Components Regression. *Lithos*, 356, Article ID: 105371. <https://doi.org/10.1016/j.lithos.2020.105371>
- Li, X., Zhang, C., Behrens, H., & Holtz, F. (2020b). Corrigendum to “Calculating Biotite Formula from Electron Microprobe Analysis Data Using a Machine Learning Method Based on Principal Components Regression” [Lithos 356-357 (2020) 105371]. *Lithos*, 362, Article ID: 105506. <https://doi.org/10.1016/j.lithos.2020.105506>
- Li, X., Zhang, C., Behrens, H., & Holtz, F. (2020c). Calculating Amphibole Formula from Electron Microprobe Analysis Data Using a Machine Learning Method Based on Principal Components Regression. *Lithos*, 362, Article ID: 105469. <https://doi.org/10.1016/j.lithos.2020.105469>
- Luhr, J. F., Carmichael, I. S. E., & Varekamp, J. C. (1984). The 1982 Eruptions of El Chichón Volcano, Chiapas, Mexico: Mineralogy and Petrology of the Anhydritebearing Pumices. *Journal of Volcanology and Geothermal Research*, 23, 69-108. [https://doi.org/10.1016/0377-0273\(84\)90057-x](https://doi.org/10.1016/0377-0273(84)90057-x)
- Luttinen, A., Kurhila, M., Puttonen, R., Whitehouse, M., & Andersen, T. (2022). Periodicity of Karoo Rift Zone Magmatism Inferred from Zircon Ages of Silicic Rocks: Implications for the Origin and Environmental Impact of the Large Igneous Province. *Gondwana Research*, 107, 107-122. <https://doi.org/10.1016/j.gr.2022.03.005>
- Marsh, B. D. (1996). Solidification Fronts and Magmatic Evolution. *Mineralogical Magazine*, 60, 5-40. <https://doi.org/10.1180/minmag.1996.060.398.03>
- Martel, C., Champallier, R., Prouteau, G., Pichavant, M., Arbaret, L., Balcone-Boissard, H. et al. (2013). Trachyte Phase Relations and Implication for Magma Storage Conditions in the Chaîne Des Puys (French Massif Central). *Journal of Petrology*, 54, 1071-1107. <https://doi.org/10.1093/petrology/egt006>
- Matzen, A. K., Woodland, A., Beckett, J. R., & Wood, B. J. (2022). Oxidation State of Iron and Fe-Mg Partitioning between Olivine and Basaltic Martian Melts. *American Mineralogist*, 107, 1442-1452. <https://doi.org/10.2138/am-2021-7682>
- McDowell, S. D., & Wyllie, P. J. (1971). Experimental Studies of Igneous Rock Series: The Kungnat Syenite Complex of Southwest Greenland. *The Journal of Geology*, 79, 173-194. <https://doi.org/10.1086/627607>
- Millhollen, G. L. (1971). Melting of Nepheline Syenite with H₂O and H₂O + CO₂, and the Effect of Dilution of the Aqueous Phase on the Beginning of Melting. *American Journal of Science*, 270, 244-254. <https://doi.org/10.2475/ajs.270.3.244>
- Mitchell, R. H. (1990). A Review of the Compositional Variation of Amphiboles in Alkaline Plutonic Complexes. *Lithos*, 26, 135-156. [https://doi.org/10.1016/0024-4937\(90\)90044-2](https://doi.org/10.1016/0024-4937(90)90044-2)
- Mitchell, R. H., & Platt, R. G. (1979). Nepheline-Plagioclase Integrowths of Metasomatic Origin from the Coldwell Complex. *The Canadian Mineralogist*, 17, 537-540.
- Moussallam, Y., Oppenheimer, C., Scaillet, B., & Kyle, P. R. (2013). Experimental Phase-Equilibrium Constraints on the Phonolite Magmatic System of Erebus Volcano, Antarctica. *Journal of Petrology*, 54, 1285-1307. <https://doi.org/10.1093/petrology/egt012>
- Namur, O., Hatert, F. G., Long, G. J., Krins, N., Fransolet, A. V. A., & Charlier, B. (2009). Ti Substitution Mechanisms in Phlogopites from the Suwalki Massif-Type Anorthosite, NE Poland. *European Journal of Mineralogy*, 21, 397-406. <https://doi.org/10.1127/0935-1221/2009/0021-1894>
- Nash, W. P., & Wilkinson, J. F. G. (1970). Shonkin Sag Laccolith, Montana. *Contributions to Mineralogy and Petrology*, 25, 241-269. <https://doi.org/10.1007/bf00399286>

- Oberti, R., Hawthorne, F. C., Cannillo, E., & Camara, F. (2007). Long-Range Order in Amphiboles. *Reviews in Mineralogy and Geochemistry*, 67, 125-171. <https://doi.org/10.2138/rmg.2007.67.4>
- Parsons, I. (1981). The Klokken Gabbro-Syenite Complex, South Greenland: Quantitative Interpretation of Mineral Chemistry. *Journal of Petrology*, 22, 233-260. <https://doi.org/10.1093/petrology/22.2.233>
- Powell, M., & Powell, R. (1974). An Olivine-Clinopyroxene Geothermometer. *Contributions to Mineralogy and Petrology*, 48, 249-263. <https://doi.org/10.1007/bf00951333>
- Putirka, K. (2016). Amphibole Thermometers and Barometers for Igneous Systems and Some Implications for Eruption Mechanisms of Felsic Magmas at Arc Volcanoes. *American Mineralogist*, 101, 841-858. <https://doi.org/10.2138/am-2016-5506>
- Putirka, K. D. (2008). Thermometers and Barometers for Volcanic Systems. *Reviews in Mineralogy and Geochemistry*, 69, 61-120. <https://doi.org/10.2138/rmg.2008.69.3>
- Rees, G. (1960). *The Geology of West Marangudzi. S. Rhodesia*. Ph.D. Thesis, University of London.
- Ridolfi, F., & Renzulli, A. (2012). Calcic Amphiboles in Calc-Alkaline and Alkaline Magmas: Thermobarometric and Chemometric Empirical Equations Valid up to 1130°C and 2.2 GPa. *Contributions to Mineralogy and Petrology*, 163, 877-895. <https://doi.org/10.1007/s00410-011-0704-6>
- Righter, K., & Carmichael, I. S. E. (1996). Phase Equilibria of Phlogopite Lamprophyres from Western Mexico: Biotite-Liquid Equilibria and P-T Estimates for Biotite-Bearing Igneous Rocks. *Contributions to Mineralogy and Petrology*, 123, 1-21. <https://doi.org/10.1007/s004100050140>
- Shagalov, E. S., Holodnov, V. V., Sustavov, S. G., & Kiseleva, D. V. (2021). Cl-Rich Amphiboles and Micas in Rocks of the Middle Riphean Kusa-Kopan Complex of Mafic Layered Intrusions (Southern Urals, Russia). *Mineralogy and Petrology*, 115, 391-409. <https://doi.org/10.1007/s00710-021-00742-2>
- Speer, J. A. (1984). 9. Micas in Igneous Rocks. In S. W. Bailey (Ed.), *Micas* (pp. 299-356). De Gruyter. <https://doi.org/10.1515/9781501508820-013>
- Storey, B. C. (1995). The Role of Mantle Plumes in Continental Breakup: Case Histories from Gondwanaland. *Nature*, 377, 301-308. <https://doi.org/10.1038/377301a0>
- Sun, J., Yang, Y., Ingrin, J., Wang, Z., & Xia, Q. (2022). Impact of Fluorine on the Thermal Stability of Phlogopite. *American Mineralogist*, 107, 815-825. <https://doi.org/10.2138/am-2022-8051>
- Tilley, C. E. (1954). Nepheline-Alkali Feldspar Parageneses. *American Journal of Science*, 252, 65-75. <https://doi.org/10.2475/ajs.252.2.65>
- Tuttle, O. F., & Bowen, N. L. (1958). *Origin of Granite in the Light of Experimental Studies in the System NaAlSi₃O₈-KAlSi₃O₈-SiO₂-H₂O* (pp. 11, 153). The Geological Society of America.
- Uchida, E., Endo, S., & Makino, M. (2007). Relationship between Solidification Depth of Granitic Rocks and Formation of Hydrothermal Ore Deposits. *Resource Geology*, 57, 47-56. <https://doi.org/10.1111/j.1751-3928.2006.00004.x>
- Ventrucci, G., Caggianelli, A., Festa, V., & Langone, A. (2020). Crystal Chemistry of Barian Titanian Phlogopite from a Lamprophyre of the Gargano Promontory (Apulia, Southern Italy). *Minerals*, 10, Article 766. <https://doi.org/10.3390/min10090766>
- Wilson, A. D. (1955). A New Method for the Determination of Ferrous Iron in Rocks and Minerals. *Bulletin Geological Survey of Great Britain*, 9, 56-58.
- Wones, D. R. (1981). Mafic Silicates as Indicators of Intensive Variables in Granitic Magmas.

Mining Geology, 31, 191-212.

Yoder, H. S., & Tilley, C. E. (1962). Origin of Basalt Magmas: An Experimental Study of Natural and Synthetic Rock Systems. *Journal of Petrology*, 3, 342-532.
<https://doi.org/10.1093/petrology/3.3.342>