Journal of African Earth Sciences 164 (2020) 103769

Contents lists available at ScienceDirect

Journal of African Earth Sciences

journal homepage: www.elsevier.com/locate/jafrearsci

Petrology and geochemistry of selected nepheline syenites from Malawi and their potential as alternative potash sources

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ARTICLE INFO

Keywords:
Potassium
Nepheline syenite
Davidsmithite
SEM-EDS
Malawi
Geophysical gamma ray spectrometry

ABSTRACT

The Sub Saharan Africa agricultural sector is one of the most disadvantaged regions, partly due to high fertiliser import costs from the northern hemisphere. Malawi is one such country which faces these fertiliser challenges for the agricultural sector growth and food crop production. However, Malawi has numerous intrusive alkaline rocks, nepheline syenites, especially within the Chilwa alkaline province. This study was therefore conducted to assess these nepheline syenites for their potential as potassium sources. We used Malawi's new airborne geophysical gamma ray data acquired in 2013, coupled with satellite remote sensing, to identify nepheline syenites suitable as possible sources for alternative silicate K-fertiliser, and carried out geochemical analysis of whole rock samples. Results show that the K_2O content for the nepheline syenites varies from 3.17 wt % to 9.14 wt % with an average of 5.22 wt %. The K_2O/Na_2O ratio for Malawi's nepheline syenites ranges from 0.41 to 1.28 with an average of 0.65 showing that the nepheline syenites are mostly sodic but with variable composition. In addition to nepheline, the calcium feldspathoid davidsmithite ($(Na,Ca)AlSiO_4$) was identified in the syenites using scanning electron microscopy with energy dispersive analysis. Although the different intrusive complexes are not homogenous, our results show that, generally, the nepheline syenites from Malawi have similar geochemistry and mineralogical composition to those which have been used as crushed-rock fertilisers in other parts of the world.

1. Introduction

The global community faces several major challenges concerning food security. One of these is the cost of conventional fertiliser, particularly potassium (commonly called potash; K_2O), which is currently so expensive that it is inaccessible to many farmers, especially in Africa, on the grounds of purchase price and transport costs (Fuentes, 2013). By 2020, without any increase in fertiliser use and amidst increased crop production, leading to soil nutrient deficiency, annual depletion rates of potassium in Africa will likely increase to 36 kg ha^{-1} K (Sheldrick and Lingard, 2004). However, alternatives are available, which may help farmers to replenish the potassium removed by crops (Manning, 2015, 2017), including the use of nepheline syenites (Goldschmidt, 1922; Jena et al., 2014).

1.1. Situational context

By 2004, all but only four African countries (Botswana, Namibia, Somalia and Niger) were K deficient (Sheldrick et al., 2002). Because most potassium fertiliser is imported from the northern hemisphere, costs are largely determined by the import and transport costs. Other additional costs are associated with fertiliser distribution within the country as well as the trader and agro-dealer margins (Chirwa and Dorward, 2013; Fuentes, 2013). The situation has worsened in the last decade due to the global economic recession, fertiliser price adjustments and increasing poverty levels in Africa. An average African farmer pays for potassium fertiliser nearly twice as much as their counterparts in Europe and America. This is partly because the First World dominates fertiliser production (Roberts and Vilakazi, 2014). Malawi, in particular, faces severe fertiliser challenges for her agricultural sector growth. The Government introduced the farm input fertiliser subsidy program (FISP) in early 2000s to help vulnerable

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https://doi.org/10.1016/j.jafrearsci.2020.103769
Received 20 July 2019; Received in revised form 13 January 2020; Accepted 21 January 2020
Available online 28 January 2020

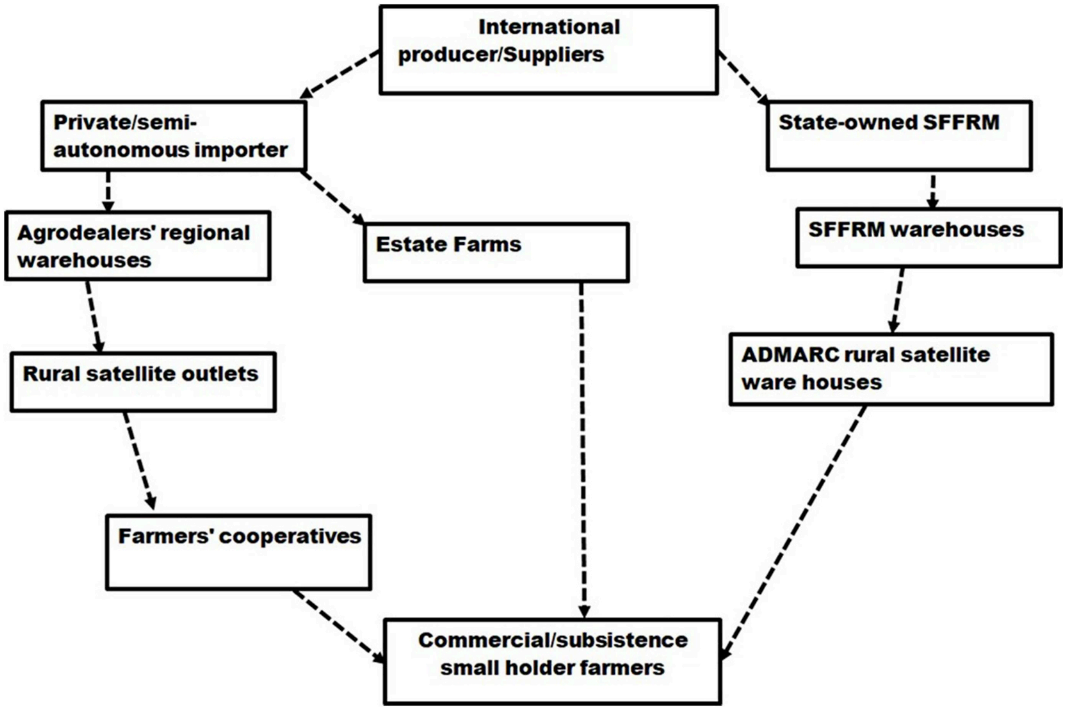

Fig. 1. Malawi's fertiliser supply chain showing long route to smallholder farmers hence high farm-gate fertiliser prices (based on Fuentes, 2013).

farmers. The scheme faces challenges including corruption, dependency on donor funding (Vinet and Zhedanov, 2010) and a long supply chain (Fig. 1). Two key state-owned local fertiliser suppliers are the Smallholder Farmers Fertiliser Revolving Fund of Malawi (SFFRM) and the Agricultural Development and Marketing Corporation (ADMARC).

Previous work has shown that crushed rocks offer a viable alternative to chemical fertilisers, especially in highly weathered and leached environments (Harley and Gilkes, 2000; Theodoro and Leonardos, 2006; van Straaten, 2007; Priyono and Gilkes, 2008; Mohammed et al., 2015; Ciceri et al., 2015; Gupta, 2015; Manning, 2010, 2017). Use of locally available crushed rocks, termed 'remineralizers', for agriculture in tropical soils is established in Brazil. In Brazil, it is particularly attractive to small farmers who produce food (especially horticultural crops) for their own consumption and for domestic markets (Manning and Theodoro, 2018). Crushed rocks release nutrients more slowly than chemical fertilisers (Harley and Gilkes, 2000), which are vulnerable to fast removal due to leaching and erosion. A number of studies have shown that rocks containing biotite and nepheline demonstrably provide potassium for plant uptake (Gautneb and Bakken, 1995; Bakken et al., 2000; Mohammed et al., 2015). Although other silicates containing potassium are common rock-forming minerals, the nutrient release from these minerals, such as feldspars, is slow compared to chemical fertilizers such as KCl (Priyono and Gilkes, 2008; Manning, 2010; Mohammed et al., 2015). This deters their use except where particular soil requirements are favorable and where rock powder properties have been improved to required standards (Harley and Gilkes, 2000).

The suitability of silicate rocks as alternative source for potassium does not depend on their absolute content but rather the dissolution rates of their potassium-bearing minerals (Manning, 2010). Although potassium feldspars have greater absolute contents of potassium than nepheline, their suitability as a source of K is limited (Priyono and Gilkes, 2008). This can be attributed to their slow dissolution rates. Other experimental studies suggest that the dissolution of silicate minerals, particularly nepheline, is largely influenced by the acidic conditions in the soil (Priyono and Gilkes, 2008; Jena et al., 2014). Dissolution rates also depend on the minerals' surface area, and can therefore be enhanced by grinding or milling, which means adding extra capital and production costs.

Few plant growth trials have been conducted using nepheline syenite compared to potassium feldspar (Manning, 2010; Manning et al., 2017). Bakken et al. (1997) carried out field trials with crushed rock containing orthoclase, nepheline and biotite, and mine tailings from nepheline syenite production at North Cape (Norway), to assess their potential to release potassium to support Italian ryegrass growth over a six months period. The plant growth was highest from nepheline followed by biotite, then orthoclase and mine tailings, suggesting fastest potassium release from nepheline. This also suggests that there was slow breakdown and dissolution from the tailings, hence the inability of the plants to extract sufficient nutrients from them. While agreeing that biotite release is higher than most soluble potassium sources, Bakken et al. (1997) reported that there was a slower release for biotite sources compared to nepheline. These findings agree with experimentally determined dissolution rates for silicate minerals as reported by Palandri and Kharaka (2004), which found the highest dissolution rates in nepheline (Table 1).

Pessoa et al. (2015) also assessed the solubility of nepheline syenite as a function of organic matrices, using coffee husk in Brazil. Results showed that regardless of potassium content, when a nepheline syenite-organic mixture was incubated, potassium solubility was high, especially when extracted with 2% citric acid compared with water. The physical properties, notably particle size and surface area of the potassium-bearing silicate minerals (Priyono and Gilkes, 2008; Mohammed et al., 2015), play an added role in accelerating their dissolution and suitability as potassium sources. The use of nepheline syenites as an alternative to K-feldspars is also supported by studies on Colombian Savanna native grasses (*Brachiaria dyctioneura*) and the legume *Pueraria phaseoloides* (Gautneb and Bakken, 1995). In their studies of these grasses' dry matter yield, Gautneb and Bakken (1995) and Sanz Scovino and Rowell (1988) found that only about 10% of the feldspar's K was absorbed by plants in 14 months, compared to 25–68% of KC1 uptake from the crops in the same period. Since the dissolution rate is also dependent on temperature (Harley and Gilkes, 2000), nepheline syenites would be suited in tropical areas. The high tropical temperatures, unlike Norway and other cold areas where the rocks have

Table 1
Silicate minerals and their dissolution rates (after Palandri and Kharaka, 2004).

Mineral	Molecular Formula	Weight % K	Dissolution rate, log mol m^{-2} S^{-1}	Relative dissolution rate
Potassium feldspar	$KAlSi_3O_8$	14.00	−10.06	1
Leucite[a]	$KAlSiO_6$	17.9	−6.00	10,000
Nepheline[a]	(Na, K) $AlSiO_4$	8.30	−2.73	20,000,000
Muscovite[b]	$KAl_3Si_3O_{10}(OH)_2$	9.00	−11.85	0.01
Biotite[b]	$K_2Fe_6Si_6Al_2O_{20}(OH)_{24}$	7.60	−9.84	1

[a] Feldspathoid family.
[b] Mica family (release K through cation exchange).

been tested (Bakken et al., 1997), would support more rapid dissolution of the nepheline.

This study compares, for the first time, the geochemical composition of nepheline syenites from Malawi with examples used elsewhere in studies of the potential of nepheline-bearing rocks as a source of K. Given the wider occurrence of nepheline syenites within the East African Rift System, the results have broader application. At present, most nepheline syenite intrusions, especially in Africa, have not been exploited for this role. More widely, our aim is to demonstrate that airborne geophysical gamma ray data coupled with petrological and geochemical analysis of rock samples collected in the field can be used to identify and map nepheline syenites suitable for consideration as sources for potassium as fertiliser. Fig. 2 shows the areas considered in this study. Fig. 2 also shows that some intrusions which were identified as possible nepheline syenites or syenites that had not been documented as alkaline rocks prior to this study. The nepheline syenites and alkaline rocks of Malawi are distributed all over the country (Woolley, 2001) although most of them occur largely in the Chilwa Alkaline Province (CAP) of Early Jurassic to Late Cretaceous age. The CAP largely comprises plutonic rocks in the form of syenites, nepheline syenites, carbonatites, and some volcanic vents associated with carbonatite bodies, feldspathic rocks, breccias and agglomerates outcrop in a number of parts of the country (Mshali, 2009).

1.2. Regional geological setting of the study area

Malawi lies within the Mozambican Mobile Orogenic Belt, which is associated with reworked meta-volcanic and meta-sedimentary rocks of Late Precambrian to Early Palaeozoic age (Carter and Bennet, 1973; Mshali, 2009), locally known as the Malawi Basement Complex (MBC). The MBC has been affected by three orogenic episodes, namely the "Ubendian" cycle (2100–1950 Ma), the "Irumide" cycle (1600–900 Ma) and the "Mozambican" cycle (700–400 Ma). The Malawi Rift is part of the Miocene-Quaternary East African Rift System (EARS). This is associated with faulting and the linear graben that covers most of east of the country (Thatcher and Walter, 1968; Mshali, 2009). Fig. 3 shows a simplified regional geological map of the study area.

There is little published information about the petrology and geochemistry of these nepheline syenites. Therefore, this paper is important because it provides the much-needed information on the distribution of Malawi's nepheline syenites, permitting assessment of their potential as a K silicate fertiliser. The sampled areas in Kasungu (Fig. 3 A) occur in the central region. The other areas fall within the Chilwa Alkaline Province, S. Malawi.

2. Materials and methods

2.1. Data used in the study

In order to label these rocks as possible nepheline syenite targets, airborne gamma-ray spectrometry data and partly ASTER digital terrain models were used. Malawi's most recent countrywide airborne gamma-ray spectrometry data were acquired by Sanders Geophysics Limited as part of Malawi's countrywide geophysical mapping programme, using the Exploranium GR-820 gamma-ray spectrometers (Bates and Mechenneff, 2013). The pixel size on the ground depends on the number of samples collected per second by the sensors. Most airborne geophysical surveys are conducted at a sampling rate of 1 count per second (1 Hz; Bates and Mechenneff, 2013) which is equivalent to 50–80 m pixel size on the ground (Horsfall, 1997; Beamish, 2014). Malawi's airborne geophysical gamma-ray data was acquired at a line spacing of 250 m and 60 m flying height (Bates and Mechenneff, 2013) and was gridded at 50 m grid cell size (Bates and Mechenneff, 2013).

2.2. Identification of potential areas for sampling

Data for petrological and geochemical analyses were acquired from the fieldwork conducted by the authors in key locations in Malawi. The fieldwork survey areas were selected largely based on results from gamma-ray airborne geophysics, remote sensing data (especially digital terrain models), and review of previous geological information of Malawi. The potential nepheline syenite areas were selected for fieldwork based on results from the gamma-ray spectrometry processing and analysis. This was done using individual total count maps of three radiometric channels, namely uranium (U), thorium (Th) and potassium (K) and ternary composite maps. Geochemically, nepheline syenites show high-K content relative to Th and U (Tye et al., 2017). On ternary plots, the potential nepheline syenites and related rocks were those which showed high potassium content. The ideal areas for fieldwork, were therefore, those with high K, relative to U and Th. This was best reflected on the gamma-ray ternary plots because they combine the three radiometric channels and highlight areas where each of the channels (K, U, Th) is highest relative to the other two. Nepheline syenites, carbonatites and other alkaline rocks are usually associated with ring structures, lineaments and clusters (Jaireth et al., 2014; Woolley and Kjarsgaard, 2008). Potential areas were, therefore, those whose results were those with high K content (between 3.43 wt% to 7.52 wt%) on the K gamma ray total count maps. The high potential areas were selected for ground follow-up, if they had higher K content relative to Th and U on the gamma ray ternary maps and showed ring structures and/or clustering on digital terrain models (DTMs).

2.3. Field sampling

Thirteen areas were surveyed during the fieldwork. Two areas were from central Malawi (9 and 10), three from the carbonatite associated areas (32,33 and 35), four from southern Malawi (25–28) and three from south-east Malawi (undocumented) in Fig. 2. During the survey, different rock types were sampled. Emphasis was on nepheline syenites and related alkaline rocks to assess their potential as potassium silicate fertiliser sources.

2.4. Ground gamma ray geophysics

Field gamma-ray data were collected using an RS 125 gamma-ray field spectrometer manufactured by Terraplus Inc. This instrument was

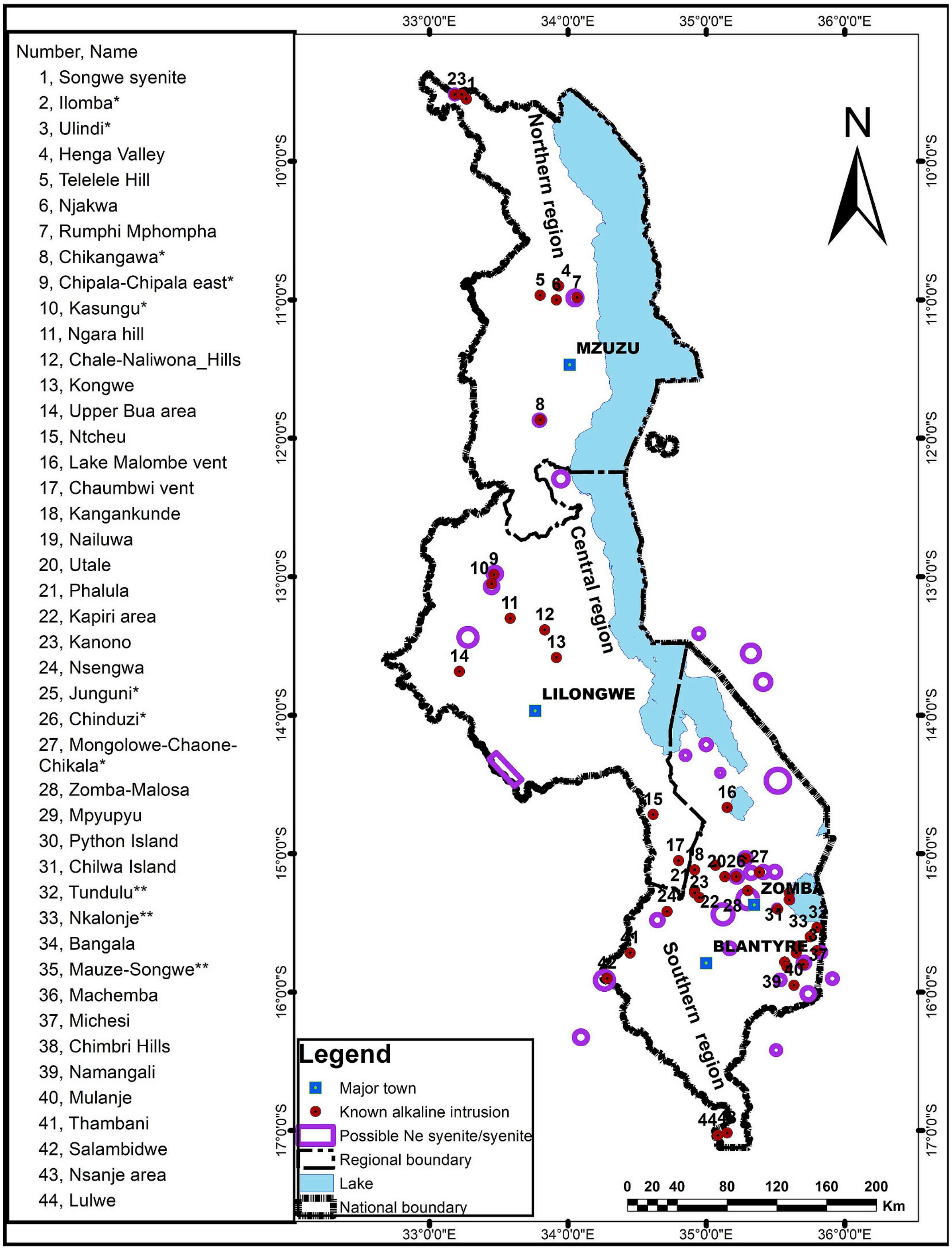

Fig. 2. Map of Malawi showing known alkaline rock intrusions across the country (data for alkaline rocks extracted from Woolley (2001)). The intrusions indicated with asterisk (*) are known nepheline syenites while those indicated with double stars (**) comprise both carbonatite and nepheline syenite.

used to obtain K, U and Th concentrations from different rocks in the areas surveyed. The spectrometer has assay mode readout for K in %, and U and Th in ppm (Madi et al., 2014). We used the Total Count readout at 1×/sec rate in the Survey Mode (www.terraplus.com/products/pdf/rs-125-portalbe-super-gamma-ray-spectrometer.pdf) and the sample time was set at 60 s.

2.5. Petrography

A detailed petrographic study of the samples was carried out on thin sections prepared by the Sample Preparation Facility of the School of Geosciences, The University of Edinburgh. Samples were studied using a Nikon Eclipse e200 conventional petrographic microscope and the Zeiss SIGMA HD VP Field Emission scanning electron microscope (SEM) hosted at Edinburgh University (https://www.ed.ac.uk/geosciences/facilities/sem/specification). Semi-quantitative mineral chemistry in the samples was measured using the Oxford AZtec energy dispersive spectrometer (EDS) fitted to the system, calibrated on a cobalt standard.

2.6. X-ray ray fluorescence (XRF) analysis

Major and trace elements were analysed using the Panalytical PW2404 X-Ray fluorescence (XRF) instrument hosted at the School of Geosciences, The University of Edinburgh (https://www.ed.ac.uk/

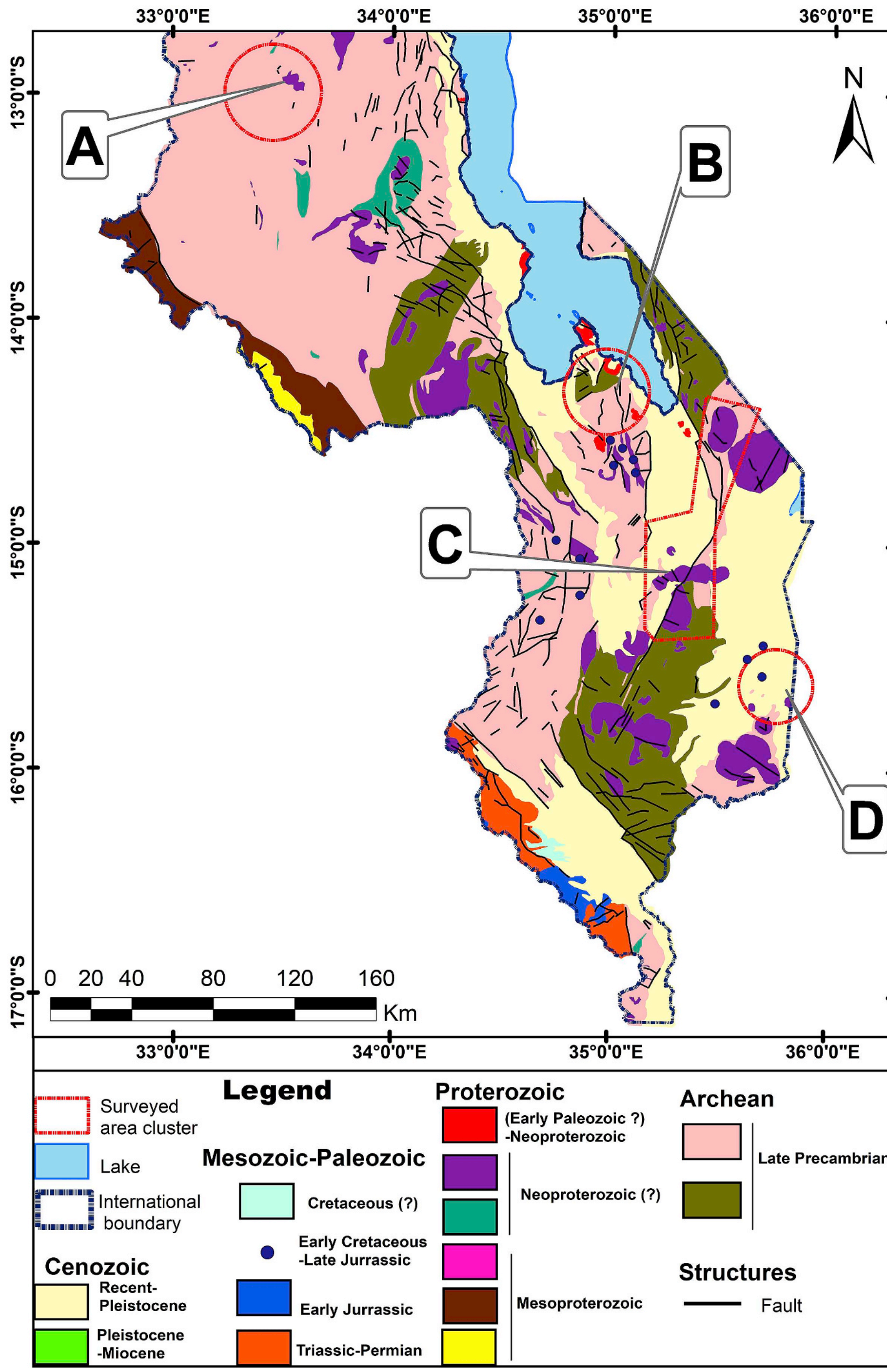

Fig. 3. Regional geology showing location of areas which were identified for fieldwork (revised after Bloomfield, 1966). These areas are clustered as (A) central Malawi nepheline syenites (B) S.E Malawi quartz syenites; (C) S. Malawi nepheline syenites and syenites; (D) Carbonatite-associated nepheline syenites.

geosciences/facilities/xrayfluorescence). The rock samples were firstly finely ground using a tungsten carbide grinding mill and an agate mill. While both mills were used to produce a fine powder from the rock samples, the tungsten carbide mill was needed for grinding very hard rock chips to a fine powder of around 120 µm. Major-element concentrations were measured on 40 mm-diameter fused glass discs; about 0.9 g of sample powder was mixed with a borate flux using a 5:1 (flux: sample) dilution procedure Gill (2014). Thereafter, the samples were fused and heated in Pt-5% Au crucibles at 1100 °C. The trace element concentrations were measured on pressed pellets with ~8 g of powder used to make a 40 mm-diameter pellets.

2.7. *Weathering intensity of the rocks*

The Parker chemical alteration index (CIA) and the plagioclase alteration index (PIA) (Nordt and Driese, 2010; Meunier et al., 2013; Mohanty et al., 2016) were used to determine the alteration states of the rocks and whether K_2O and nepheline abundance could be related to this. The CIA degree of alteration ranges from 0 to 100. The optimum index value for fresh/less altered rock is < 50 whereas 100 is the maximum index value for 'complete' alteration (Price and Velbel, 2003). The PIA focusses more on plagioclase alteration. Using molecular proportions of elemental oxides the two indices are calculated (Price and Velbel, 2003) as:

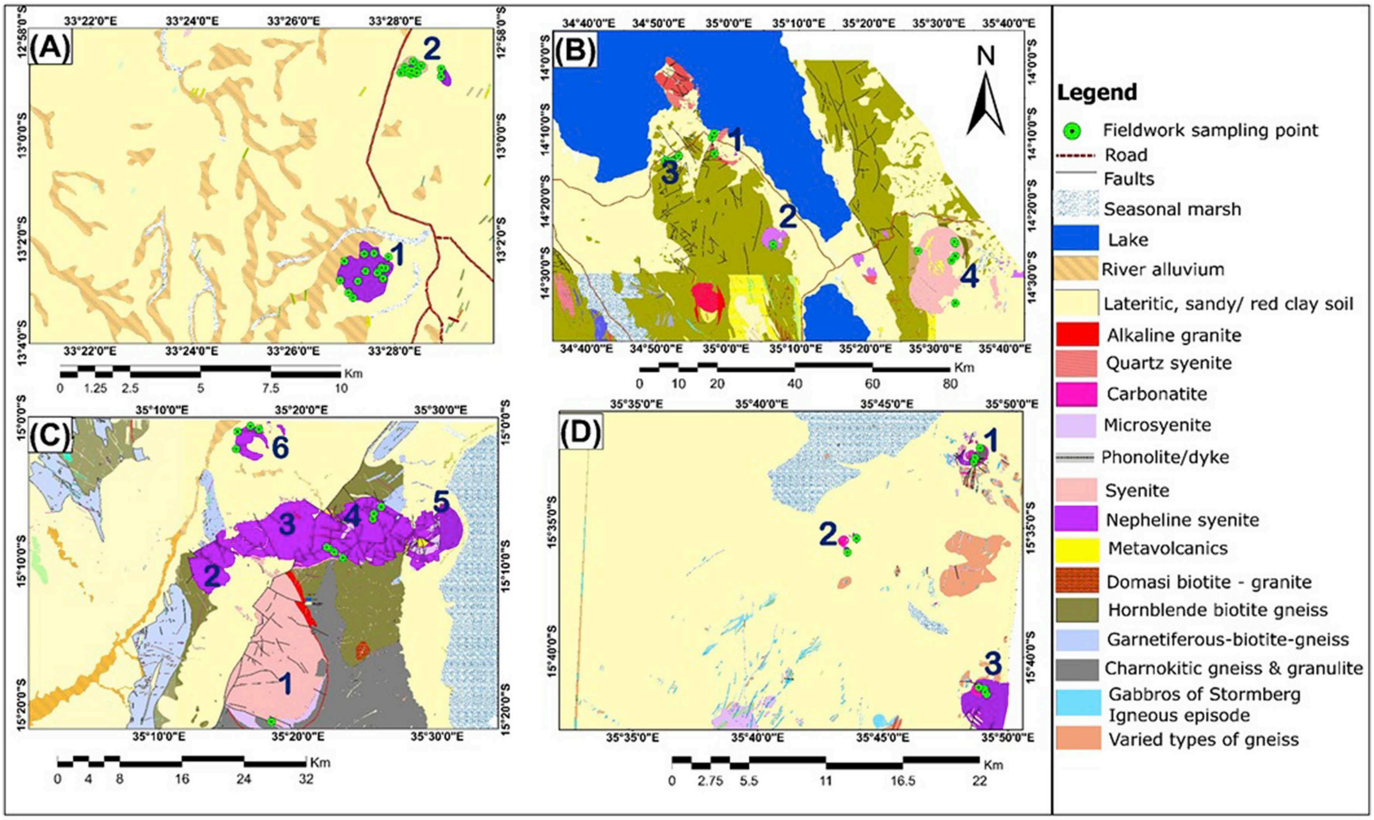

Fig. 4. General geology of clusters A, C, D, E. of Fig. 3 namely (A) central Malawi nepheline syenite namely, 1. Kasungu hill, 2. Kasungu-Chipala hill areas (after Peters, 1969); (B) South-east Malawi quartz syenites namely, 1. Nkhuzi bay 2. Mauni, 3. Chantulo, 4. Mangochi Hill syenite. (after King and Dawson, 1976); (C) South east nepheline syenites and syenite namely: (1) Zomba syenite, (2) Chinduzi, (3) Mongolowe, (4) Chaone, (5) Chikala and (6) Junguni nepheline syenites (modified after Eby et al., 1998); (D) the carbonatite-associated nepheline syenite area, namely: 1. Tundulu, 2. Nkalonje, 3. The Songwe-Mauze, intrusions.

$$CIA = \left((100)^{*}\left(\frac{Al_2O_3}{Al_2O_3O + K_2O}\right)\right), \tag{3}$$

$$PIA = \left(100 * \left[\frac{(Al_2O_3 - K_2O)}{Al_2O_3 + \text{ CaO } + Na_2O{-}K_2O}\right]\right) \tag{4}$$

3. Results

3.1. Geology and field observations of the surveyed areas

The samples of nepheline syenites, syenites and other rock types were collected from the different areas that were surveyed. As shown in Fig. 2, the areas were grouped in clusters based on the locations where they occur. Fig. 4(A-D) shows the general geology of four of clusters which were surveyed. The maps in Fig. 4 are only for clusters which included at least a nepheline syenite or syenite intrusion.

3.1.1. Central Malawi nepheline syenites (Fig. 4 (A))

The central Malawi unit comprises the Kasungu and Kasungu-Chipala nepheline syenites (areas 1 and 2 respectively in Fig. 4A), which were intruded in a suite of medium to high-grade metamorphic rocks of the Mozambique Orogenic Belt, dated ~500 Ma (Eby et al., 1998). In hand specimens, nepheline syenites from both intrusions are medium to coarse-grained and contain xenolithic inclusions of gneisses and diorites. Mesocratic, very coarse-grained nepheline syenites, which grade into syeno-granites, occur sparsely. The rocks are variably weathered; lichens and small herbaceous plants are abundant.

The Kasungu-Chipala nepheline syenites (2 in Fig. 4A), are in some localities bounded by diorites, although the contact zone between these rock types is not clear (Peters, 1969). Localized faulting with some heavily folded biotite schist and fenites along the nepheline syenite-diorite contact zone occur in few locations. This may suggest a contact metasomatism event, which might have preceded micro-faulting and later quartzitic vein development (Peters, 1969).

3.1.2. South East Malawi quartz syenites and Mangochi hill syenite (Fig. 4 (B))

The south-eastern quartz syenites and syenite include the Nkhuzi Bay and Mauni intrusions (Fig. 4B; 1 and 2 respectively). These are part of a chain of some NNE trending oval-shaped undulating hills located on the western side of Mangochi town. The Nkhuzi Bay area is characterized by coarse-grained-mesocratic-weathered quartz syenite. The weathered rocks are more altered and show a pale colour while the fresher specimens are more pinkish. King and Dawson (1976) reported that the quartz syenites in this area occur together with syenites but during this fieldwork only quartz syenites were observed. In hand specimens, the quartz syenites show more K-feldspars ($\geq$40%), plagioclase ($\leq$25%), quartz ($\geq$15%), muscovite, biotite (10%), minor occurrences of hornblende plus other unidentified minerals.

The Mangochi Hill syenite (Fig. 4 B (4)), which is located further north-east of the Junguni intrusion, shows similar mineralogy to the Zomba syenite although the Mangochi Hill syenite has more K-feldspar.

Fig. 5. Examples of outcrops from which rock samples were collected from the field: (A) nepheline syenite from Kasungu (KU-009), (B) nepheline syenite from Kasungu-Chipala (KUCP-008), (C) nepheline syenite from Chaone (CHA-002), (D) nepheline syenite from Junguni (JUN-003).

The Mangochi Hill syenites are coarse to medium-grained and mesocratic. Hand specimens of the rocks mainly show K-feldspars (≥50%), plagioclase and micas.

3.1.3. South Malawi nepheline syenites and syenites (Fig. 4C)

These nepheline syenites comprise the Junguni hill and a 36 km-long east-west-trending Chikala-(Ch), Chaone (Ca)–Mongolowe (Mo)–Chinduzi (Ci) structural chain located north-east of the Chilwa Alkaline Province (Fig. 4 (C)). These intrusions have been dated between 98 Ma-137 Ma (Eby et al., 1998; Swinden and Hall, 2012) and they mainly comprise a series of small syenite intrusions, quartz syenites and nepheline syenites. Nepheline abundance appears to increase to the west in this alkaline structural chain (Woolley, 2015). Samples were collected from the Junguni, Chaone and Mongolowe intrusions.

The Chinduzi and Chikala intrusions (area 2 and 5 respectively, in Fig. 4C) were not surveyed during the present fieldwork. The Chaone ring structure ("4" in Fig. 4C), comprises coarse grained, leucocratic-mesocratic, nepheline syenite bounded by orthogneisses. The nepheline syenites are largely weathered, with lichen and moss growth evident on some of the outcrops. In some localities, the nepheline syenites have inclusions of diorite xenoliths, which shows that the nepheline syenites are younger. The alkali granites/syenogranites probably occur within contact zones of the gneisses and nepheline syenites. This shows the possible interaction between the gneisses and nepheline syenites. The Mongolowe intrusion sits in the middle-western part of the Chinduzi-Mongolowe-Chaone-Chikala structural chain of igneous intrusions. The intrusion mainly comprises medium-coarse-grained, mesocratic weathered nepheline syenite rocks. Some outcrops are heavily weathered and show coarse-grained biotite and muscovite mica.

The Junguni nepheline syenite ("6" in Fig. 4C) is a horseshoe-shaped 2.5 km diameter intrusion, situated about five km north of the Chikala-Mongolowe hills (Woolley, 2015). It comprises coarse-medium grained mesocratic nepheline syenites with K-feldspar, nepheline, biotite and pyroxene. The grain size increases uphill and field gamma-ray measurements for K_2O values also tend to be higher in the southward direction and toward the summit of the intrusion. The Zomba Mountain ("1" in Fig. 4C) is predominantly a syenite intrusion, which also has other rocks including quartz syenites and charnockitic gneisses.

3.1.4. Carbonatite-associated nepheline syenites (Fig. 4D)

Carbonatite-associated nepheline syenites from the Tundulu, Nkalonje and Songwe-Mauze complexes were also studied and sampled (Fig. 4D). The nepheline syenites at Tundulu ("1" in Fig. 4D), are coarse to very coarse grained, mesocratic to slightly melanocratic, less altered and occur adjacent to carbonatites. In hand specimen these rocks are coarse-grained, mesocratic to melanocratic, and little weathered. The key porphyritic minerals in hand specimens include coarse-grained K-feldspars, mostly orthoclase (≥35%), nepheline (≥15%), plagioclase (≥20%), biotite (10%) and pyroxenes (5%). The nepheline syenites at Nkalonje Complex (2 in Fig. 4 (D)) occur south west of this complex and are also coarse-grained, and less weathered but are slightly melanocratic compared to the ones at Tundulu complex.

The Songwe-Mauze complex ("3" in Fig. 4D), contains fine-grained, mesocratic to light-reddish, highly weathered carbonatite rocks, which are localized on the Songwe-Mauze area. The nepheline syenites occur east of the Songwe-Mauze Hill and on Mauze Hill. The complex is also characterized by fenites, which occur mostly along the carbonatite and nepheline syenite contact zones. The fenites are fine-medium grained, mesocratic to light reddish weathered rocks consisting of calcite and quartz, with some mafic minerals banded with orthoclase and

Table 2
Description of rocks' hand specimens based on field observations.

Location	Sample Code	Minerals (in order of decreasing abundance)	Grain Size	Colour	Lithology Description	Rock Name
South Malawi Nsy	CHA 002	Kfs, Pl, Bt, Ne (?)	Medium to coarse grained	Mesocratic/pinkish-pale light grey	Highly weathered rocks associated with coarse-grained syeno-granite and/diorite xenocrysts.	Nepheline syenite
South Malawi Nsy	JUN 001	Kfs, Bt, Ne (?), Px	Coarse-medium grained	Mesocratic-leucocratic	Slightly weathered to weathered rocks.	Nepheline syenite
South Malawi Nsy	JUN 002	Kfs, Bt, Ne, Px	Medium-coarse grained	Mesocratic	Less weathered to weathered rock	Nepheline syenite
South Malawi Nsy	JUN 004	Kfs, Bt, Ne, Px	Coarse grained	Mesocratic-pinkish toward hill summit	Slightly weathered rocks with increasing Kfspar uphill.	Nepheline syenite
Central Malawi Nsy	KU 002	Kfs, Pl, Ne, Ms	Medium-coarse grained	Melano-mesocratic	Weathered rocks with lichens growth.	Nepheline syenite
Central Malawi Nsy	KU 003	Qtz, Pl, Bt, hbl	Medium grained	Mesocratic	Weathered with inclusions of dolerite	Quartz syenite
Central Malawi Nsy	KU 006	Kfs, Pl, Ne, Bt, Ms	Coarse-v. coarse grained	Mesocratic	Weathered rock with pegmatitic veins	Nepheline syenite
Central Malawi Nsy	KU 011	Kfs, Pl, Ne, biot.	V. coarse-coarse grained	Mesocratic	Mixed with gneisses in some parts	Nepheline syenite
Central Malawi Nsy	KUCP 001	Qtz, Pl, Bt, Ms hbl, grnt	Medium to coarse grained	Mesocratic	Weathered with pegmatitic inclusions and quartz veins.	Diorite
Central Malawi Nsy	KUCP 005	Qtz, Pl, Bt, Ms hbl, grnt	Medium grained	Meso-melanocratic	Weathered with pegmatitic inclusions and quartz veins.	Quartz syenite
Central Malawi Nsy	KUCP 006	Kfs, Pl, Ne, px/ol (?)	Medium grained	Meso-melanocratic	Weathered rocks with developed soils	Nepheline syenite
Central Malawi Nsy	KUCP 007	Kfs, Pl, Ne, px/ol (?)	Medium grained	Meso-melanocratic	Weathered rocks with much developed soils.	Nepheline syenite
Central Malawi Nsy	KUCP 008	Kfs, Pl, Ne green minerals, ol (?)	Medium to coarse grained	Meso-melanocratic	Nsy bodies bounded by quartz-feldspathic gneisses with sharp contact between Nsy and gneisses.	Nepheline syenite
S.E Malawi Syenite	MANGO 002	Kfs, Pl, Ms Bt, hbl	Coarse grained	Mesocratic- pinkish	Weathered to highly weathered rocks, much K-Feldspar (pinkish colour)	Syenite
S.E Malawi quart-syenite	MAU 001	Kfs, Qtz, Bt, Px	Coarse-v. coarse grained	Mesocratic	Highly weathered to weathered rocks. Sporadic fine-medium grained granites in some places	Syenogranite/Quartz syenite
South Malawi Nsy	MOG 001	Kfs, Pl, Bt, hbl, Ne	Coarse grained	Mesocratic-leucocratic	Weathered rocks with relatively well-developed soils	Nepheline syenite
S.E Malawi quart-syenite	NKHU 002	Kfs, Pl, Qtz, Ms Bt, hbl	Coarse grained	Mesocratic	Weathered rocks with altered showing pale colour and fresher specimens show pinkish colour	Quartz syenite
S.E Malawi quart-syenite	NKHU 003	Kfs, Pl, Qtz, Ms Bt, hbl	Coarse grained	Mesocratic	Weathered rocks with abundant K-Feldspar	Quartz syenite
Carbonatite- associated Nsy	SONG 002	Kfs, Pl, Bt, Ms Ne	Coarse-v. coarse grained	Mesocratic- lightly-red coloured	Fine grained, slightly red coloured fenites along contact of Mauze and Songwe-Mauze	Nepheline syenite
Carbonatite-associated Nsy	TUND 001A	Kfs, Pl, Bt, Ms Ne	medium-coarse grained	Mesocratic-slightly melanocratic	Relatively fresh rocks, occur mostly on S to SW edge of Tundulu	Nepheline syenite
South Malawi Nsy	ZA 002	Kfs, Pl, Bt, Ms Ne	Coarse-medium grained	Mesocratic	Weathered rocks	Syenite
South Malawi Nsy	ZA 003	Kfs, Pl, Bt, Ms Ne	Coarse-medium grained	Meso-melanocratic	Less weathered	Syenite

Note: Samples collected from following locations CHA = Chaone; JUN = Junguni; KU = Kasungu; KUCP = Kasungu- Chipala; MANGO = Mangochi Forest Hill; MAU = Mauni Hill; MOG: Mongolowe; NKHU = Nkhuzi bay; SONG: Songwe-Mauze; TUND = Tundulu; ZA = Zomba.

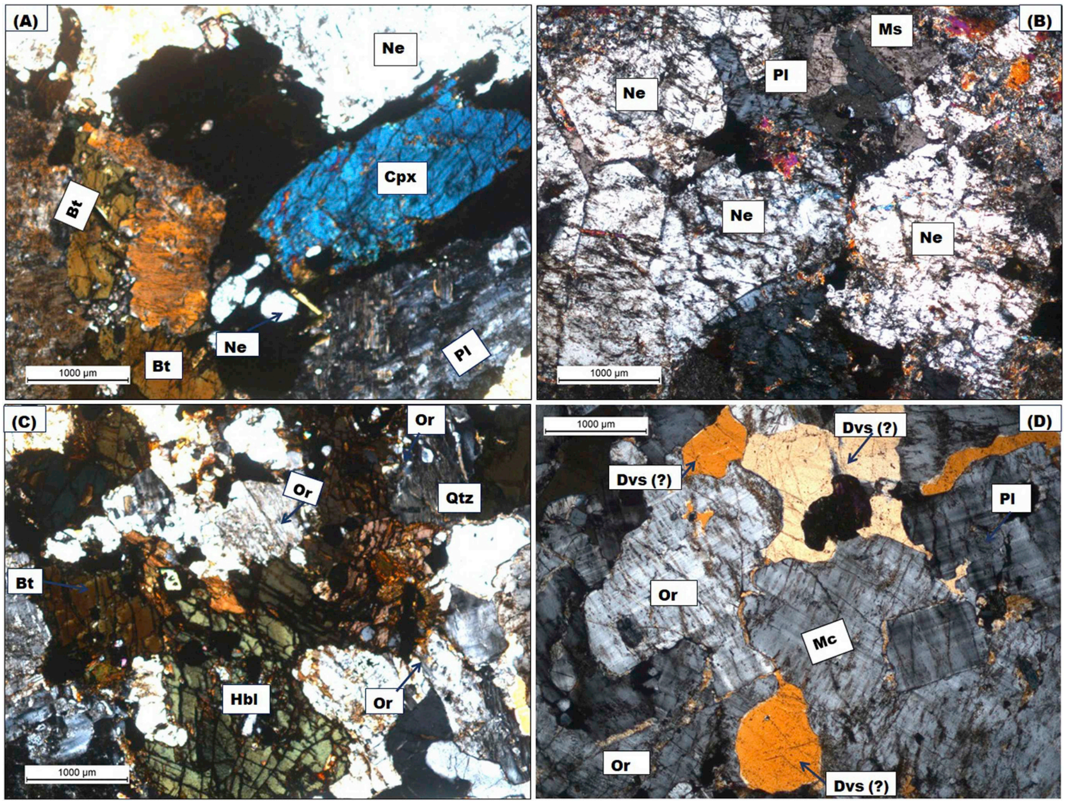

Fig. 6. Photographs of selected rocks showing minerals in thin sections of selected rocks for (A) Junguni nepheline syenite {JUN-004}; (B) Tundulu nepheline syenite {TUND-01A}; (C) Mangochi syenite {MANGO-002} and (D) Nkhuzi bay foid syenite {NKHU-002} showing (davidsmithite (dvs ?)), Scale: x1000 μm.

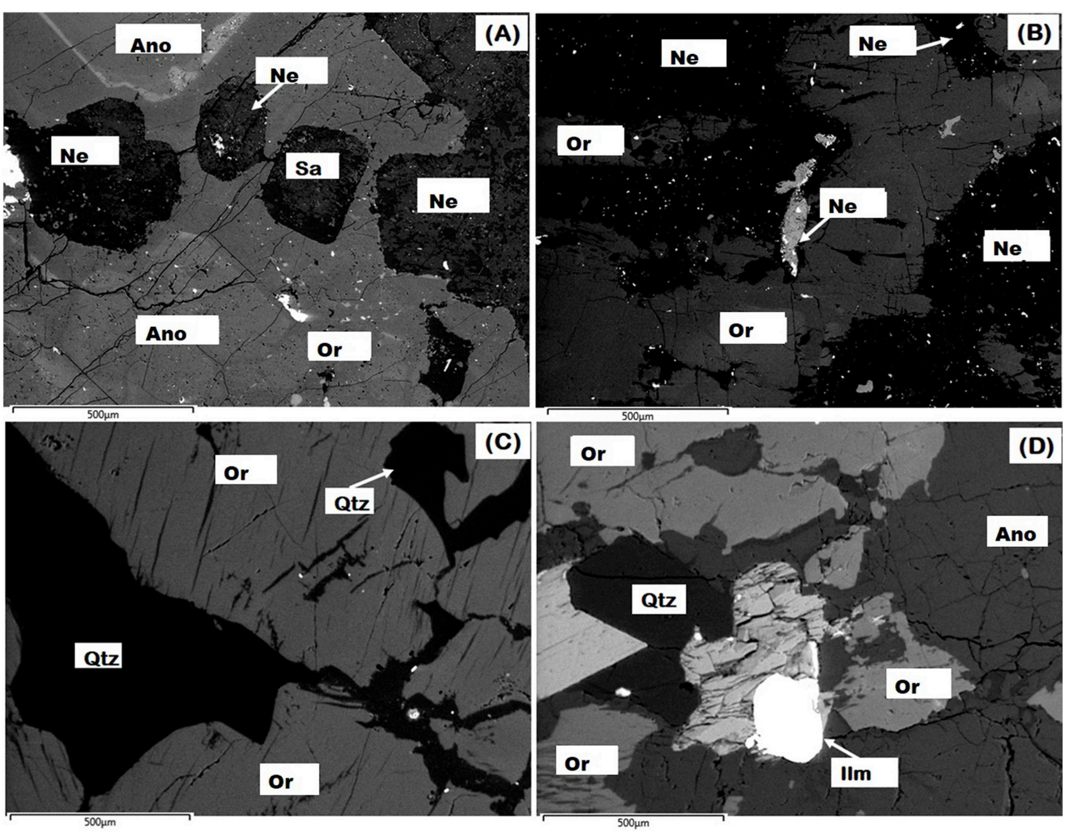

Fig. 7. Back-Scattered electron (BSE) images of selected rocks showing minerals for (A) Songwe-Mauze Nsy {SONG-002}; (B) Tundulu Nsy {TUND-01A}; (C) Nkhuzi bay Qtz Sy {NKHU-002} and (D) Mangochi Sy {MANGO 002002}}; Scale: x500μm.

Table 3
Composition, mode of minerals and brief description of selected rock samples in thin sections.

Location	Sample location & Code	Minerals and relative mode	Grain Size	Brief description	Rock Name
South Malawi Nsy	Chaone and Mongolowe	30%Pl, 25% Or, Bt,5% Ne,5–15% Ms.	Medium to coarse grained	Dominated by plagioclase which is etched on edges and altered to clays. Nepheline less visible and interlocking with plagioclase	Nepheline syenite
South Malawi Nsy	Junguni JUN04	25%Ne, 15% Or, 20% Bt; 10% Pyx, 10% Pl, 10% Opq	Coarse-medium grained	Much altered, feldspars and micas show replacement by secondary minerals (as shown in Fig. 4C)	Nepheline syenite
Central Malawi Nsy	Kasungu (KU03)	15% Or,10% Ne, 10% Pl; % 20% Bt, 5% Ms 20% Opq	Medium-coarse grained	Highly weathered with nepheline and feldspars replaced by secondary minerals hence abundance of opaque minerals.	Nepheline syenite
Central Malawi Nsy	Kasungu-Chipala (KUCP08)	15% Or,15% Ne, 10% Pl; % 20% Bt, 5% Ms, 20% Opq	Very coarse grained	Highly weathered with nepheline and feldspars replaced by secondary minerals hence abundance of opaque minerals	Nepheline syenite
S. East Malawi Syenite	Mangochi Hill (MANGO02)	20% Or, 15%Mc, 15%, 15% Bt; 10% Pl; % 10%Pyx, 5% Qtz	Coarse grained	Weathered to highly weathered rocks, much K-feldspar (pinkish colour).	Syenite
S. East Malawi quart-syenite	Nkhuzi Bay (NKHU03)	20% Or, 15% Mc, 15% Bt; Plag; %,5% Qtz, 4% Pyx, 3% Dvs (?)	Coarse grained	Weathered rocks with altered showing pale colour and fresher specimens show pinkish colour (see Fig. 4D)	Foid syenite
Carbonatite- associated Nsy	Mauze-Songwe (SONG02)	25%Ne, 18% Mc; 15% Or, 5% Pyx, 15% Bt; 10%; Pl 3% Dvs (?),%; 10% Opq	Coarse- very coarse grained	Relatively less altered, dominated by nepheline K-feldspar.; minor davidsmithite (?) occurrence (see Fig. 4B). Abundance of microcline suggests exsolution of albite (Na-rich) out of a K-feldspar host.	Nepheline syenite
Carbonatite-associated Nsy	Tundulu (TUND01A)	35%Ne, 18% Mc; 15% Or, 10% Pl, 5% Pyx, 15% Bt; 3% Dvs (?),	Medium-coarse grained	Less altered, dominated by nepheline K-feldspar; minor davidsmithite (?) occurrence (see Fig. 4B). Abundance of microcline suggests exsolution of albite (Na-rich) out of a K-feldspar host.	Nepheline syenite

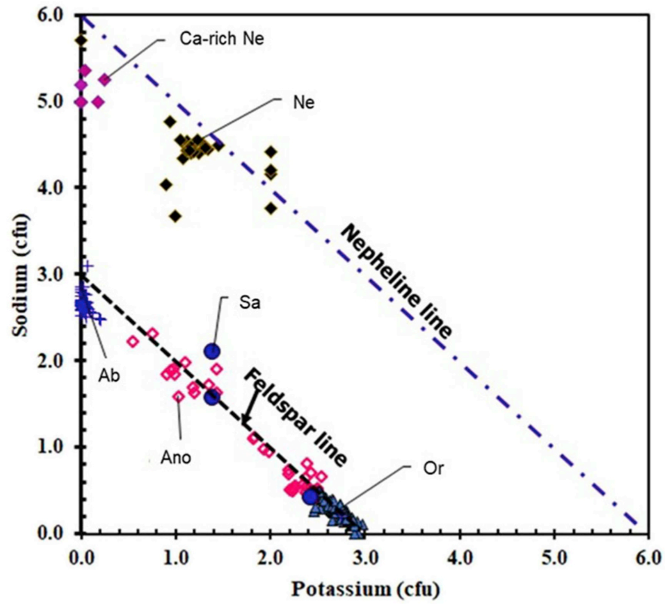

Fig. 8. K (at prop) vs Na (at prop) plot for modal feldspars and nepheline showing fields for orthoclase (Or), anorthoclase (Ano), sanidine (Sa), Albite (Ab), nepheline (Ne) and Ca-rich nepheline (Ca-rich Ne).

plagioclase. The fenites which occur close to the Mauze nepheline syenite intrusion are dark-coloured suggesting nepheline syenite metasomatism while those closer to or on the edges of Songwe-Mauze Hill carbonatite are light-reddish coloured suggesting carbonatite metasomatism with the country rocks or carbonatite-nepheline syenite interaction (Swinden and Hall, 2012). These authors have also argued that mineralisation in this complex is associated with potassic fenitisation alteration and low temperature hydrothermal/carbohydrothermal secondary alteration. The occurrence of these carbonatites and nepheline syenites may suggest carbonatite-nepheline syenite magma liquid immiscibility (Robb, 2005). Field spectrometry found that in these three complexes fenites in the carbonatite complexes are more potassic than the nepheline syenites.

3.1.5. *General description of the rocks in hand-specimens*

The nepheline syenite samples collected from the field show differences in colour, grain size, texture and mineral compositions. In hand specimen, nepheline crystals are not easily identifiable in most of the nepheline syenites. Weathering varied in intensity and samples were taken from outcrops for which visible weathering was limited to a thin (< 1 cm) zone. Fig. 5(A-D) shows typical photographs of the outcrops from which rock samples were collected.

Table 2 provides a summary of the rocks based on the observations in the field. For the purpose of grain size classification, the hand specimens were classified as fine-grained (< 1 mm), medium-grained (< 3 mm) and coarse-grained (> 3 mm) according to Gill (2010). The mineral proportions are classified and given in their order of abundance.

3.2. *Petrography*

Twenty-three thin sections were studied for their minerals. In most nepheline syenite thin sections, nepheline is etched around the grain boundaries and shows alteration. Orthoclase and plagioclase also show alteration to clays. Fig. 6 shows examples of thin sections for selected rocks, and Fig. 7 shows back-scatter electron images. Nepheline is clearly identifiable in the Tundulu nepheline syenite (Figs. 6B, 7A and 7B). Some opaque minerals also are also present in some highly altered rocks such as Junguni (Fig. 6C). In terms of composition, modal

Table 4
Analyses for selected nepheline and number of cations for nepheline based on 4 oxygens for Kasungu (KU) and Songwe-Mauze (SONG) intrusions.

a). Nepheline analyses (wt. %)

Element (Wt%)	Sample ID																			
	KU 09	KU 09	KU 09	KU 09	KU 09	KU 09	KU 09	KU 09	KU 09	KU 09	KU 09	SONG 02	SONG 02	SONG 02	SONG 02	SONG 02	SONG 02	SONG 02	SONG 02	SONG 02
SiO_2	45.79	42.76	48	42.43	42.96	42.79	42.75	46.34	45.66	42.67	42.76	41.21	45.96	48.06	41.35	43.48	43.25	41.97	43.68	41.31
Al_2O_3	34.26	34.62	31.64	34.79	35.13	34.54	34.46	32.52	32.97	35.03	34.79	35.05	37.48	31.37	35.33	34.13	34.18	35.01	34.11	32.48
Fe_2O_3	–	–	–	–	–	–	–	–	–	–	–	–	0.55	0.23	0.3	–	0.31	–	–	–
CaO	1.04	0.51	0.61	0.4	0.43	0.38	0.26	0.61	0.52	0.49	0.5	–	0.44	–	–	–	–	–	–	5.83
Na_2O	13.41	15.78	14.78	15.98	15.62	16.06	15.73	15.09	15.21	15.83	15.88	15.9	7.71	13.67	15.8	16.06	15.83	15.89	15.94	20.38
K_2O	5.51	6.34	4.96	6.4	5.87	6.23	6.79	5.44	5.64	5.98	6.07	7.84	7.85	6.67	7.23	6.33	6.44	7.13	6.28	–
TOTAL	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

b). Number of cations for nepheline based on 4 oxygens

Element (Wt%)	Sample ID																			
	KU 09	KU 09	KU 09	KU 09	KU 09	KU 09	KU 09	KU 09	KU 09	KU 09	KU 09	SONG 02	SONG 02	SONG 02	SONG 02	SONG 02	SONG 02	SONG 02	SONG 02	SONG 02
Si	1.079	1.027	1.129	1.02	1.027	1.027	1.028	0.934	0.934	1.022	1.025	1	0.934	1	1.042	1.038	1.013	1.046	1.071	0.995
Al	0.951	0.98	0.877	0.986	0.989	0.977	0.977	0.922	0.922	0.989	0.983	1.003	0.922	1.007	0.964	0.967	0.995	0.962	1.03	0.922
Ca	0.026	0.013	0.015	0.01	0.011	0.01	0.007	0.016	0.013	0.012	0.013	0	0	0	0	0	0	0	0.011	0.151
Na	0.612	0.734	0.674	0.745	0.724	0.747	0.734	0.693	0.7	0.735	0.738	0.748	0.626	0.741	0.746	0.736	0.743	0.74	0.348	0.952
K	0.165	0.194	0.149	0.196	0.179	0.191	0.208	0.333	0.333	0.333	0.186	0.243	0.333	0.223	0.194	0.197	0.219	0.192	0.234	0
K/(NaK)	0.213	0.209	0.181	0.209	0.198	0.203	0.221	0.325	0.323	0.312	0.201	0.245	0.347	0.231	0.206	0.211	0.228	0.206	0.401	0

nepheline ranges from 10 to 35% in the nepheline syenite thin sections as shown in Fig. 6B, Table 3. In some foid-bearing syenites and nepheline syenites, a mineral first taken to be quartz appears yellower than the normal first-order interference colour quartz (Fig. 6D). If this were due to the thin section thickness, adjacent feldspars would also show similar interference colours. SEM analysis showed that this high birefringence mineral might be davidsmithite, a Ca-bearing nepheline (see later). Composition of most rocks in thin sections (as shown in Table 3) confirm the field observations of the rocks' mineralogy in hand specimens (shown in Table 2).

Confirming the petrographic observations using EDS, the key minerals in the nepheline syenites include anorthoclase, albite, actinolite, nepheline, orthoclase, sanidine, sphene, fluorapatite, calcite, biotite and iron oxide. Fig. 8 shows the K/Na bivariate x-y graph for atomic proportions of Na and K, calculated from the EDS output, for the K-feldspars and nepheline. While alkali feldspars show a continuous range, nepheline clusters around $(K_{0.25}Na_{0.75})$ $AlSiO_4$.

As shown in Fig. 8, and Table 4, some of the nepheline syenites (from the EDS analyses) also appear to contain a calcium-rich nepheline $(Na,Ca)AlSiO_4$ or $(KNa)_8CaAl_8Si_8O_{32}$, whose occurrence has not been previously reported in Malawi. We suspect this mineral to be davidsmithite, an uncommon silicate mineral of the nepheline group. Davidsmithite is associated with the heterovalent replacement of Ca^{2+} for K^+ (and is therefore K-deficient; Kechid et al., 2017; Rossi et al., 1989), whose occurrence has been reported in few areas.

3.3. Geochemistry

3.3.1. Major elements

The geochemical analytical results (Table 5) show that Malawi's nepheline syenites and syenites are heterogeneous. There are some marked differences between and among the rocks from the different localities. The whole rock geochemistry shows that the rocks are generally silica-undersaturated and their SiO_2 content ranges from 44.6 wt % to 69.57 wt% with an average of 57.69 wt%. They also have low CaO content (0.56 wt% to 6.86 wt%, average 2.79 wt %), MgO (0.07 wt % to 2.78 wt %, average 1.23 wt %), TiO_2 (0.25 wt % to 2.05 wt % average 1.18 wt %), very low MnO (0.16–0.27 wt %, average 0.17 wt %) and P_2O_5 (0.03 wt% to 0.80 wt%, average 0.40).

Based on the CIPW norm (Johannsen, 1939; Gillespie and Styles, 1999; Verma et al., 2002), normative nepheline appears in 16 of the 22 samples and ranges from 4.6 wt% to 40.26 wt% with an average of 16.11 wt%, as shown in Table 6. Normative leucite varies from 0 wt % to 45.90 wt%, average 29.92 wt%, and normative orthoclase from 0 to 45.95 wt% average 23.85 wt%.

The 16 samples which showed normative nepheline plot as nepheline syenites on the TAS plot for intrusive rocks (Wilson, 1989, Fig. 9). Based on Shand's (1943) alkalinity index, the rocks analysed in this study are mostly metaluminous with Al-(KNaCa) values ranges of between −205 up to 0. This is consistent with the presence of biotite and augite among the modal minerals.

Oxides versus SiO_2 variation diagrams are presented in Fig. 10. From this figure, some of the intrusions show similar geochemical composition. The central Malawi nepheline syenites are the least potassic of all the clusters but they have high TiO_2 and FeO contents. Geochemical analyses reported by Eby et al. (1998) and this study for the central Malawi nepheline syenites show similar results.

The R_1- R_2 classification scheme for intrusive rocks (De la Roche, Leterrier, Granclaude and Marchal, 1980) shows that most of the rocks are nepheline syenites (Fig. 11 and Table 7). Based on this classification, two major groups of nepheline syenites can be identified, classified as group A and group B (Fig. 11). Group A, which includes the Tundulu, Songwe-Mauze, and Junguni and Mongolowe intrusions, has a higher nepheline and potassium content.

However, the nepheline syenites are heterogeneous and may be classified into three main categories: (I) the central Malawi nepheline

Table 5
Major and trace elements analyses by XRF method for representative alkaline rocks from Malawi.

Sample Element	KUCP −01	KUCP −05	KUCP −06	KUCP −07	KUCP −08	KU02	KU03	KU06	CHA-02	KU-11	MANG −02	MAU-01	MOG-03	NKHU −02	NKHU −03	SONG-02	TUND −01	JUN-01	JUN-02	JUN-04	ZA-02	ZA-04
Major elements (wt. %)																						
SiO_2	55.20	53.81	54.50	55.75	58.76	54.30	53.69	54.11	61.36	56.33	58.04	65.58	56.12	64.51	69.57	53.07	44.60	54.19	56.57	60.94	67.27	60.83
Al_2O_3	17.08	17.34	19.10	16.57	17.44	17.58	17.85	16.16	18.95	18.23	16.95	16.31	21.21	15.72	14.40	21.25	18.39	23.53	20.72	18.49	14.75	15.12
Fe_2O_3	8.17	8.37	6.92	8.21	6.43	8.05	7.87	8.62	2.94	6.86	6.90	4.14	3.64	4.55	1.43	4.24	6.20	2.16	3.61	3.42	4.43	7.57
MgO	2.01	2.12	1.69	1.85	1.64	2.08	2.15	2.78	0.76	1.66	1.78	0.42	0.31	0.90	0.35	0.22	1.71	0.07	0.33	0.93	0.20	1.11
CaO	3.68	4.10	3.26	3.70	3.47	3.96	3.18	4.90	1.43	3.31	3.58	2.18	1.62	1.50	0.56	1.59	6.86	0.76	1.60	1.59	1.49	2.99
Na_2O	6.65	7.18	8.30	6.88	4.62	6.99	7.41	6.38	6.37	7.60	4.61	4.48	10.40	4.19	1.59	7.14	7.98	12.26	10.58	6.24	4.82	4.76
K_2O	3.542	3.364	3.437	3.869	5.001	3.642	3.190	3.418	6.318	3.169	4.893	5.605	5.067	6.235	11.32	9.136	6.285	5.508	5.033	6.314	5.628	4.885
TiO_2	1.845	1.854	1.494	1.673	1.486	1.688	1.720	2.053	0.783	1.611	1.636	0.549	0.585	0.987	0.252	0.562	1.750	0.330	0.577	0.907	0.424	1.117
MnO	0.208	0.228	0.184	0.226	0.131	0.209	0.198	0.240	0.110	0.173	0.138	0.068	0.243	0.089	0.016	0.160	0.268	0.079	0.243	0.127	0.138	0.187
P_2O_5	0.682	0.652	0.509	0.553	0.638	0.544	0.648	0.705	0.230	0.453	0.675	0.147	0.131	0.359	0.172	0.026	0.802	0.047	0.131	0.257	0.087	0.412
LOL	0.57	0.77	0.25	0.29	0.40	0.43	1.83	0.18	0.54	0.49	0.29	0.29	0.58	0.78	0.15	2.32	4.95	1.01	0.80	0.35	0.53	0.58
Total	**99.63**	**99.78**	**99.64**	**99.56**	**100.0**	**99.47**	**99.74**	**99.55**	**99.8**	**99.89**	**99.49**	**99.77**	**99.91**	**99.81**	**99.80**	**99.72**	**99.80**	**99.94**	**100.2**	**99.57**	**99.77**	**99.58**
Trace Elements (ppm)																						
Zn	96	105.4	86.2	103.6	143.5	102.2	112.8	85.9	46.4	96	149.9	79.5	91	111.1	18.2	64.8	125.7	17.5	164.6	56.1	142.7	112.1
Cu	5.6	3.9	4.6	6.4	5.4	7.9	3.4	10.5	2.4	6.3	4.7	3.5	2.1	4.3	4.3	3.8	6.9	2	2.6	3.2	3.9	6.2
Ni	1	2.3	0.1	1.7	2.4	1.2	2.2	1.2	−1.4	0.4	2.7	−0.7	−2.6	0.4	1.1	0.4	3.1	−3.4	−0.4	−0.4	0.7	1.4
Cr	2.4	3.4	2.5	5.2	2.9	2.6	2.9	1.1	4.6	2.2	3.2	3.7	3.1	5.1	13.9	2.4	0.8	4.6	5.8	6	8.7	4.3
V	55.7	59.9	45.6	50.5	51	59.9	68	71.4	4.1	50.6	50.4	4	0.2	6.9	16.7	62.5	129.9	6.9	13.4	5.7	1.6	30
Ba	624.1	607.5	614.8	578.8	3146	528.1	670.8	602.8	894.5	630.1	3049	2206	99.6	2802	679.8	4917	2407	68.5	602.1	901.2	343	837.9
Sc	6.4	5.2	4.1	5.2	14	4.4	5.3	6.1	4.8	4.5	14	6.1	0.5	11.6	2	−1.3	3	−0.1	0.7	4.9	2.7	10
La	55.3	70.4	76.6	85.6	143.7	76.6	98.7	95	33.6	78.1	150.5	30.4	45.7	99.6	48.1	107.1	130.5	16.7	78.3	38.3	131	91.1
Ce	112.1	130.5	157.1	174.1	275.4	148.6	150.7	185.7	58.9	154.2	290.6	70.7	88.7	243.4	74.7	120.6	240	36.9	137.5	66.2	256.8	182.3
Nd	42.7	48	60.2	66	124.9	53.8	85.6	71.3	19.8	56.1	134.4	37.1	28.9	95.1	23.6	19	86.4	11.1	39.3	25.4	116.3	81.1
U	5.9	3.4	6.3	1.4	0.4	8.5	14.8	1.5	0.5	5.3	0.5	1.7	1.3	2	2.9	0.8	1.8	1.6	10.3	0.4	3.7	1.8
Th	19.3	11.5	20.8	11	4.1	29.1	19.6	8.9	3.2	18.8	4.3	4.6	5.2	11.1	42.1	9.9	7.6	4.6	34.3	3.3	17.4	8.5
Pb	11.8	11.3	12	6.9	29.2	14.7	10.5	7.8	5.3	10.8	28.9	22.7	14.3	28.7	17.7	7.5	5.2	7.6	27.7	5.2	14.4	11.4
Nb	247.6	222.2	191.5	190.7	43.7	240	219	257.1	34.9	213.4	45.8	32.5	122	68.2	11.2	54.2	250.9	52.2	225.9	40.7	91.2	70
Zr	973.3	528.7	715.1	613.2	741.9	1068	937.3	562.5	125.6	650.7	784	480.5	218.1	739.7	256.3	166.6	532.9	164.3	982.4	127.6	771	667.1
Y	52.9	52.5	49.4	48	66.1	49.3	60.7	58.7	13.8	51.2	71	32.5	24.3	54	12.4	15.4	36.5	8.9	43	16.5	91.8	53.4
Sr	408.5	454.8	397.5	353.7	820.1	555.5	560.4	560.5	283	520.3	819.6	492.7	32.9	297.2	75.8	2501	2047	109	605.2	279.7	51.7	189.9
Rb	129	116.1	148.5	126.2	81.6	144	146.6	81	57.9	120.1	80.8	134.9	112.8	149.1	292.8	172.9	202.3	107.7	182.7	59.3	126.6	77.7

Table 6
CIPW normative minerals of Malawi alkaline rocks. The key minerals of interest for this study are indicted by an Asterix (*).

Sample Mineral (Wt %)	KUCP-01	KUCP-05	KUCP-06	KU5P-07	KUCP-08	KU02	KU03	KU06	CHA-02	KU-11
Quartz	0	0	0	0	0.2	0	0	0	0	0
Albite	42.68	37.32	37.34	40.51	39.09	36.82	40.61	37.17	45.41	45.9
Anorthite	6.07	4.93	4.49	2.69	10.94	5.64	5.78	5.14	4.13	6.04
Orthoclase*	21.39	20.32	20.76	23.28	31.84	21.91	19.34	20.64	37.99	19.19
Nepheline*	7.36	12.7	17.82	9.59	0	12.09	11.97	9.11	4.6	9.97
Leucite*	0	0	0	0	0	0	0	0	0	0
Diopside	6.47	9.3	6.98	10.01	1.92	8.74	4.88	12.13	1.27	6.23
Hypersthene	0	0	0	0	9.61	0	0	0	0	0
Olivine	7.41	6.84	5.81	6.09	0	6.81	8.09	7.2	3.03	5.83
Larnite	0	0	0	0	0	0	0	0	0	0
Acmite	0	0	0	0	0	0	0	0	0	0
Na_2SiO_3	0	0	0	0	0	0	0	0	0	0
Ilmenite	3.51	3.52	2.84	3.18	2.82	3.21	3.27	3.9	1.49	3.06
Magnetite	0.83	0.85	0.7	0.83	0.65	0.81	0.8	0.87	0.3	0.69
Apatite	1.58	1.51	1.18	1.28	1.48	1.26	1.5	1.63	0.53	1.05
Zircon	0.14	0.08	0.11	0.09	0.11	0.16	0.14	0.08	0.02	0.1

Sample Mineral (Wt %)	MANGO-02	MAU-01	MOG-03	NKHU-02	NKHU-03	SONG-02	TUND-01	JUNG-01	JUNG-02	JUNG-04	ZA-02	ZA-04
Quartz	0	10.25	0	9.03	16.2	0	0	0	0	0	12.5	4.17
Albite	38.38	37.91	27.48	35.45	10.59	0	0	16	27.25	44.25	40.78	40.28
Anorthite	10	7.04	0	4.65	0	0	0	0	0	3.47	1.86	5.16
Orthoclase*	31.13	34.73	30.02	38.88	67.37	45.95	0	32.6	30.18	37.97	33.51	29.48
Nepheline*	0.34	0	28.9	0	0	29.84	31.39	40.26	27.57	4.63	0	0
Leucite*	0	0	0	0	0	9.11	30.49	0	0	0	0	0
Diopside	2.94	2.43	5.93	0.43	1.38	6.92	22.14	2.88	5.97	2.32	4.1	5.8
Hypersthene	9.89	4.42	0	6.62	1.8	0	0	0	0	0	3.66	8.31
Olivine	0	0	1.62	0	0	1.59	0	0.9	1.62	3.32	0	0
Larnite	0	0	0	0	0	0	0.5	0	0	0	0	0
Acmite	0	0	0.73	0	0.29	0.85	1.25	0.44	0.73	0	0	0
Na_2SiO_3	0	0	1.48	0	0.59	1.02	1.9	3.01	2.46	0	0	0
Ilmenite	3.11	1.04	1.11	1.88	0.48	1.07	3.33	0.63	1.1	1.72	0.81	2.12
Magnetite	0.7	0.42	0	0.46	0	0	0	0	0	0.35	0.45	0.76
Apatite	1.56	0.34	0.3	0.83	0.4	0.06	1.86	0.11	0.3	0.6	0.2	0.95
Zircon	0.12	0.07	0.03	0.11	0.04	0.02	0.08	0.02	0.15	0.02	0.11	0.1

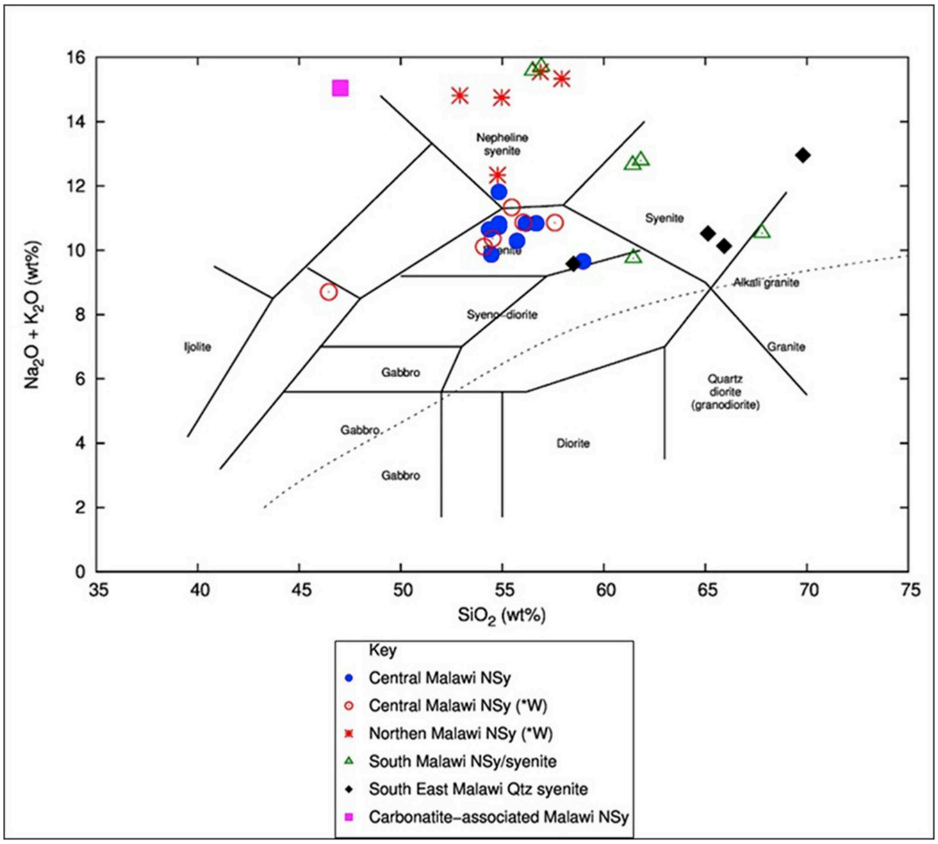

Fig. 9. Total silica alkali (TAS) for the nepheline syenites and other alkaline rocks from Malawi (after Cox et al. (1979) and modified by Wilson (1989).

syenites in the Malawi basement complex, (II) South Malawi and north Malawi rift-associated nepheline syenites and (III) carbonatite-associated nepheline syenites which may overlap with either (I) or (II). Group B is slightly silica-rich (Fig. 11) and comprises mostly the Central Malawi nepheline syenites. The carbonatite-associated nepheline syenites plot in group A on the R1-R2 but some plot into B on the TiO_2 vs P_2O_5 plot (Alle, 2007).

The K_2O/Na_2O ratio for the nepheline syenites varies from 0.41 to 1.28 with an average of 0.65, which shows the nepheline syenites are more sodic than potassic, with variable K_2O and Na_2O content. The K_2O content for all the rock units varies from 3.17 wt % to 9.14 wt % with an average of 5.22 wt %. The K_2O content for nepheline syenites only ranges from 3.17 wt% to 11.32 wt % with an average of 5.22 wt %. The total alkali content for the nepheline syenites ranges from 9.62 wt% to 17.77 wt% with an average of 13.26 wt% while the average content for all the rock units is 11.92 wt%.

3.3.2. Trace elements

The nepheline syenite and related rocks from Malawi contain varying amounts of trace elements (Table 5). The South Malawi and carbonatite associated intrusions tend to be more enriched in LREEs in contrast with the rocks from the north and central areas of Malawi. The trace element concentration is typical of alkaline rocks with an abundance of large ion lithophile (LIL) elements such as Rb, Sr, Ba, Nb, Ta, Th compared to the high field strength REEs (Fig. 12). Fig. 12 shows an abundance of Ba and Rb which suggests replacement of K in K-feldspar, micas or hornblende (Deer et al., 1982). The abundance of Rb in some rocks, notably the carbonatite-associated Northern Malawi and the Central Malawi nepheline syenites, could be attributed to the chemical similarities of K and Rb. This enables cations of elements like Rb to be substituted for K in the alkali feldspar structures during crystallisation of the magmatic rocks, and Ba is further enriched by weathering of these rocks (Ollila et al., 2014).

Some elements may be toxic above certain concentrations, which makes nepheline syenites with low concentrations, if used as fertilizers, much safer for humans and the environment. Fig. 13 shows variations in terms of selected trace elements, which could be important for agriculture, versus relation to K_2O content in the rocks. All decrease with increasing K content. The rocks have low amounts of the elements except the central Malawi nepheline syenites, which have comparatively high U and Th values.

3.3.3. Weathering intensity of the rocks

Based on the Parker's chemical alteration index (CIA) scale, almost all the rocks were relatively fresh with their CIA < 50 (Fig. 14 and Table 7). The Tundulu nepheline syenite was the least altered sample whereas the Nkhuzi Bay, Chaone and Kasungu nepheline syenites had some of the most altered rocks. The results show almost no association between the chemical index of alteration and nepheline abundance in the rocks. This suggests that nepheline concentration is not related to the intensity of weathering. However, a weak positive association is noted between the chemical index of alteration and normative orthoclase.

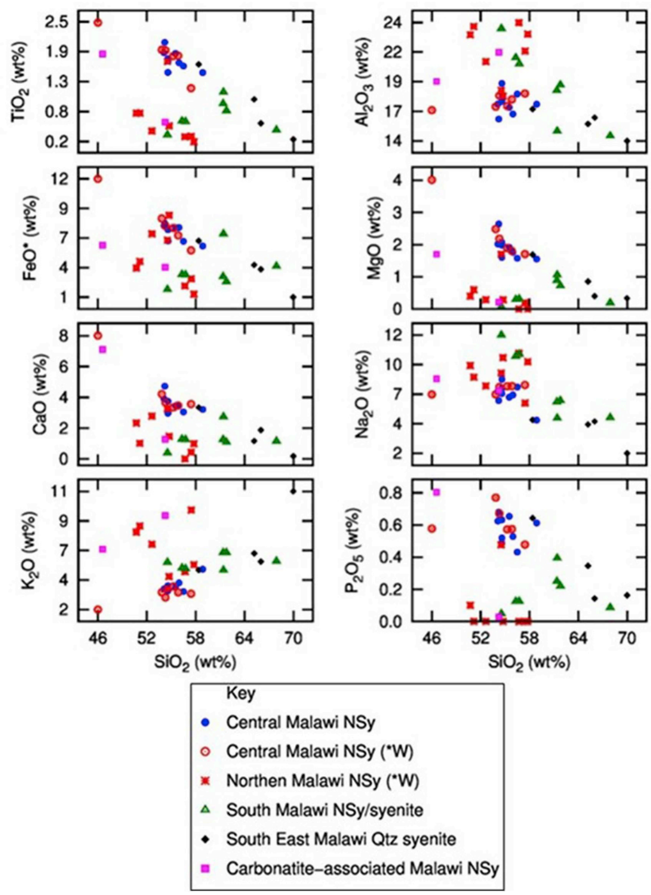

Fig. 10. Harker diagrams for major elements diagrams. *W denotes data from Eby et al. (1998).

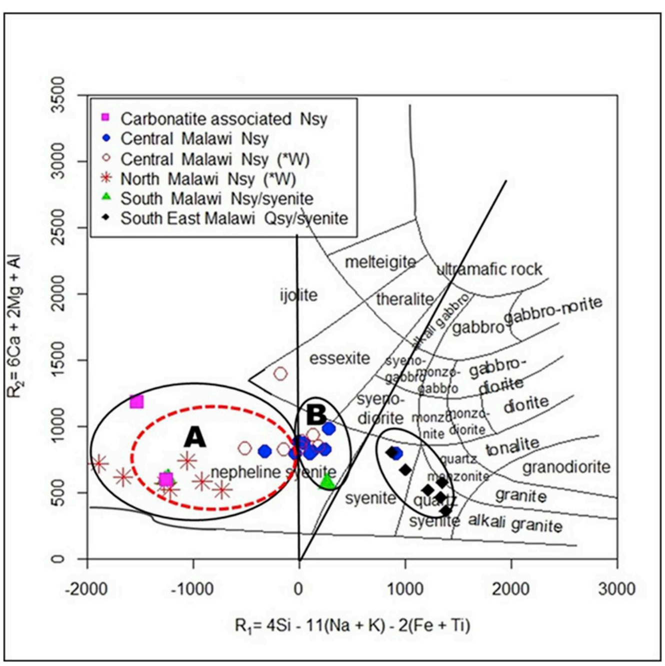

Fig. 11. Classification of alkaline rocks from Malawi after De la Roche et al. (1980). *W stands for data from Eby et al. (1998). Red-dashed area shows the region for alkaline rocks from other parts of the world. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.3.4. Comparison of XRF results with airborne and ground gamma ray spectrometry

Some similarities and differences were noted in the data acquired from the airborne and ground spectrometry compared to laboratory XRF analyses (Table 8). The XRF K_2O values vary from 3.17 to 11.32 wt% (average 5.22 wt %). The airborne gamma K_2O values range from 0 to 5.62 wt% with an average of 2.78 wt%, while the ground gamma ray spectrometry gave K_2O values which range from 3.40 to 8.98 wt% and an average of 4.89 wt%. The U values from X-ray fluorescence (XRF) analyses range from 0.40 to 14.80 ppm and an average of 3.49 ppm. Airborne gamma U values range from 0 to 7.46 ppm and an average of 2.95 ppm, while the ground gamma ray spectrometry show U values which range from 0.73 to 9.36 ppm and an average of 3.06 ppm. The XRF Th values range from 3.20 to 42.10 ppm and an average of 13.60 ppm. The airborne gamma Th values range from 0 to 22.81 ppm and an average of 10.27 ppm while the ground gamma ray spectrometry shows Th values which range from 0 to 22.81 ppm and an average of 18.42 ppm.

The field gamma-ray spectrometry has also shown that the nepheline syenites and alkaline rocks vary considerably in their K content. Table 8 shows summary descriptive statistics of the data for the ground field spectrometry survey and the XRF analyses of the same samples. For the rock samples which were acquired by field spectrometry, the South Malawi nepheline syenites from Junguni area (Table 8) showed the highest K_2O content. For the XRF analyses, the highest K_2O content was found in the carbonatite-associated nepheline syenites (from the Songwe-Mauze Complex) as shown in Fig. 15 and Table 8.

Fig. 15 summarises the K, U and Th content in the areas surveyed during this study's fieldwork. As further shown in Table 9, the results also show that there is a weak correlation between data analysed by XRF instrument and the gamma-ray field spectrometer for potassium. There is however no significant correlation for U–Th pairs of data acquired using the field gamma ray spectrometer and the XRF laboratory instrument.

4. Discussion

Our results show that, in general, there is a moderate positive agreement for most rocks between the K content (recalculated as K_2O wt.%) reported by the field gamma ray spectrometer and the results obtained using XRF (Table 8). The results show that the direct measurement of radioactive elements using the field ground geophysical survey was effective in detecting the radioactive elements. However, we also observed that carbonatites showed poor agreement, and this may be due to sample heterogeneity or weathering. The results suggest that hand-held field spectrometry can be used to identify rocks with high K_2O content when laboratory XRF analysis is not available.

While some of the carbonatite-associated and the South Malawi nepheline syenites, (particularly the Junguni, Tundulu and Songwe-Mauze nepheline syenites) are similar (Fig. 11), the rocks from the Junguni intrusion have the highest amount of normative nepheline (40 wt%) as seen in Table 6. These results agree with petrographic studies done by Woolley (2015), who found up to > 60 wt% normative nepheline in some rocks of the Junguni intrusion, with strong peralkalinity characterized by normative acmite values of up to 28 wt%.

The Songwe-Mauze and Tundulu intrusions also show high normative nepheline coupled with the presence of normative leucite. The positive correlation of normative nepheline with the normative K-feldspar (especially orthoclase), as reflected in the results, suggests that in mapping nepheline syenites it is likely that the other alkaline rocks or those closely related to the nepheline syenite could be mapped together with nepheline syenites. Alternatively, this suggests that field spectroscopy is not fully effective in distinguish clearly members of the silicate family from each other, as found in some previous studies (Hecker, der

Table 7
Chemical alteration index (CIA) for selected individual samples.

Sample ID	R1	R2	Chemical index of alteration (CIA)	Intrusion Name	Location group/cluster
CHA-02	255.39	562.43	49.44	Chaone	South Malawi Nsy/Sy
JUNG-01	−2092.63	546.34	46.21	Junguni	South Malawi Nsy/Sy
JUNG-02	−1269.41	594	44.88	Junguni	South Malawi Nsy/Sy
JUNG-04	259.38	578.97	48.82	Junguni	South Malawi Nsy/Sy
KU-02	39.59	871.77	45.17	Kasungu	Central Malawi Nsy
KU-03	−40.83	797.08	47.31	Kasungu	Central Malawi Nsy
KU-06	272.36	979.23	43.01	Kasungu	Central Malawi Nsy
KU-11	100.43	794.13	46.62	Kasungu	Central Malawi Nsy
KUCP-01	236.62	828.53	46.26	Kasungu-Chipala	Central Malawi Nsy
KUCP-05	−7.72	884.03	44.82	Kasungu-Chipala	Central Malawi Nsy
KUCP-06	−331.05	807.33	46.38	Kasungu-Chipala	Central Malawi Nsy
KUCP-07	118.53	812.72	44.21	Kasungu-Chipala	Central Malawi Nsy
KUCP-08	906.02	794.76	49.48	Kasungu-Chipala	Central Malawi Qsy
MANGO-02	871.33	803.86	48.81	Mangochi	South East Malawi Sy
MAU-01	1349.56	574.02	48.9	Mauni	South East Malawi Qtz Sy
MOG-11	−1244.37	604.76	45.68	Mongolowe	South Malawi Nsy/Sy
NKHU-02	1212.87	513.51	50.31	Nkhuzi Bay	South East Malawi Qtz Sy
NKHU-03	1382.28	359.75	48.2	Nkhuzi Bay	South East Malawi Qtz Sy
SONG-02	−1255.08	597.87	46.48	Songwe-Mauze	Carbonatite associated Nsy
TUND-01A	−1530.15	1179.58	37.62	Tundulu	Carbonatite associated Nsy
ZA-02	1331.89	458.68	47.17	Zomba	South East Malawi Sy

Meijde and van der Meer, 2010).

The weathering indices have further shown that the rocks are weakly altered, with three clusters. One cluster comprises the rocks from Junguni and Mongolowe (the South Malawi nepheline syenites) and those from Tundulu and Songwe-Mauze (carbonatite-associated nepheline syenites) which are relatively less altered while another cluster has some of the Kasungu, Kasungu-Chipala (the Central Malawi nepheline syenites) and some of the Junguni nepheline syenites and these are more altered. The third group is for the most altered nepheline syenites and includes the Chaone (the South Malawi nepheline syenites) and some of the Kasungu-Chipala nepheline syenites. The carbonatite-associated nepheline syenite at Tundulu differs characteristically from all the other intrusions. Whether this is due to the level of alteration or geochemical composition is not clear. Both factors may apply because it is also the only sample which does not show normative orthoclase as already shown in Table 5.

In terms of chemical composition, the nepheline syenites from Malawi, especially those the Illomba, the Junguni, Chaone, Songwe-Mauze and Tundulu complexes, show similar geochemical composition to the nepheline syenites from Cape Dome in British Columbia and

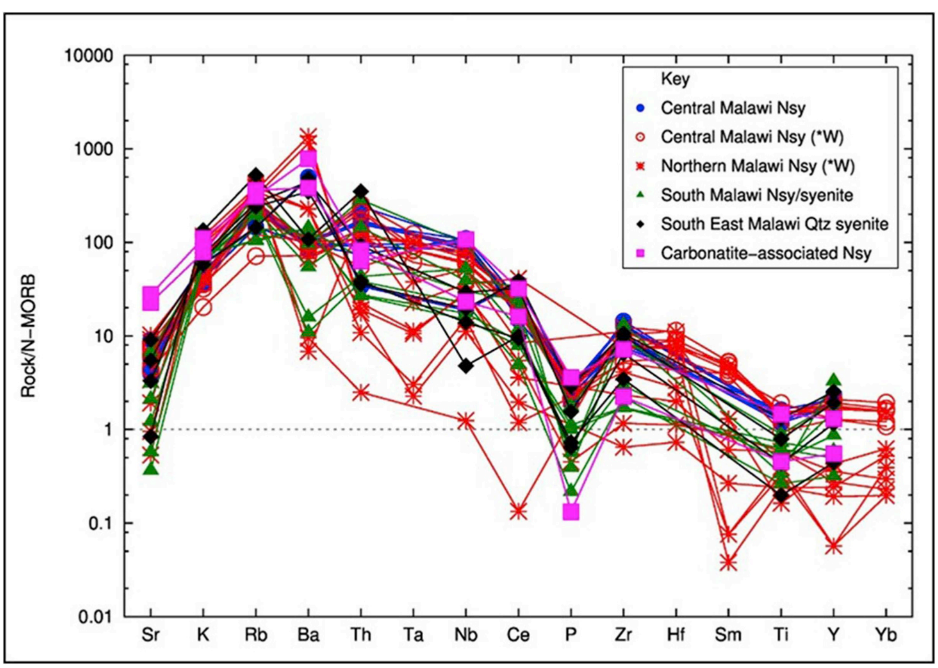

Fig. 12. Spider diagram of normalized-MORB showing LIL and HFs REE after Pearce (1983) according to Sun and Mc Donough (1989) reconstructed using the PINGU tool by Cortes and Palma (2014).

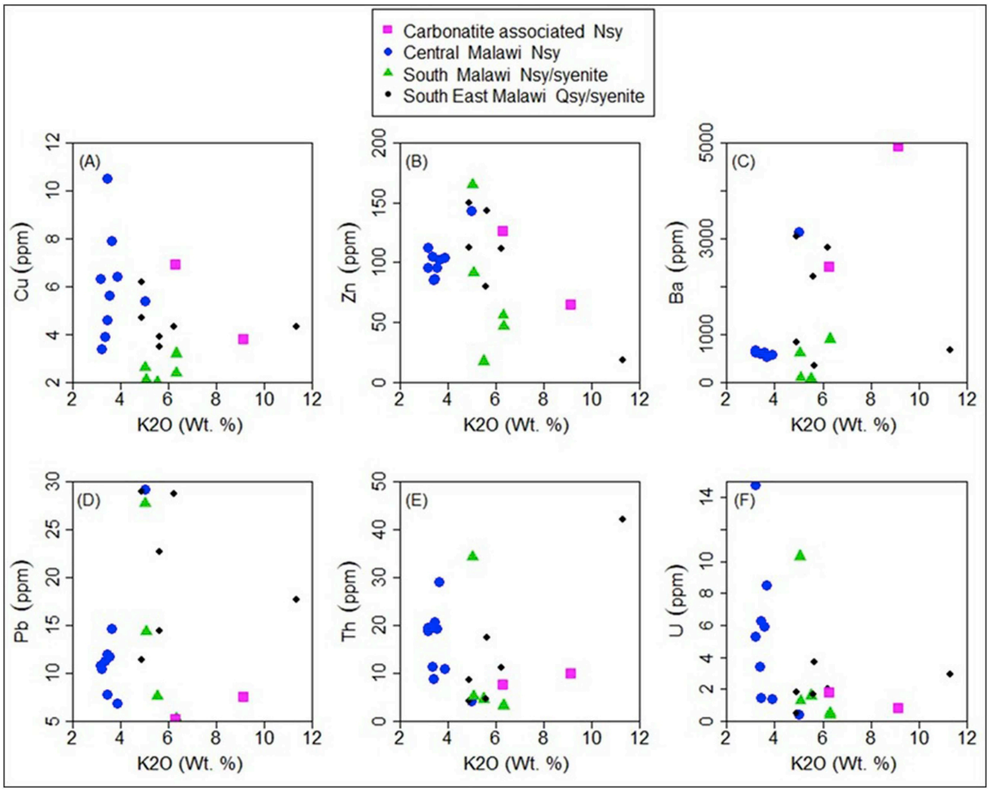

Fig. 13. Concentration of some trace elements of relative to K_2O in Malawi's alkaline rocks.

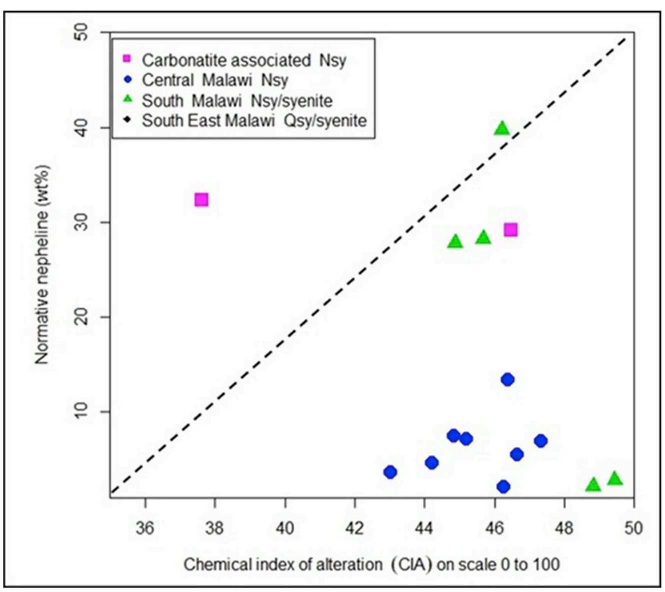

Fig. 14. The chemical alteration index (CIA) vs normative nepheline content for the rocks.

North Cape in Norway (Fig. 11) that have been used in previous studies relating to soil fertility. Based on this geochemical similarity, our results therefore offer strong confidence that Malawi's nepheline syenites would equally be suited for this project goal. This has further demonstrated that Malawi with her numerous alkaline rocks could be an important source of alternative potassium fertiliser using both the nepheline syenites and carbonatite resources as candidates.

The results have also shown that the Tundulu complex is quite different from the other studied nepheline syenites. The distinctive characteristics of the Tundulu nepheline syenite may be interpreted as possible evidence of the carbonatite–nepheline melt mixing/interaction, perhaps like the nepheline syenites that surround the apatite-rich carbonatite on Nathace Hill (Malawi; Broom-Fendley et al., 2016). In addition, we note that some of the areas had previously been wrongly mapped on geological maps of Malawi. For example, the Nkhuzi Bay and Mauni quartz syenites (from the South-east Malawi quartz syenites) are mapped as granites on the existing Geological Survey's geological maps. This shows that there is a need to re-map the country's geology, as proposed by the Geological Survey of Malawi.

The results further show relationships between geographically dispersed rocks based on the R_1-R_2 (De la Roche et al., 1980) classification of igneous rocks. As shown in Fig. 11, the X-ray fluorescence analyses for the Junguni, Chaone, Songwe-Mauze and Tundulu complexes, are closely related and form one cluster, which is geochemically different from the other intrusions. Similar results were obtained by Eby et al. (1998) who also mapped the |Central Malawi nepheline syenite (Kasungu and Chipala intrusions) and the Northern Malawi intrusions (Ilomba and Ulindi nepheline syenites). Based on these secondary data, we conclude that the two Northern Malawi intrusions also have potential as potassium fertiliser sources. If fully exploited as soil remineralizers, the potassium silicate resources in Malawi and other rift tectonic settings of the world could greatly contribute to achievement of Sustainable Developmental Goal (SDG) 2 of ending hunger and achieving global food security.

In addition, the results of the geochemical analyses of the rocks from

Table 8
Descriptive statistics for data from the field gamma ray survey and laboratory XRF sample analysis.

Parameter	K_2O (Wt. %) XRF	K_2O (Wt. %) ground	Th (ppm) XRF	Th (ppm) ground	U (ppm) XRF	U (ppm) ground	Th/U (ppm) XRF	Th/U (ppm) ground
Mean	5.22	4.89	13.6	18.42	3.49	3.06	5.66	7.73
SD	1.99	1.69	10.65	4.7	3.71	2.02	3.37	3.53
RSD	38.12	34.49	78.3	25.53	106.23	66.23	59.57	45.72
Sum	114.86	107.53	299.2	405.2	76.8	67.24	124.54	170.02
Min	3.17	3.4	3.2	6.67	0.4	0.73	1.32	1.71
Max	11.32	8.98	42.1	30.43	14.8	9.36	14.52	16.89
Count	22	22	22	22	22	22	22	22

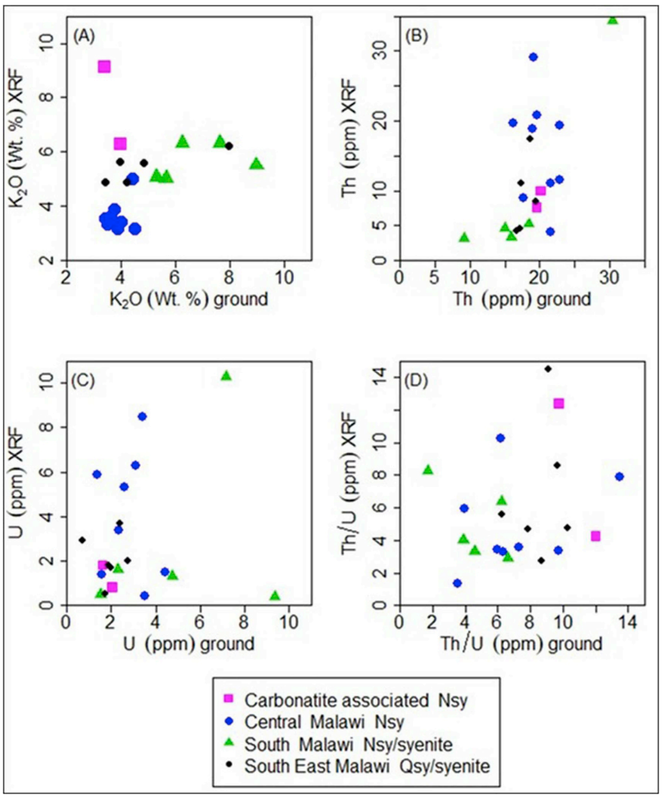

Fig. 15. Discrimination plots of gamma-ray data measured by ground (field) spectrometry vs XRF data for (a) potassium; (b) thorium. (c) uranium (d) thorium/uranium.

Malawi have shown similarities in chemistry between geographically dispersed rocks based on the R_1-R_2 (De la Roche et al., 1980) classification of igneous rocks (Fig. 11). In addition, the previous geochemical data by Eby et al. (1998) for some of northern Malawi nepheline syenites, such as the Illomba, the Ullindi show similar plots to some samples analysed in this study. The geochemical analyses further show that some of the South Malawi and carbonatite-associated nepheline syenites are similar in geochemical composition to the nepheline syenites from other parts of the world. For example, the geochemical compositions of Chaone, Songwe-Mauze, Junguni and Tundulu nepheline syenites are similar other countries such as the North Cape nepheline syenites of Norway, and others from British Columbia. These nephelines syenites have been tested and found to be viable potash sources. The results, therefore, suggest that Malawi's nepheline syenites have potential for use just like those from other areas in other parts of the world. Such information opens doors for further exploration and exploitation of these agro-minerals by potential investors.

5. Conclusions

The results have shown that Malawi's nepheline syenites have potential as sources of potassium for crop nutrition and may be classified into two major groups. Group A nepheline syenites show higher potential as an alternative potassium source due to their high nepheline content than Group B nepheline syenites. In addition, Group A nepheline syenites have similar geochemistry to the rocks used as potassium sources in other areas, such as the North Cape and Cape Dome nepheline syenites. This suggests that Malawi has potential for alternative potassium reserves derived from nepheline syenites. Novel alternative potassium sources in Malawi and other parts of Africa will greatly benefit millions of farmers in the developing world, particularly in Sub-Saharan Africa (SSA), a region affected by high fertiliser costs. Further work is needed, such as detailed sampling and field gamma ray spectrometry to assess the available nepheline syenite resources in Malawi, and plant growth trials to fully ascertain the suitability of these rocks as potash sources. The identification of davidsmithite in Malawi is also another significant finding, which needs further investigation. Finally, this study has shown that some areas were previously wrongly or inconsistently mapped as shown on the documented geological maps of Malawi. This implies that there is a need to re-map the country's geology, as also proposed by the Geological Survey of Malawi.

Table 9
Correlation coefficients for pairs of gamma-ray data measured by ground (field) spectrometry vs XRF data for (a) potassium; (b) thorium. (c) uranium (d) thorium/uranium. In addition, Fig. 15 and Table 10 show that, generally, higher values were acquired using the gamma ray field spectrometer for all the three elements.

Sample	K_2O (Wt. %) XRF	K_2O (Wt. %) ground	Th (ppm) XRF	Th (ppm) ground	U (ppm) XRF	U (ppm) ground	Th/U (ppm) XRF	Th/U (ppm) ground
K_2O (Wt. %) XRF	1.00	**0.46***	0.17	−0.51	−0.39	−0.18	0.74	0.04
K_2O (Wt. %) ground	**0.46***	1.00	−0.02	−0.51	−0.22	0.09	0.11	−0.34
Th (ppm) XRF	0.17	−0.02	1.00	**0.07**	0.64	0.00	0.06	0.03
Th (ppm) ground	−0.51	−0.51	**0.07**	1.00	0.30	0.29	−0.37	0.17
U (ppm) XRF	−0.39	−0.22	0.64	0.30	1.00	**0.25**	−0.52	−0.18
U (ppm) ground	−0.18	0.09	0.00	0.29	**0.25**	1.00	−0.15	−0.73
Th/U (ppm) XRF	0.74	0.11	0.06	−0.37	−0.52	−0.15	1.00	**0.10**
Th/U (ppm) ground	0.04	−0.34	0.03	0.17	−0.18	−0.73	**0.10**	1.00

Table 10
Summary of gamma-ray data measured by ground (field) spectrometry vs XRF data for (a) potassium, (b) thorium. (c) uranium (d) thorium/uranium.

Location Group	Sample Location	K_2O (Wt. %) XRF	K_2O (Wt. %) ground	Th (ppm) XRF	Th (ppm) ground	U (ppm) XRF	U (ppm) ground	Th/U (ppm) XRF	Th/U (ppm) ground
South Malawi. Nsy	Chaone	6.32	7.65	3.20	9.18	0.50	1.53	6.40	6.24
South Malawi. Nsy	Junguni	5.51	8.98	4.60	15.00	1.60	2.30	2.88	6.62
South Malawi. Nsy	Junguni	5.03	5.66	34.30	30.43	10.30	7.17	3.33	4.59
South Malawi. Nsy	Junguni	6.31	6.25	3.30	15.92	0.40	9.36	8.25	1.71
Central Malawi. Nsy	Kasungu	3.64	3.62	29.10	19.15	8.50	3.40	3.42	5.97
Central Malawi. Nsy	Kasungu	3.19	3.86	19.60	16.25	14.80	4.60	1.32	3.57
Central Malawi. Nsy	Kasungu	3.42	3.62	8.90	17.65	1.50	4.45	5.93	3.97
Central Malawi. Nsy	Kasungu	3.17	4.50	18.80	18.90	5.30	2.60	3.55	7.27
Central Malawi. Nsy	Kasungu-Chipala	3.54	3.43	19.30	22.80	5.90	1.35	3.27	16.89
Central Malawi. Nsy	Kasungu-Chipala	3.36	3.49	11.50	22.90	3.40	2.35	3.38	9.74
Central Malawi. Nsy	Kasungu-Chipala	3.44	3.98	20.80	19.63	6.30	3.10	3.30	6.33
Central Malawi. Nsy	Kasungu-Chipala	3.87	3.74	11.00	21.60	1.40	1.60	7.86	13.50
Central Malawi. Nsy	Kasungu-Chipala	5.00	4.40	4.10	21.60	0.40	3.50	10.25	6.17
South East Malawi. syenite	Mangochi	4.89	3.40	4.30	16.63	0.50	1.73	8.60	9.64
South East Malawi. Qsy	Mauni	5.60	4.84	4.60	17.18	1.70	1.98	2.71	8.66
South Malawi. Nsy	Mongolowe	5.07	5.30	5.20	18.45	1.30	4.75	4.00	3.88
South East Malawi. Qsy	Nkhuzi Bay	6.23	7.95	11.10	17.33	2.00	2.77	5.55	6.27
South East Malawi. Qsy	Nkhuzi Bay	1.32	7.31	42.10	6.67	2.90	0.73	14.52	9.09
Carbonatite-associated Nsy	Songwe-Mauze	9.14	3.41	9.90	20.17	0.80	2.07	12.38	9.76
Carbonatite-associated Nsy	Tundulu	6.29	3.98	7.60	19.63	1.80	1.63	4.22	12.02
South East Malawi. syenite	Zomba	5.63	3.94	17.40	18.63	3.70	2.37	4.70	7.87
South East Malawi. syenite	Zomba	4.89	4.22	8.50	19.50	1.80	1.90	4.72	10.26

Note: Nsy = nepheline syenite; Qsy = quartz syenite.

Acknowledgements

The authors would like to thank the Faculty of Science, Agriculture and Engineering (SAgE) of Newcastle University, the Society of Economic Geologists (SEG), and the Geological Survey of Malawi for their financial, material and technical support the study. We are also greatly grateful to Nick Odling and Nicola Cayzer both from the School of Geosciences, University of Edinburgh, for the help with the XRF and SEM-EDS sample analyses, respectively.

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