

MINERALOGY AND GEOCHEMISTRY OF THE KANGANKUNDE,
TUNDULU AND NKALONJE CARBONATITES OF THE CHILWA
ALKALINE PROVINCE, MALAWI: IMPLICATIONS FOR
THEIR GENESIS AND ASSOCIATED RARE EARTH
ELEMENTS MINERALIZATION

デンソン, マクウェラ

<https://hdl.handle.net/2324/7396233>

出版情報 : Kyushu University, 2025, 博士 (工学), 課程博士
バージョン :
権利関係 :



**MINERALOGY AND GEOCHEMISTRY OF THE
KANGANKUNDE, TUNDULU AND NKALONJE
CARBONATITES OF THE CHILWA ALKALINE
PROVINCE, MALAWI: IMPLICATIONS FOR THEIR
GENESIS AND ASSOCIATED RARE EARTH
ELEMENTS MINERALIZATION**

MINERALOGY AND GEOCHEMISTRY OF THE
KANGANKUNDE, TUNDULU AND NKALONJE
CARBONATITES OF THE CHILWA ALKALINE
PROVINCE, MALAWI: IMPLICATIONS FOR THEIR
GENESIS AND ASSOCIATED RARE EARTH ELEMENTS
MINERALIZATION

Denson Makwela

A dissertation submitted in partial fulfilment of the requirements for the
degree: Doctor of Engineering

Department of Earth Resources Engineering
Graduate School of Engineering
Kyushu University
Fukuoka, Japan

July 2024



Abstract

Demand for rare earth elements (REEs) will continue to increase in the future due to its application in green energy. Carbonatite REEs deposits are a primary target for exploration as they are more enriched with REEs compared to other igneous rocks. The carbonatites mostly occur in cratonic and non-cratonic extension settings associated with Archean and Proterozoic/Phanerozoic rocks. Carbonatite forms in response to magmatism in shallow crust and associated volcanism and hydrothermal processes. This makes both magmatic and hydrothermal processes responsible for REEs mineralization. However, there is debate on the roles of primary and secondary processes, as researchers have to choose either of the two processes or all.

This study examines and compares the Kangankunde carbonatite representing western belt carbonatites and Tundulu and Nkalonje carbonatites representing the eastern belt carbonatites in the Chilwa Alkaline Province (C.A.P) to understand the source of carbonate magma, its evolution paths and implication to REEs mineralization. The tectonic setting of the Malawi basement complex (MBC) of southern Malawi is a subducted crust of island arc setting. Pan-African magmatism was responsible for the extension along the boundary between the Unango and Lilongwe subdomains, which resulted in the thickening and thinning of the Lilongwe and Unango subdomains, hosting the western belt carbonatites and eastern belt carbonatites respectively.

The Kangankunde carbonatite complex was emplaced as a ring structure through magmatic differentiation. Four carbonatite lithotypes were identified including: beforosite, magnesio-carbonatite, ferro-carbonatite, and ferruginous calcio-carbonatite. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ stable isotope results show a wide range of -7.7 ‰ to -0.7 ‰, and of +4.4 ‰ to +26.7 ‰, respectively indicating the magmatic origin and involvement of hydrothermal component of the system. Although silicates rocks were observed outside the complex, suggesting the carbonatite magma formed from immiscibility of carbonate-silicate derived from the mantle. Petrographic and geochemical results suggest that the initial magma was Mg- and P-rich. Two trends of magmatic differentiation were identified. The first differentiation trend was from beforosite through magnesio-carbonatite to ferro-carbonatite. The second trend was possibly from beforosite to ferruginous calcio-carbonatite.

The main REE-bearing mineral in Kangankunde is monazite and minor REE-bearing minerals include apatite, synchysite, goyazite, and daqingshanite. The REEs mineralization in Kangankunde carbonatite occurs as dissemination, wispy veinlets, and patchy forms within almost all identified carbonatite rocks, as well as acicular form in magnesio-carbonatite. The primary REEs mineralization occurred during magmatic differentiation, evidenced by the occurrence of monazite as inclusions or filling interstices between dolomite while the second stage of mineralization occurred in late-magmatic-hydrothermal stage. The average chondrite-normalized of lanthanum and ytterbium (La/Yb_N) ratios decrease from magnesio-carbonatite (681), ferro-carbonatite (488), to ferruginous calcio-carbonatite (248). This trend suggests that REEs enrichment was controlled by primary magmatic processes, particularly fractional crystallization of dolomite, apatite, siderite, ankerite, monazite fluorite and synchysite. In addition hydrothermal process were localized.

The Tundulu carbonatite complex was emplaced as a ring structure with three igneous centers through magmatic differentiation and is accompanied by nepheline syenite. Three carbonatite lithotypes were identified: calcio-carbonatite, ferruginous calcio-carbonatite, and magnesio-carbonatite. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ stable isotope results show a narrow span of -3.6 ‰ to -2.92 ‰, and from +3.59 ‰ to +13.9 ‰, respectively. The Tundulu carbonatite initial magma was Ca- and P-rich formed from immiscibility of carbonate-silicate derived from the mantle evidence from the spatial association of syenite and carbonatites. This is also supported by depleted contents of Nb (5.3-3600 ppm) and Zr (1.3-321) and enriched contents of P_2O_5 (0.1-13.5 wt. %) in carbonatites and enriched contents of Nb (99-48647 ppm) and Zr (231-524 ppm) and depleted contents of P_2O_5 (0.1-0.5 wt. %) in nepheline syenite. Petrography and geochemical data suggest the magma differentiated from calcio-carbonatite that fractionated calcite and apatite to ferruginous calcio-carbonatite that fractionated ankerite, and calcite and magnesio-carbonatite that fractionated siderite and dolomite.

The main REE bearing mineral in Tundulu carbonatite is synchysite and mineralization occurred as disseminated form. Primary mineralization occurred during magmatic differentiation evidenced by zoned synchysite with high Ti content and an intergrowth texture in association with magnetite, calcite and apatite in calcio-carbonatite. The second mineralization stage is late-magmatic-hydrothermal

characterized by hexagonal pseudomorphs that are filled with synchysite strontianite barite and quartz forming glomeroporphyritic texture in ferruginous calcio-carbonatite and synchysite overprinting quartz and recrystallized calcite and fluorapatite in ferruginous calcio-carbonatite and magnesio-carbonatite. The $(La/Yb)_N$ in calcio-carbonatite range from 33 to 289, ferruginous calcio-carbonatite from 30 to 56 and magnesio-carbonatite from 122 to 3035. These ranges suggest LREE are more enriched in magnesio-carbonatite and mineralization was controlled by magmatic process while the negative Y anomaly in magnesio-carbonatite suggest that hydrothermal processes particularly localized redistribution may have also influence REEs enrichment.

The Nkalonje carbonatites occurred as a vent with only calcio-carbonatite and accompanied by a nepheline syenite. The $\delta^{18}O$ and $\delta^{13}C$ stable isotope results show a narrow range from -3.67 to -3.11 ‰ and from +1.95 to +8.61 ‰ respectively and plots within and outside the primary igneous carbonatite field indicating its magmatic origin and involvement of a hydrothermal component. Calcio-carbonatite showed depleted contents of Nb, (0.72 to 5.39 ppm), Zr (0.19-19.73 ppm) and while syenite showed enriched contents of Nb (0.59-19.60 ppm), Zr (46.69-58.27 ppm). These observations suggest that carbonatite magma formed from immiscibility of a mantle derived calc-silicate. The initial carbonatite magma was Ca-rich. The carbonatite is less evolved and was altered by high temperature fluids. Petrography and geochemical data suggest the magma differentiated calcio-carbonatite that fractionated calcite and apatite.

REE mineralization at the Nkalonje carbonatite occurred as disseminated form. Primary mineralization occurred during magmatic-hydrothermal stage characterized by synchysite replacing apatite that shows corrosive texture and synchysite occurring in equilibrium with crystallized or altered calcite.

The Irumide and Pan-African tectonic might have influenced the observed less evolved nature of carbonatites in the eastern belt through thinning of the Unango subdomain and faulting that may have directed carbonatite magma ascent and emplacement. On the other hand, the thickening of Lilongwe subdomain and transposition of the early alkaline intrusion into Malawi basement complex may have influence magma underplating, assimilation and REE enrichment on western belt carbonatites. The close association of the syenite and carbonatite on the eastern belt suggest use of same conduit during magma ascent while presence of orthoclase

suggest immiscibility to have occurred at shallow depth. The absence of alkaline rocks within the western belt carbonatite possibly suggest non exposure of alkaline rock or use of different conduits.

I dedicate this to my Family.

Table of Content

Abstract.....	i
Table of Content.....	vi
List of Figures.....	x
Acknowledgments.....	xvii

Chapter 1 : Introduction.

1.1 General introduction.....	1
1.1.1 Rationale and objectives.....	1
1.1.2 Thesis organization.....	5
1.1.3 Scientific contributions from this study.....	6
References.....	6

Chapter 2 : Regional Geology and Tectonic setting

2.1 The Malawi basement complex (MBC) and metamorphism.....	10
2.2 Early alkaline magmatism.....	19
2.3 Chilwa Alkaline Province.....	20
2.3.1 Petrogenesis of the Chilwa Alkaline Province.....	23
References.....	25

Chapter 3 : Sample description and methodology

3.1 Introduction.....	28
3.2 Samples collection and preparation.....	30
3.3.1 Petrographic analysis.....	33
3.3.2 Geochemical analysis.....	33
3.3.3 Isotope analysis.....	34
References.....	35

Chapter 4 : Petrochemistry of the Kangankunde carbonatite

4.1 Introduction.....	36
4.2 Samples description.....	39
4.3 Results.....	42
4.3.1 Drill core and outcrop observations.....	42
4.3.2 Petrography.....	45
4.3.3 Whole-rock geochemistry.....	48
4.3.4 Carbon and Oxygen isotope.....	55
4.4 Discussion.....	57
4.4.1 Origin of carbonatite magma.....	57
4.4.2 Evolution of carbonatite magma.....	59
4.4.3 Implications to REEs mineralization.....	63
4.5 Summary.....	68
Reference.....	69

Chapter 5 : Petrochemistry of the Tundulu carbonatite

5.1 Introduction.....	79
5.2 Results.....	82
5.2.1 Field observation.....	82
5.2.2 Petrography.....	84
5.2.3 Whole-rock geochemistry.....	87
5.2.4 Carbon and Oxygen isotope.....	95
5.3 Discussion.....	97
5.3.1 Origin of the carbonatite magma.....	97
5.3.2 Evolution of the carbonatite magma.....	98
5.3.3 Implication to REEs mineralization.....	100
5.4 Summary.....	105

Reference.....	106
Chapter 6 : Petrochemistry of the Nkallonje carbonatite	
6.1 Introduction.....	110
6.2 Results.....	112
6.2.1 Field observations.....	112
6.2.2 Petrography.....	114
6.2.3 Whole-rock geochemistry.....	117
6.3 Discussion.....	125
6.3.1 Origin of carbonatite magma.....	125
6.3.2 Evolution of the magma.....	127
6.3.3 Order of emplacement between syenite and carbonatite.....	127
6.3.4 Implications to REE mineralization.....	127
6.4 Summary.....	130
Reference.....	131
Chapter 7 Conclusions	
8.1. Regional and local Tectonic setting.....	134
8.2. Origin of the carbonatite magma.....	134
8.3. Implications of magmatic and hydrothermal processes on REEs mineralization.....	135
8.4. Proposed genetic model of magma differentiation of the carbonatites.....	136
Appendix A1 XRD pattern of representative samples from Kangankunde carbonatite.....	138
Appendix A2 XRD pattern of representative samples from Tundulu carbonatite.....	141
Appendix A3 XRD pattern of representative samples from Nkallonje carbonatite...	144
Appendix A4 Major, minor and trace element compositions of carbonatite rocks in Kangankunde.....	147

Appendix A5 Major, minor and trace element compositions of carbonatite rocks in Tundulu.....	163
Appendix A6 Major, minor and trace element compositions of carbonatite rocks in Nkalonje.....	171
Appendix A7 Carbon and Oxygen Isotope composition for Kangankunde, Tundulu and Nkalonje carbonatites.....	175

List of Figures

Chapter 1

Fig. 1-1 Map of southern Malawi showing carbonatites occurrence in the Chilwa Alkaline Province (C.A.P). Insert Map of the central and southern parts of Africa showing the location of Malawi within the East Africa Rift System. (modified after Duraiswami & Shaikh, 2014.) 4

Chapter 2

Fig. 2-1 Map of Malawi showing the Malawi basement complex domains. Insert geological setting of Malawi in western and south Gondwana within the East African belt. (modified after Fullgraf et al., 2022).11

Fig. 2-2 Map of central and southern Malawi showing structures and tectonic subdomain (adapted from Fullgraf et al., 2022). 13

Fig. 2-3 Map of part of Central and Southern Malawi showing regional geology (modified after Bloomfield et al., 1966; Tsunogae et al., 2021). 14

Fig. 2-4. (a) South (left) to north (right) schematic cross-section across Malawi showing the proposed plate tectonic setting during late Mesoproterozoic (CA 1070-1040), (b) Schematic structural stack of Malawian subdomains after the Irumide orogeny (Modified after Fullgraf et al., 2022). 18

Fig. 2-5: Map of South Malawi showing structural and igneous geology. The major igneous centres of the Chilwa Alkaline Province are shown, as well as the dyke swarm and basaltic and rhyolitic lavas of late Karoo age (modified from Woolley, 1987). 22

Fig. 2-6. Plot of SiO₂ vs CaO (wt. %) for rocks of the Chilwa Alkaline Province. Most of the data are for the northern part of the province, and a few are for the southern part. The three-magma series of the rock groups (adapted from Woolley, 1987). 24

Chapter 3

Fig. 3-1 Photographs of representative samples (a) drill core sample of leucocratic, fine to medium grained magnesio-carbonatite from Kangankunde carbonatite, (b) outcrop sample of leucocratic, coarse grained calcio-carbonatite from Tundulu carbonatite, (c) outcrop of mesocratic fine to medium grained beforosite from Kangankunde, (d) outcrop

sample of mesocratic, fine to medium grained calcio-carbonatite, (e) outcrop of melanocratic, fine to medium grained magnesio-carbonatite, (f) drill core sample of leucocratic agglomerate with feldspar xenocryst.	29
Fig. 3-2 Product of samples prepared. (a) thin section, (b) pellet, (c) glass bead	32

Chapter 4

Fig. 4-1. Map of Kangankunde carbonatite showing local geology, drilled hole collar and sampling point (modified after Garson 1965). Drill collar coordinates from Lindian Resources Limited.	38
Fig. 4-2 Section of exploration drilled cores showing lithological variation, total rare earth element (TREE ₂ O ₃) distribution at depth and sampling locations.	40
Fig. 4-3 Representative photos of drill core and rock chip samples. (a) beforsite, the earliest carbonatite rock, (b) magnesio-carbonatite in whitish to light grey color, and magnesio-carbonatite with greenish spots of weathered phlogopite and magnesio-carbonatite with highly resorbed feldspar xenolith, (c) ferro-carbonatite, (d) ferruginous calcio-carbonatite that formed at a later stage of emplacement, (e) late carbonatite dyke that cut early carbonatite, (f) colloform texture on ferro-carbonatite indicating hydrothermal activity, (g) agglomerate/breccia with carbonatite and feldspar clast. Abbreviation: Ap - apatite, Phl— phlogopite, Dol — dolomite, Mnz — monazite.....	41
Fig. 4-4 Photographs of representative samples showing the mode of occurrence of the mineralization in Kangankunde. (a-b) monazite disseminated in ferro-carbonatite, (c-d) acicular monazite in magnesio-carbonatite, (e-f) magnesio-carbonatite showing patchy mineralization and miarolitic cavities indicating the presence of the magmatic-hydrothermal fluid phase. Abbreviation: Ank— ankerite. Brt—barite, Dol—dolomite, Fe-oxide — iron oxide, Mnz—monazite, Str—strontianite.	44
Fig. 4-5 Backscattered electron images and photomicrographs of mineral assemblages of samples studied. (a-b) beforsite— earliest-formed apatite-rich carbonatite with associated accessory silicate minerals, (c) magnesio-carbonatite with monazite occurring interstitial between Fe-bearing dolomite, (d) magmatic magnesio-carbonatite with corroded monazite inclusion, (e) magnesio-carbonatite having zoned quartz with monazite inclusion, overprinted by strontianite that enveloped monazite (f) magnesio-carbonatite with monazite replacing strontianite, (g) magnesio-carbonatite with	

pyrochlore associated with goyazite and Fe-bearing dolomite, (h) magnesio-carbonatite with greenish spots of weathered phlogopite associated with pyrochlore, (i) ferro-carbonatite with Mg-bearing siderite with dissolution texture and strontianite replacing monazite. (j) ferro-carbonatite with pyrolusite vein, goyazite replacing Fe-bearing dolomite, (k) ferruginous calcio-carbonatite showing ankerite with amorphous texture replacing dolomite and dissolution of synchysite, and formation of fluorite and strontianite, (l) ferruginous calcio-carbonatite with hematite in association with monazite overprinting Fe-bearing dolomite occurring together with ankerite in ferruginous calcio-carbonatite, (m) ferruginous calcio-carbonatite with quartz having apatite inclusions and overprinted by strontianite enveloped monazite, (n) ferruginous calcio-carbonatite with monazite wisp veining, and (o) magnesio-carbonatite with disseminated monazite overprinting dolomite, (p) fenite with biotite occurring as shred and turbid orthoclase and Abbreviation: Ap - apatite, Ank— ankerite. Brt—Baryte, Cal— calcite, Daq—daqingshanite, Dol—dolomite, Fe— iron, Fl— fluorite, Goy— goyazite, Hem- hematite, Mag— magnetite, Mnz—monazite, Mll— melilite, Mtc— monticellite, Pcl— pyrochlore, Pyl—pyrolusite, Phl— phlogopite, Qz— quartz, Str— strontianite. Kfs— orthoclase, Bt— biotite..... 48

Fig. 4-6. Carbonatite classification using major oxides. (a) classification using molar proportion defined by Gittins and Hammer (1997), (b) tetrad plot using weight percent defined by Mitchel (2022) in comparison with silicate-bearing carbonatite, magnesio-carbonatite with Fe-bearing dolomite and ferro-carbonatite with Mg-bearing siderite, where Di and TFP are the ideal compositions (quaternary wt. %) of diopside and tetraferriphlogopite, respectively. Dol - dolomite; MS - magnesian siderite. 50

Fig. 4-7 Whole-rock REEs and trace element patterns for magnesio-carbonatite, ferro-carbonatite and ferruginous calcio-carbonatite. (a) chondrite-normalized REEs patterns, (b) primitive mantle normalized LILE and HFSE elements. Chondrite and primitive mantle values from McDonough and Sun (1995). 52

Fig. 4-8 Bivariate plots of major and trace element oxides against total rare earth elements oxides. (a) P_2O_3 vs. $TREE_2O_3$, (b) SrO vs. $TREE_2O_3$, (c) Ba vs. $TREE_2O_3$, (d) $(Fe+Mn)/(Fe+Mn+Ca+Mg)$ vs. $TREE_2O_3$, and (e) Nb vs. $TREE_2O_3$. R^2 means the linear correlation coefficient..... 54

Fig. 4-9 Histogram of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope analysis of ankerite and calcite from the ferruginous-carbonatite, and strontianite from the magnesio-carbonatite.....	56
Fig. 4-10 The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions of the Kangankunde carbonatites The filled symbol are form this study. The open symbols are supplement composition data form Broom-Fendley et al. (2017c). Arrows indicate possible principal controls on carbonatite O and C isotope ratio after Deines (1989) and Demény et al. (2004). The mantle field is adapted from Kyser (1990), Deines (1992), and Cartigny et al. (1998). Primary igneous carbonatite (P.I.C) field from Ray & Ramesh (2006).	58
Fig. 4-11 Paragenetic sequence for the Kangankunde carbonatite.....	64
Fig. 4-12 A cross section of the Kangankunde carbonatite facing NW. Cross section line A-B on Fig. 4-1 highlighting the magnesio-carbonatite. Section inferred form Fig 4-1 and carbonatite emplacement model by Garson 1965.....	67

Chapter 5

Fig. 5-1 Map of the Tundulu carbonatite showing the geology and sampling points (adapted from Garson, 1962).....	81
Fig. 5-2 Representative photos of rock samples. (a-c) calcio-carbonatite with foliated feldspar, barite vein, spinifex texture, (d-f) ferruginous calcio-carbonatite with pyrite, and siderite, (g-h) apatite-rich magnesio-carbonatite with comb and porphyritic texture, (i-j) apatite-poor magnesio-carbonatite with veins composed of calcite, hematite, biotite, (k) hematite dyke in apatite-poor carbonatite, (l) agglomerate crystalline quartz, (m) syenite. Abbreviation: Ap - apatite, Cal— calcite, Kfs —K-feldspar., Sd- Siderite, Bt- biotite, Hem- hematite, Ank- ankerite, Brt- barite, Py- pyrite.....	83
Fig. 5-3 Backscattered electron images and photomicrographs of mineral assemblages of samples studied. (a-b) calcio-carbonatite from Tundulu Hill first igneous center with foliated feldspar blebs, and synchysite with glomeroporphyritic texture. (c) calcio-carbonatite with calcite and idiomorphic texture of apatite over printing magnetite, (d) calcio-carbonatite with differentiation between Fe and P_2O_5 rich melt, (e) synchysite inclusion in calcio-carbonatite, (f). ferruginous calcio-carbonatite with hexagonal pseudomorph indicating magmatic REE mineralization, (g) ferruginous calcio-carbonatite with brecciated ankerite, (h) ferruginous calcio-carbonatite with apatite overprinting brecciated ankerite, and celestine interstitial between ankerite and apatite,	

(i) ferruginous calcio-carbonatite with apatite overgrowth and dissolution textures, quartz filling spaces between apatite and ankerite, synchysite and barite overprinting quartz, and brecciated pyrochlore overprinting quartz (j) ferruginous calcio-carbonatite with recrystallized calcite overprinted by synchysite, (k) ferruginous calcio-carbonatite with calcite contaminated with REE, (l) ferruginous calcio-carbonatite with pyrite unwedged texture, (m) Apatite-rich magnesio-carbonatite with dolomite replacing siderite, (n) apatite-rich magnesio-carbonatite with synchysite overprinting quartz, (o) apatite-rich magnesio-carbonatite with skeletal texture of siderite alteration, (p) apatite-poor magnesio-carbonatite with fibrous texture of synchysite having rhodochrosite on rim and calcite, (q) apatite-poor magnesio-carbonatite with dolomite replacing siderite, (r) agglomerate with Fe-oxides filling calcite (s) agglomerate with quartz and calcite veins, (t) syenite with consertal texture. Abbreviation: Ap - apatite, Ank— ankerite. Brt—Baryte, Cal— calcite, Str—Strontianite, Py— Pyrite, Dol—dolomite, Fe-oxide — iron, Syn— Synchysite, Qz— Quartz, Mag— magnetite, Clt—Celestine, Bt— Biotite, Kfs— Orthoclase, Pcl— pyrochlore, Pyl—pyrolusite. All photomicrographs are crossed polarized.	87
Fig. 5-4 Carbonatite classification using major oxide molar proportion defined by Gittins and Hammer (1997).	89
Fig. 5-5 Whole-rock REE and trace element patterns for magnesio-carbonatite, calcio-carbonatite and ferruginous calcio-carbonatite. (a) Chondrite-normalized REE patterns. (b) Primitive mantle normalized LILE and HFSE elements. Chondrite and primitive mantle values from McDonough and Sun (1995).	91
Fig. 5-6 Chondrite-normalized diagrams of REE ratios $(La/Yb)_N$ versus Y/Ho (chondrite values from McDonough & Sun, (1995). Adapted from Bau (1996) (primary and alteration fields from Zheng et al., 2023)	92
Fig. 5-7 Bivariate plots of major oxides and trace elements against total rare earth elements oxides. (a) P_2O_3 vs. $TREE_2O_3$, (b) SrO vs. $TREE_2O_3$, (c) Ba vs. $TREE_2O_3$, (d) $(Fe+Mn)/(Fe+Mn+Ca+Mg)$ vs. $TREE_2O_3$, (e) Nb vs. $TREE_2O_3$. R^2 means the linear correlation coefficient.	94
Fig. 5-8 Histogram of $\delta^{13}C$ and $\delta^{18}O$ isotope analysis of calcite from calcio-carbonatite, ankerite and strontianite from ferruginous-carbonatite.	96

Fig. 5-9. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions of the Tundulu carbonatites. Arrows indicate possible principal controls on carbonatite O and C isotope ratio after Deines (1989) and Demény et al. (2004). The mantle field is adapted from Kyser (1990), Deines (1992), and Cartigny et al. (1998). Primary igneous carbonatite (PIC) field from Ray & Ramesh (2006).	97
Figure 5-10 Paragenetic sequence for the Tundulu carbonatite	101
Fig. 5-11 Cross section of Tundulu carbonatite facing NW. Cross section line A-B on Fig. 5-1 highlighting the magnesio-carbonatite. Section inferred from Fig 5-1 and carbonatite emplacement model by Garson 1965.....	104

Chapter 6

Fig. 6-1 A map of the Nkalonje carbonatite showing the geology of the carbonatites..	111
Fig. 6-2 Representative photos of rock chip samples. (a) calcio-carbonatite dyke, (b) whitish calcio-carbonatite with spinifex texture, (c) dark calcio-carbonatite, (d-e) feldspathic breccia with large and small feldspar xenolith cemented by pyrolusite (f) agglomerate with pseudotrachytic matrix, (g) quartz-fluorite, (h) fenitized gneiss with remnant of foliated and magmatic texture, (i) phonolite with sanidine phenocryst, (j-k) nepheline syenite, Abbreviation: Cal— calcite, Kfs —K-feldspar., Fl– Fluorite, Aeg– aegirine, Aug— augite.....	113
Fig. 6-3 Photo micrographs, Backscatter electron image of samples from Nkalonje carbonatite (a – j) Calcio-carbonatite, (k – n) Feldspathic agglomerate and breccia, (o – p) Fenite, (q-s) Nepheline syenite. Abbreviations: Ap – apatite, Aeg- aegirine, Brt- Barite, Clt- Celestine, Bt – biotite, Kfs – albite, Cal – calcite, Fl- fluorite, Mag – magnetite, Sd – siderite, Hem- hematite, Str – strontianite, Qz – quartz, Px- pyroxene, Nph- nepheline, Aug-Augite, Note: all photomicrographs are cross-polarized light....	116
Fig. 6-4 Carbonatite classification using major oxides molar proportion defined by Gittins and Hammer (1997).....	118
Fig. 6-5 Plot of SiO_2 vs CaO (wt. %) for rocks of the Chilwa Alkaline Province. Most of the data are for the northern part of the province, and a few are for the southern part. The three-magma series of the rock groups was modified after Woolley (1987). The green dot represents this study.....	118

Fig. 6-6 Whole-rock REEs and trace element patterns for calcio-carbonatite, agglomerate, and breccia, and syenite. (a) Chondrite-normalized REE patterns. (b) Primitive mantle normalized LILE and HFSE elements: Chondrite and primitive mantle values from McDonough and Sun (1995).	120
Fig. 6-7 Scatter diagrams of $(La/Sm)_N$ versus Y/Ho. The CHARAC fields and other carbonatites were adapted after Zheng et al. (2023).	121
Fig. 6-8 Bivariate plots of major oxides and trace elements against total rare earth elements oxides. (a) P_2O_3 vs. $TREE_2O_3$, (b) SrO vs. $TREE_2O_3$, (c) Ba vs. $TREE_2O_3$, (d) $(Fe+Mn)/(Fe+Mn+Ca+Mg)$ vs. $TREE_2O_3$, (e) Nb vs. $TREE_2O_3$. R^2 means the linear correlation coefficient.	123
Fig. 6-9 Histogram showing $\delta^{13}C$ and $\delta^{18}O$ isotope analysis of calcite from calcio-carbonatite.	124
Fig. 6-10. The $\delta^{13}C$ and $\delta^{18}O$ compositions of the Nkalonje carbonatites. Arrows indicate possible principal controls on carbonatite O and C isotope ratio after Deines (1989) and Demény et al. (2004). Mantle field is adapted from Kyser (1990), Deines (1992), and Cartigny et al. (1998). Primary igneous carbonatite (PIC) field from Ray & Ramesh (2006).	126

Chapter 7

Fig. 7-1 Simplified model for the origin of the carbonatite magma and differentiation paths for the (a) western belt and (b) Eastern belt carbonatite of the Chilwa Alkaline Province, Malawi.	137
---	-----

Acknowledgments

I want to express my profound gratitude to my supervisor, Professor. Akira Imai, for his guidance, support, and patience with me. I have learned a lot from you in the past 3 years. I am grateful to my co-supervisors, Associate Prof. Kotaro Yonezu and Associate Assistant Professor Akane Ito, for your unconditional assistance and encouragement. When times were tough, you still had faith in me. You all were available anytime I needed to see you. I really appreciate it. Dr. Mami Mampuku, thank you for your kind support and coordination during the doctoral program.

I am greatly indebted to the Japan International Cooperation Agency (JICA) for the financial support through the Human Resource Development in the Mining Sector (KIZUNA) Scholarship Program. I am also grateful to Lindian Resources Limited, Optichem Limited, and Mkango Resources Limited for allowing me to conduct research in their tenement areas and providing access to data and drill core. Fieldwork was no success without coordination and support from the Geological Survey of Malawi and the JICA Malawi Office.

This work would not be done without mention of the following friends and colleagues, Dr. E. Nopeia, Dr. J. Chisambi, Dr. S. Juri Dr. F. Chikanda, Alistair Stephens, Chrispine Ngwena, Sera Msuku, Alexander Lemon, Paul Armitage, Burton Kachinjika, Symon Kalupya, Ketrina Chunga, Dyton Saidi, Cathrine Mboga, and members of the Economic Geology Laboratory of Kyushu University. All your support is appreciated.

Lastly, I would like to thank my Dad, Mum, sisters, and brothers for their prayers and constant moral support.

Above all, I thank GOD for giving me the wisdom and intelligence to undertake this work.

Chapter 1 : Introduction

1.1 General introduction

1.1.1 Rationale and objectives

Rare earth elements (REEs) are the lanthanide series elements (Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb) and Lutetium (Lu), plus Scandium (Sc) and Yttrium (Y.) (Balaram, 2019). Scandium and yttrium are included because of their similar characteristic to the lanthanides (Nabyl et al., 2020). There is increasing demand for REE due to energy transition requirements (e.g. Stegen, 2015; Dushyantha et al., 2020). Carbonatites are a primary target for REEs exploration as they are generally enriched in REE compared to other igneous rocks (Loubet et al., 1972; Nelson et al., 1988; Woolley & Kempe, 1989).

Carbonatite usually refers to igneous rocks derived from the mantle with carbonate mineral volume ≥ 30 vol. % primary magmatic carbonate minerals (Mitchell, 2005). There are two hypotheses on carbonatite formation process; (1) derivation from a primary carbonatitic magma by low-degree partial melting of carbonate-bearing mantle (Wallace & Green, 1988; Bell & Simonetti, 2010), (2a) derivation from a carbonate-bearing silicate magma by either fractional crystallization (Lee & Wyllie, 1994; Mitchell, 2005; Tappe et al., 2017) (2b) separation of a carbonatitic magma from a carbonate-bearing silicate magma by liquid-immiscibility (Veksler et al., 1998; Mitchell, 2005).

Carbonatite REEs mineralization remains a contentious topic as both magmatic and hydrothermal process are known to contribute to enrichment of REE mineralization (Yang et al., 2011; Moore et al., 2015; Cheng et al., 2018; Patel et al., 2023). However, carbonatites REEs budget is accounted for during the initial short-lived magmatic intrusion and do not accumulate additional REEs over time (Anenburg et al., 2021). Studies on carbonatites based on field observation and thermodynamic modelling suggest that either metamorphic and hydrothermal processes may transform REEs mineral assemblage or chemical signatures and result in REEs redistribution (e.g. Castor,

2008b; Broom-Fendley et al., 2016b; Migdisov et al., 2016; Anenburg et al., 2021). However, most carbonatites REEs are concentrated and influenced by magmatic processes (Chen et al., 2017; Nabyl et al., 2020).

Carbonatites are classified as calcio-carbonatite, magnesio-carbonatite, ferro-carbonatite and ferruginous calcio-carbonatite based on dominant carbonate oxide (Gittins & Harmer, 1997). The magmatic calcio-carbonatite is more common while magnesio-carbonatite and ferruginous-calcio-carbonatite are less common (Giebel, 2019).

Overprinting of magmatic processes by hydrothermal or metamorphic process and scarcity of magmatic magnesio-carbonatite and ferruginous calcio-carbonatite limit understanding of carbonatite evolution and REEs mineralization. This promotes many debates and controversies about carbonatite's geological background, genetic characteristics, and metallogenic processes. Therefore, it is necessary to summarize the tectonic background, petrology and geochemical characteristics of carbonatite-related REEs deposits so as to better understand the genesis of the deposits and provide guidance for mineral exploration (Wang et al., 2020).

More than 500 carbonatites are reported, of which 88% and 10.5% are emplaced on cratonic and non-cratonic extension settings, respectively (Brauch et al., 2018). The carbonatites are associated with Archean and Proterozoic rocks or Phanerozoic rocks underlain by a Precambrian basement (Pirajno, 2000; Woolley & Kjarsgaard, 2008; Wang et al., 2020; Bank et al., 2021). Malawi lies at the southern end of the East African Rift System with Mesoproterozoic rocks, within tectonic mobile belts and cretaceous carbonatites and peralkaline igneous rocks. Seventeen carbonatite occurrences are reported in southern Malawi, associated with the Chilwa Alkaline Province (C.A.P; Garson, 1966; Fig. 1-1). The carbonatites occur as ring complexes, agglomerates, and vents ranging from 400 m to 1600 m in diameter (Dixey, 1955). Carbonatite variation on mode of occurrence may indicate difference in the stage and depth of the emplacement cycle of a carbonatite, as described by Walter et al. (2021), having either the same or different magma source. Structurally, the carbonatite in the C.A.P forms two main belts. The eastern belt is comprised of an irregular chain of volcanic necks with associated alkaline plugs. The western belt is comprised of carbonatitic intrusions (Garson, 1965). Exploration of these carbonatites dates four

decades, and some were mined (e.g. Garson, 1965; Holt, 1965). Kangankunde carbonatite occurred on the western belt while, Tundulu carbonatite and Nkalonje carbonatite occurred on the eastern belt and are associated with nepheline syenites.

Kangankunde, Tundulu, and Nkalonje carbonatites were emplaced at higher erosion levels (Garson, 1965). These characteristics provide a better laboratory for studying carbonatites in the C.A.P. There have been more studies on Kangankunde and Tundulu carbonatites than Nkalonje carbonatite. Previous studies on these carbonatites mainly focused on petrography, geochemical, geochronological, and isotopic evolution (e.g. Garson 1962; Ngwenya 1994; Duraiswami and Shaikh 2014; Broom-Fendley et al. 2017; Elliott et al. 2018; Chikanda et al. 2019). The previous studies have not been exhaustive in understanding the evolution of the carbonatites due to complex evolution processes and the limited availability of data. There have been new drill cores for Kangankunde carbonatite. Therefore, this study aims to improve understanding of the carbonatite evolution in the C.A.P with the objectives of (1) establishing the paragenetic sequence of the carbonatites, (2) providing an exhaustive description of the mode of occurrence of the REE minerals, (3) establishing the magmatic differentiation paths and its effects on mineralization, (4) Comparing the Kangankunde, Tundulu, and Nkalonje carbonatites within the C.A.P, (5) To discuss the possible genesis of REEs mineralization in the three carbonatites and (6) contribute to an ongoing discussion on REE mineralization.

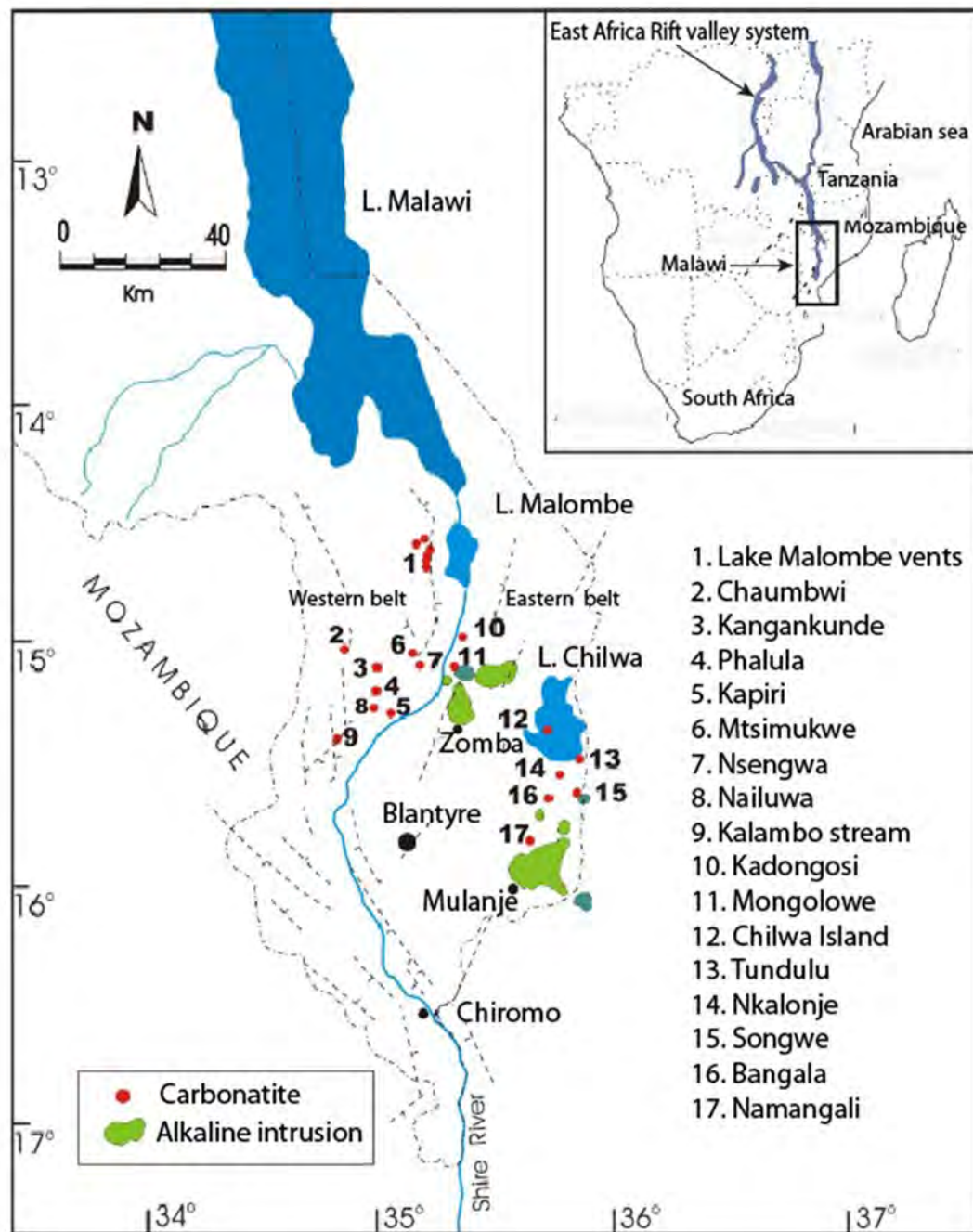


Fig. 1-1 Map of southern Malawi showing carbonatites occurrence in the Chilwa Alkaline Province (C.A.P). Insert Map of the central and southern parts of Africa showing the location of Malawi within the East Africa Rift System. (modified after Duraiswami & Shaikh, 2014.)

1.1.2 Thesis organization

The thesis is divided into 7 chapters. Chapter 1 introduces the research area, identify gaps, and state the objectives the research use to address the gap.

Chapter 2 presents the geology and tectonic setting of Southern Malawi. It provides a brief on emplacement order of main lithological group to account for age, chemical composition, and tectonic setting in Malawi. It also provides a regional overview of the C.A.P tectonic setting and highlights its litho-stratigraphy, including the carbonatites that host REEs deposits. Furthermore, the tectonic setting provides possible source of carbonatite contamination.

Chapter 3 presents the research sample type, sampling techniques, and methods used. The methods are uniform for all study area.

Chapter 4 re-evaluates the Kangankunde carbonatite and presents the local geology, petrography, and whole-rock geochemistry of carbonatites and fenite. This chapter also reclassifies the carbonatite lithotypes at Kangakunde and provides mineral paragenetic sequence and stable isotope signatures. The data are used to model the magmatic evolution paths and its implication to REEs mineralization.

Chapter 5 re-evaluates the Tundulu carbonatite and presents the local geology, petrography and whole-rock geochemistry of carbonatites, fenite and syenite. This chapter also reclassifies the carbonatite lithotypes at Tundulu and provides mineral paragenetic sequence and stable isotope signatures. The data are used also to model the magma evolution and its implication on REEs mineralization.

Chapter 6 re-evaluates the Nkalonje carbonatite and presents the local geology petrography and whole-rock geochemistry of carbonatites agglomerate breccia and syenite. This chapter also provides mineral paragenetic sequences and stable isotope signatures. These data are used to model the magma evolution and its implication on REEs mineralization.

Chapter 7 of this thesis provide major finding of the research with respect to tectonic control on the carbonatite evolution and REE sources, Origin of the carbonatite magma, implication of magmatic and hydrothermal process on REEs mineralization of the two carbonatite belts in the C.A.P. Finally, it provides a model of the Carbonatite

magma differentiation for the emplacement of carbonatite in the western and eastern belts.

1.1.3 Scientific contributions from this study

- a) Petrochemistry of the Kangankunde carbonatite in the Chilwa alkaline province; Implication of REE mineralization
- b) Paragenetic stages of rare earth elements mineralization at the Tundulu carbonatite of the Chilwa alkaline province, Malawi. Ideas and Innovations in Earth Sciences: Proceedings of the 10th International Geosciences conference of young researchers, Kyiv, Ukraine. May 23-24, 2024 page. 52-55.

References

- Anenburg, M., Broom-Fendley, S., and Chen, W. (2021). Formation of rare earth deposits in carbonatites. *Elements*, 17(5), pp.327–332.
- Balaram, V. (2019). Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. *Geoscience Frontiers*, 10(4), pp.1285–1303.
- Bank, T., Roth, E., Joward, B., and Granite, E. (2021). Geology of Rare Earth Deposits.
- Bell, K., and Simonetti, A. (2010). Source of parental melts to carbonatites-critical isotopic constraints. *Mineralogy and Petrology*, 98(1–2), pp.77–89.
- Brauch, K., Tauchnitz, M., Kopp, D., Riedel, P., G, S., Walter, B. and Weller, A. (2018). Interpretation of the geophysical data at Kaiserstuhl central carbonatite complex. *HiTech AlkCarb*.
- Broom-Fendley, S., Styles, M. T., Appleton, J. D., Gunn, G., and Wall, F. (2016b). Evidence for dissolution-reprecipitation of apatite and preferential LREE mobility in carbonatite-derived late-stage hydrothermal processes. *American Mineralogist*, 101(3), pp.596–611.
- Broom-Fendley, S., Wall, F., Spiro, B., and Ullmann, C. V. (2017). Deducing the source and composition of rare earth mineralising fluids in carbonatites: Insights from isotopic (C, O, ⁸⁷Sr/⁸⁶Sr) data from Kangankunde, Malawi. *Contributions to Mineralogy and Petrology*, 172–196, pp.1–18.
- Castor, S. B. (2008a). Rare Earth Deposits of North America. *Resource Geology*, 58(4),

pp.337–347.

- Castor, S. B. (2008b). The Mountain Pass rare-earth carbonatite and associated ultrapotassic rocks, California. *The Canadian Mineralogist*, 46, pp.779–806.
- Chen, W., Honghui, H., Bai, T., and Jiang, S. (2017). Geochemistry of monazite within carbonatite related REE deposits. *Resources*, 6(8), pp.51.
- Chikanda, F., Otake, T., Ohtomo, Y., Ito, A., Yokoyama, T. D., and Sato, T. (2019). Magmatic-hydrothermal processes associated with rare earth element enrichment in the Kangankunde carbonatite Complex, Malawi. *Minerals*, 9(7), pp.1–22.
- Dixey, F., and Campbell, S. W. (1955). The Chilwa Series of Southern Nyasaland: a group of alkaline and other intrusive and extrusive rocks and associated limestones. Government Printers, Bulletin 5 revised, 71pp.
- Duraiswami, R. A., and Shaikh, T. N. (2014). Fluid-rock interaction in the Kangankunde carbonatite Complex, Malawi: SEM based evidence for late stage pervasive hydrothermal mineralisation. *Central European Journal of Geosciences*, 6(4), pp.476–491.
- Dushyantha, N., Batapola, N., Ilankoon, I. M. S. K., Rohitha, S., Premasiri, R., Abeysinghe, B., Ratnayake, N., and Dissanayake, K. (2020). The story of rare earth elements (REEs): Occurrences, global distribution, genesis, geology, mineralogy, and global production. In *Ore Geology Reviews*, Vol 122, Elsevier. p. 103521.
- Elliott, H. A. L., Wall, F., Chakhmouradian, A. R., Siegfried, P. R., Dahlgren, S., Weatherley, S., Finch, A. A., Marks, M. A. W., Dowman, E., and Deady, E. (2018). Fenites associated with carbonatite complexes: A review. *Ore Geology Reviews*, 93(12), pp.38–59.
- Garson, M. S. (1962). The Tundulu carbonatite ring-complex in Southern Nyasaland. Government Printer, Memoir 2. 235p.
- Garson, M. S. (1965). Carbonatites in Southern Malawi. Government Printers, Bulletin 15, 128pp.
- Garson, M. S. (1966). Carbonatites in Malawi. In: *Carbonatites* (Tuttle, O.). Wiley-Interscience.
- Giebel, R. J. (2019). The petrogenesis of carbonatites: PhD Thesis, Universität Tübingen.

- Gittins, J., and Harmer, R. E. (1997). What is ferrocarbonatite? A revised classification. *Journal of African Earth Sciences*, 25(1), pp.159–168.
- Holt, D. N. (1965). The Kangankunde Hill rare earth prospect. Government Printers,
- Lee, W., and Wyllie, P. J. (1994). Experimental data bearing on liquid immiscibility, crystal fractionation, and the origin of calciocarbonatites and natrocarbonatites. *International Geology Review*, 36(3), pp.797–819.
- Loubet, M., Bernat, M., Javoy, M., and Allegre, C. J. (1972). Rare earth contents in carbonatites. *Earth and Planetary Science Letters*, 14(2), pp.226–232.
- Migdisov, A., Williams-jones, A. E., Brugger, J., and C.A.Poruscio, F. A. (2016). Hydrothermal transport, deposition, and fractionation of the REE: Experimental data and thermodynamic calculations. *Chemical Geology*, 439, pp.13–42.
- Mitchell, R. H. (2005). Carbonatites and carbonatites and carbonatites. *The Canadian Mineralogist*, 43(6), pp.2049–2068.
- Moore, M., Chakhmouradian, A. R., Mariano, A. N., and Sidhu, R. (2015). Evolution of rare-earth mineralization in the Bear Lodge carbonatite, Wyoming: Mineralogical and isotopic evidence. *Ore Geology Reviews*, 64, pp.499–521.
- Nabyl, Z., Massuyeau, M., Gaillard, F., Tuduri, J., Iacono-Marziano, G., Rogerie, G., Le Trong, E., Di Carlo, I., Melleton, J., and Bailly, L. (2020). A window in the course of alkaline magma differentiation conducive to immiscible REE-rich carbonatites. *Geochimica et Cosmochimica Acta*, 282, pp.297–323.
- Nelson, D. R., Chivas, A. R., Chappell, B. W., and Mcculloch, M. T. (1988). Geochemical and isotopic systematics in carbonatites and implications for the evolution of ocean-island sources. *Geochimica et Cosmochimica Acta*, 52(1), pp.1–17.
- Ngwenya, B. T. (1994). Hydrothermal rare earth mineralisation in carbonatites of the Tundulu complex, Malawi: Processes at the fluid/rock interface. *Geochimica et Cosmochimica Acta*, 58(9), pp.2061–2072.
- Patel, A. K., Upadhyay, D., Mishra, B., and Pruseth, K. L. (2023). Magmatic rare earth element mineralization and secondary fluid-assisted redistribution in the Kamthai carbonatite complex, NW India. *Lithos*, 456–457(7), pp.107294.
- Pirajno, F. (2000). Ore deposits and mantle plumes (1st ed.). Springer Netherlands.
- Stegen, S. K. (2015). Heavy rare earths, permanent magnets, and renewable energies:

- An imminent crisis. *Energy Policy*, 79, pp.1–8.
- Tappe, S., Romer, R. L., Stracke, A., Steenfelt, A., Smart, K. A., Muehlenbachs, K., and Torsvik, T. H. (2017). Sources and mobility of carbonate melts beneath cratons, with implications for deep carbon cycling, metasomatism and rift initiation. *Earth and Planetary Science Letters*, 466, pp.152–167.
- Veksler, I. V., Nielsen, T. F. D., and Sokolov, S. V. (1998). Mineralogy of crystallized melt inclusions from Gardiner and Kovdor Ultramafic Alkaline Complexes: Implications for carbonatite genesis. *Journal of Petrology*, 39(11–12), pp.2015–2031.
- Wallace, M. E. M. and Green, D. H. D. H. (1988). An experimental determination of primary carbonatite magma composition. *Nature*, 335(9), pp.343–346.
- Walter, B. F., Giebel, R. J., Steele-MacInnis, M., Marks, M. A. W., Kolb, J., and Markl, G. (2021). Fluids associated with carbonatitic magmatism: A critical review and implications for carbonatite magma ascent. *Earth-Science Reviews*, 215, pp.103509.
- Wang, Z. Y., Fan, H. R., Zhou, L., Yang, K. F., and She, H. D. (2020). Carbonatite-related REE deposits: An overview. *Minerals*, 10(11), pp.1–26.
- Woolley, A. R., and Kempe, D. R. C. (1989). Carbonatites: Nomenclature, average chemical compositions, and element distribution. In Bell K. (Ed.), *Carbonatite: Genesis and Evolution* (1st ed) UnwinHyman. pp.1–13.
- Yang, K. F., Fan, H. R., Santosh, M., Hu, F. F., and Wang, K. Y. (2011). Mesoproterozoic carbonatitic magmatism in the Bayan Obo deposit, Inner Mongolia, North China: Constraints for the mechanism of super accumulation of rare earth elements. *Ore Geology Reviews*, 40(1), pp.122–131

Chapter 2 : Regional Geology and Tectonic setting

2.1 The Malawi basement complex (MBC) and metamorphism

Malawi lies within the Mozambican mobile orogenic belt characterized by reworked meta-igneous and meta-sedimentary rocks of Late Precambrian to Early Palaeozoic, locally known as the Malawi Basement Complex (MBC; Carter & Bennett, 1973). The MBC is composed of Paleoproterozoic Ubendian domain in the North, Mesoproterozoic Irumide domain in the Centre and Mesoproterozoic South Irumide domain in the South (Fig. 2-1a; Fullgraf et al., 2022a).

The Ubendian domain underlies northern Malawi and is characterized by Paleoproterozoic supracrustal and intrusive rocks that were accreted between the south-west edge of the Tanzania Craton and the north-east margin of the Bangweulu block and subjected to several phases of deformation and metamorphism during the Ubendian orogeny at ~1800 Ma (Bloomfield, 1968; Fig. 2-1a-b).

The emplacement of the Irumide domain is attributed to closure of the “Irumide Ocean” and the collision of the Kalahari and Congo Cratons (Bingen et al., 2009). It is further grouped into Irumide domain and south Irumide domain. The Irumide domain covered parts of northern and central Malawi characterized by Paleoproterozoic (Ubendian) crust, which, during Late Mesoproterozoic, became an active continental margin south of the now-stabilized Bangweulu-Ubendian-Tanzania Craton block (Bloomfield, 1968; Fig. 2-1a-b). The Irumide domain was intruded by Mesoproterozoic magmatic rocks and underwent intense deformation and high-grade metamorphism at ~1050 Ma (Fullgraf et al., 2022a).

The South Irumide domain covers much of Southern Malawi (Fig. 2-1a). The South Irumide domain is composed of Late Mesoproterozoic juvenile crust, which formed in an island arc setting and underwent extensive magmatism and high-grade metamorphism (Bloomfield, 1968; Fullgraf et al., 2022). Intrusion of the supracrustal rock occurred between ~1010-1090 Ma (Bingen et al., 2009; Tsunogae et al., 2021). The Irumide orogeny in South Malawi, was overprinted by Pan-African orogeny between ~580 and 470 Ma (Fritz et al., 2013).

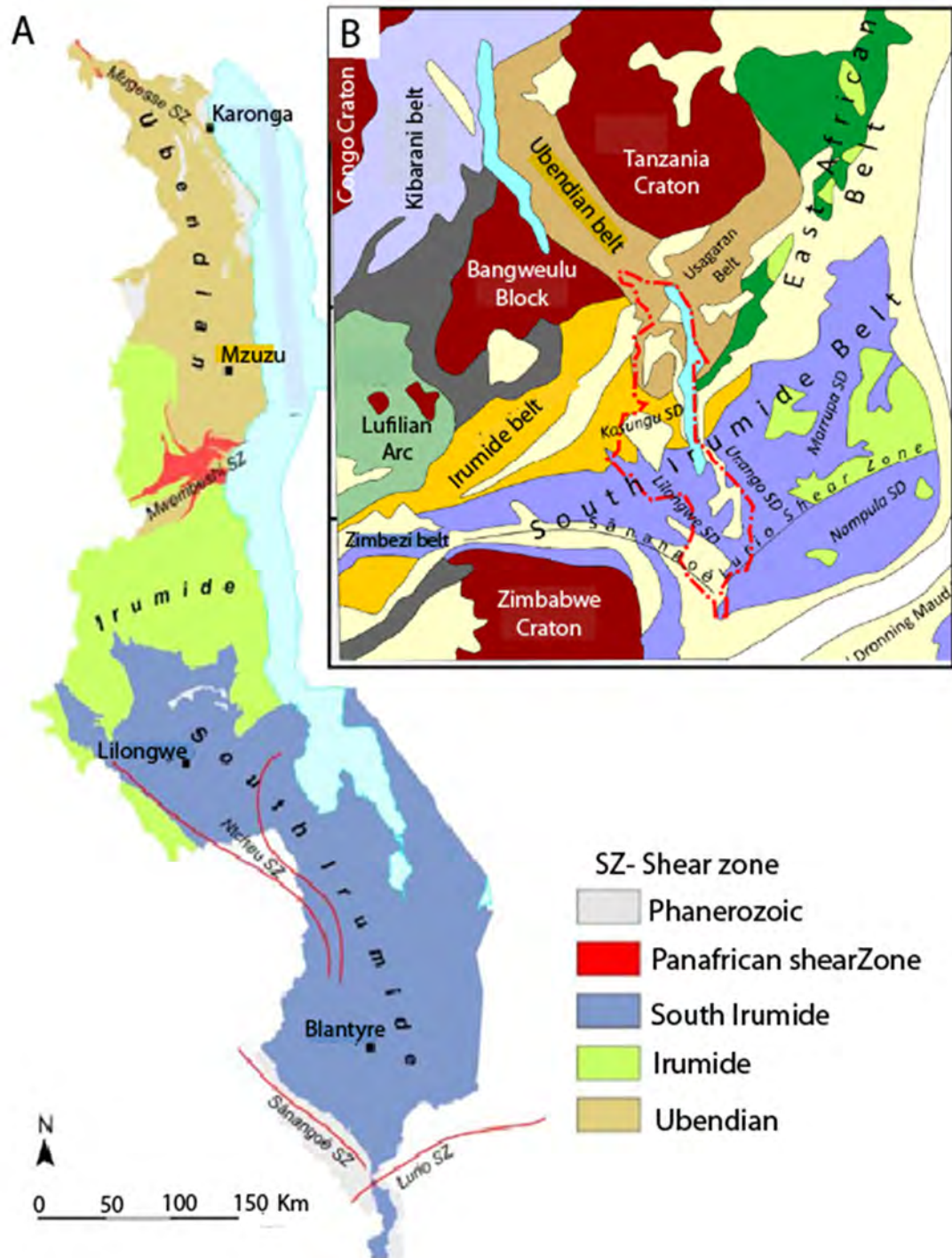


Fig. 2-1 Map of Malawi showing the Malawi basement complex domains. Insert geological setting of Malawi in western and south Gondwana within the East African belt. (modified after Fullgraf et al., 2022).

The South Irumide domain is divided into the Lilongwe, Unango and Nampula subdomains based on differences in structural style, geophysical signature, rock composition, and metamorphic conditions (Fig. 2-2; Fullgraf et al., 2022a).

The Lilongwe subdomain covers central and south-western Malawi and hosts the Kangankunde carbonatite (Fig. 2-2). The Lilongwe subdomain in central Malawi is overlaid by the Kasungu subdomain in the north and underlaid by Mchinji and Unango subdomains in the south-west and south-east, respectively. In Southern Malawi, the Lilongwe subdomain is put adjacent to the Lurio Shear Zone (LSZ) with the Nampula subdomain, whereas in the south-west it borders north-west south-east striking Sângo Shear Zone (SSZ; Fig. 2-2). The Lithology of the Lilongwe subdomain is characterized by graphite, sulfide and kyanite-bearing paragneiss and schist (Fig. 2-3; Bloomfield & Garson, 1965; Thatcher & Walter, 1968; Walter, 1972; Tsunogae et al., 2021). In the Kangankunde area, the graphite schist is separated by hornblende-biotite gneisses and to the NW is an oval-shaped mass of ultrabasic rocks orientated NW parallel to the strike of the surrounding paragneiss and surrounded by a discontinuous envelope of granitoid gneiss (Bloomfield & Garson, 1965; Walshaw, 1965).

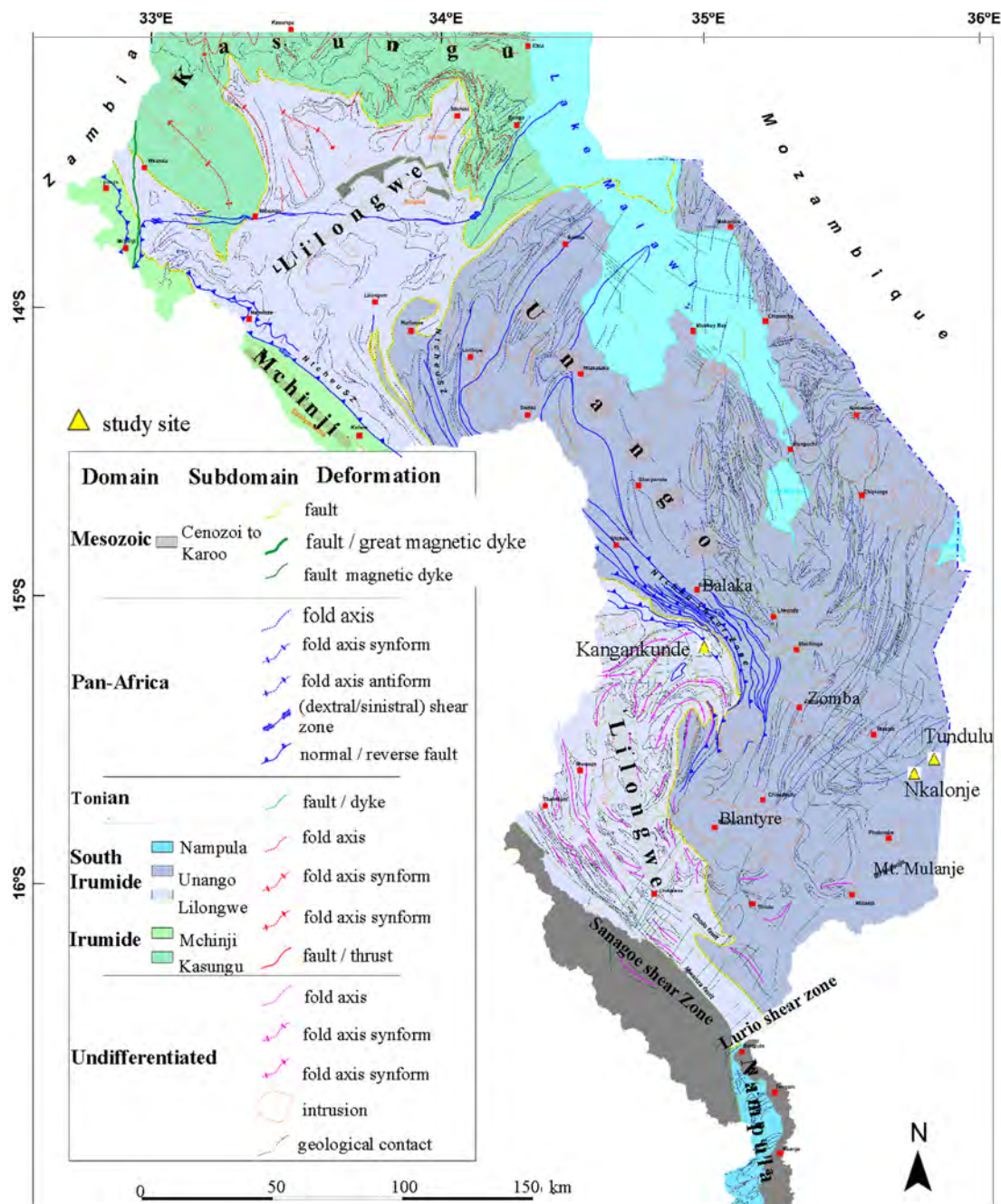


Fig. 2-2 Map of central and southern Malawi showing structures and tectonic subdomain (adapted from Fullgraf et al., 2022).

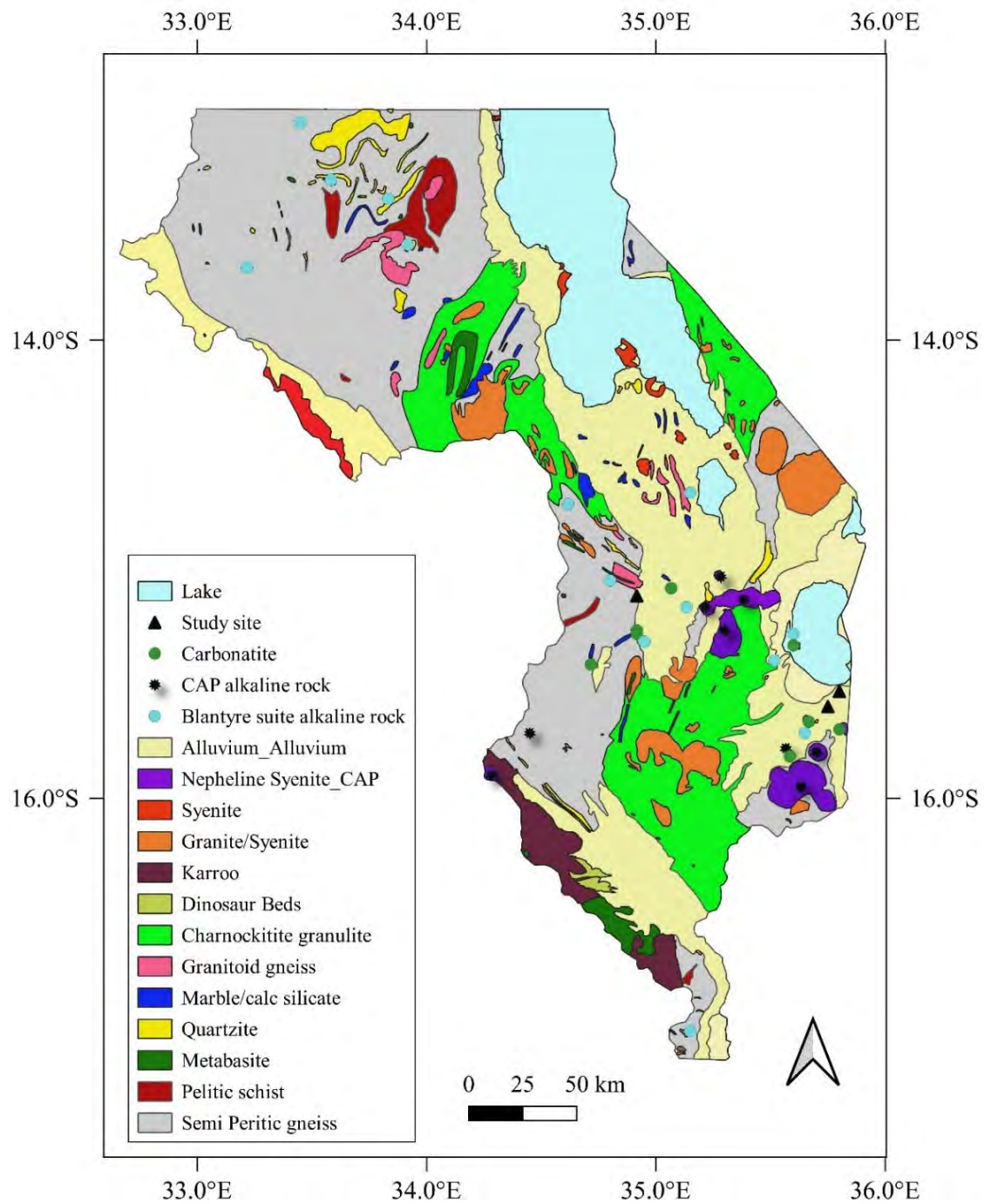


Fig. 2-3 Map of part of Central and Southern Malawi showing regional geology (modified after Bloomfield et al., 1966; Tsunogae et al., 2021).

The deformation of Lilongwe subdomain was a product of both Irumide and Pan-African deformation and metamorphism that resulted in amphibolite-grade metamorphism and limited anatexis at 1028 ± 15 Ma prior to the development of the regional gneissic fabric, which transposed pre-existing fabrics (Evans, 1965). The Lilongwe subdomain has shallow dips that suggest nappe-style tectonics, which resulted in the stacking of the Unango subdomain at the base, Lilongwe subdomain at the centre and Kasungu subdomains on the top. Subsequent polyphase folding at a regional scale bears mainly the Irumide trend of north and north-west folding while the mafic dykes of the Tonian rifting are undeformed and bears North-South trend (Fullgraf, et al., 2022). Fullgraf et al (2022a) suggest that the occurrence of Tonian rift rocks in all domains demonstrated the amalgamation stage of Precambrian rocks of Malawi.

The Pan-African deformation includes early west to north-west-directed transport, evidenced by the occurrence of the Ntcheu Shear Zone (NSZ) and thrusts around Mchinji (Fig. 2-2). Local anatexis in the deformation planes of the NSZ has been dated between 585 and 575 Ma (Fullgraf, et al., 2022a). In the south-west, the Lilongwe subdomain abuts and is dragged into the SSZ in an oblique dextral, north-east verging sense of movement, implying the lower position of the Lilongwe subdomain confirmed by dextral drag into the SSZ (Fullgraf, et al., 2022a). The SSZ has been attributed to the Kuunga phase (580-555) of Pan-African orogeny and shows that all major shear and thrust systems in Malawi were active during this stage (Goscombe et al., 2020). The circular Mlindi intrusion in the southern part of the Lilongwe subdomain constrains the minimum age of deformation at 531 ± 8 Ma (North-East-directed down-dip senses of movement in the NSZ record late-stage extension related to orogenic collapse (Tsunogae et al., 2021). These features, therefore, represent at least three times the locus of major tectonic movements, thus (1) Mesoproterozoic nappe stacking, (2) Pan-African thrusting and (3) late-Pan-African extensional shearing (Fullgraf, et al., 2022a). Hence magmatic or metamorphic episodes are recorded in high-grade metamorphic rock in the framework of East Africa and Kuunga orogens (Tsunogae et al., 2021).

Unango subdomain lithology is characterized by pyroxene granulite and charnockitic rocks, indicating granulite facies metamorphism (Fig. 2-3) (Garson & Walshaw, 1969; Carter & Bennett, 1973; Tsunogae et al., 2021). The dominant foliation

is moderate to steep and axial planes have interference folds. The western part of the subdomain is influenced mainly by the NSZ, which transported it over the Lilongwe subdomain. In the north, the Unango subdomain is overlain by the Lilongwe and Kasungu subdomains (Fullgraf, et al., 2022a).

The deformation characteristics of the Unango subdomain includes, moderate to vertical foliations associated with upright to steep fold interference and dome/basin structures overprinting all pre-existing Irumide-related tectono metamorphic fabrics (Fullgraf, et al., 2022a). The general trend of regional fold axial planes changes from north-east in the south-east through north-south in the center, returning to north-east in the north. The northern part, unaffected by Pan-African thrusting, the Unango subdomain underlies the Lilongwe and Kasungu domains. Metamorphic conditions change across the contacts from granulite facies in the Unango subdomain to amphibolite facies in the Lilongwe and Kasungu subdomains (Tsunogae et al., 2021). The variation of metamorphic facies resulted from compression from (i) NW-SE Pan-African compression followed by (ii) E-W compression in a left-lateral simple shear regime. The SSZ is truncated in the south at high angle by the east northeast-west south west trending Lurio Shear Zone (LSZ), which separates the Unango subdomain from the Nampula subdomain. These tectonic movements cause the rise of the Unango subdomain as a metamorphic dome during an early stage of deformation. The northwest-southeast compression was responsible for the fold interference shown in Figure 2-3.

Pan-African tectonism was accompanied by intrusions of the Blantyre Suite, which are variably affected by deformation. Early plutons were emplaced along the boundary with the Lilongwe subdomain, implying a first stage of extension to enable their emplacement along this crustal-scale structure, which may be associated with the rise of the metamorphic dome (Figs. 2-2, 2-3; Fullgraf et al., 2022a). In the NSZ, intrusions were subsequently transposed during west-directed thrusting into the gneissic fabric, imparting large-scale, sheet-like geometries. Late-to post-tectonic plutons are circular in shape and locally deform and steepen the enveloping gneisses. Relatively undeformed early Blantyre granite and syenite bodies in the interior of the Unango subdomain dated at 573 ± 7 Ma indicating minimum age of regional deformation and metamorphism (Fullgraf, et al., 2022a). The ages coincide with U-Pb zircon rim ages

between 569 and 557 Ma, considered to date the timing of high-temperature granulite facies in the Unango subdomain (Tsunogae et al., 2021).

The Nampula subdomain in the southernmost part of Malawi is juxtaposed with the Unango subdomain along the east-to-northeast-trending LSZ. The Nampula subdomain has been interpreted as a suture of Mesoproterozoic and / or Pan-African age (Bingen et al., 2009; Goscombe et al., 2020). The Nampula subdomain underwent regional upper amphibolite facies conditions (Engvik et al., 2007). A second phase of high-pressure granulite facies conditions Pan-African (557 ± 16 Ma, 930°C, 18 kb) characterize mafic slivers that in Mozambique are concentrated along the LSZ and were combined into the Ocu Complex (Engvik et al., 2007). In Malawi, lenses of these rocks have been mapped across the whole unit. The tectonic style is marked by moderate to steep gneissic foliations and the general northeast to east trend.

Schema is proposed on the initial tectonic setting and the stacking as a result of the orogenic belts that impacted the MBC evolution, as shown in Figure 2-4.

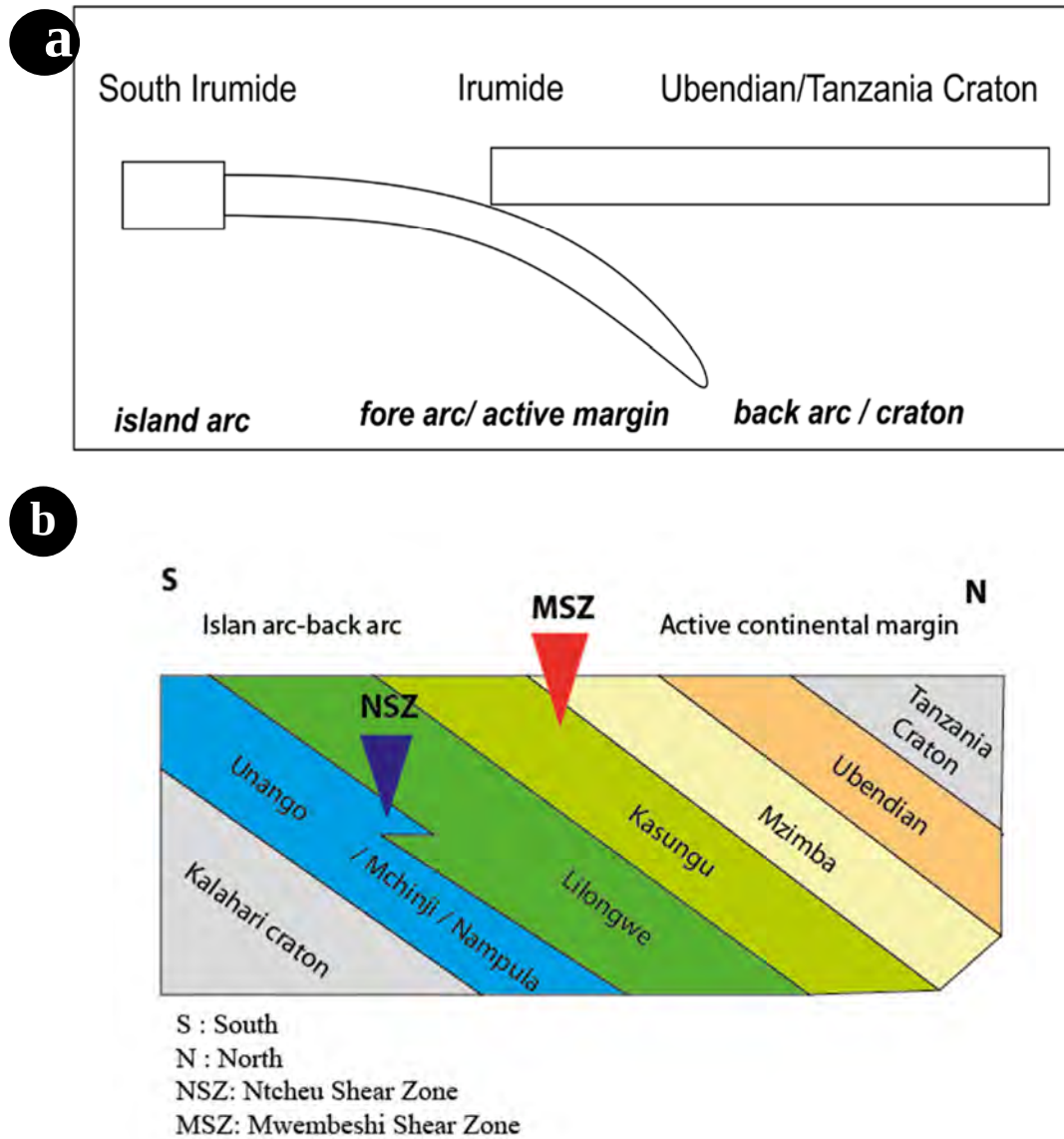


Fig. 2-4. (a) South (left) to north (right) schematic cross-section across Malawi showing the proposed plate tectonic setting during late Mesoproterozoic (CA 1070-1040), (b) Schematic structural stack of Malawian subdomains after the Irumide orogeny (Modified after Fullgraf et al., 2022).

2.2 Early alkaline magmatism

Both Irumide and South Irumide experienced magmatism during the Pan-African orogeny that emplaced the nepheline-syenite, monzonite, pegmatite granite, granodiorite and perthitic syenite and is related to the Tonian magmatism (Figs. 2-2, 2-3; Tsunogae et al., 2021) but its imprint varies between the Ubendian, Irumide and South Irumide domain. The imprints of Irumide magmatism are pronounced more in central and northern Malawi. The North Nyasa Alkaline province rocks in the Kangankunde area were dated 980-620 Ma, and are commonly gneissic, sub-alkaline, ferroan, LREE enriched and geochemically classified as intra-plate rifting (Fullgraf et al., 2022b).

The South Irumide magmatism is common in the Unango subdomain and prominent magmatism formed the Blantyre Suite, alkaline, LREE enriched and HREE depleted. The Blantyre Suite most classify geochemically as late- to post-collisional intrusions, emplaced in an intraplate setting (Fullgraf et al., 2022b).

The older plutons were transposed into the regional gneissic fabric rendered layer-parallel and subsequently folded (Fullgraf et al., 2022a). The most prominent of these structures occur in the NSZ that is dated by syntectonic migmatitic leucosome and shear-hosted granitoids at 583 ± 5 Ma and 575 ± 13 Ma, respectively (Fullgraf et al., 2022a). While younger circular bodies cut the regional fabric and locally deform the NSZ.

Rocks of the Blantyre Suite are rare in the Lilongwe subdomain and almost absent in the Kasungu subdomain (Fig. 2-2). This can be explained by (1) the variation in the metamorphic conditions between the Unango subdomain and the Lilongwe subdomain. (If the magmas are derived from crustal anatexis and implying that the metamorphism is of the Pan-African age), (2) the change in crustal stockwork (3) the variation of lithospheric thickness between Lilongwe subdomain (thick) and Unango subdomain (thin). In this model, the Unango subdomain represents a thinned lithosphere into which mantle magmas were preferably channelled (Fullgraf, et al., 2022a).

2.3 Chilwa Alkaline Province

The Chilwa Alkaline Province (C.A.P) marks the second alkaline magmatism that was emplaced during the lower Cretaceous from 138 to 105 Ma (Bloomfield, 1965; Garson & Walshaw, 1969; Carter & Bennett, 1973). The C.A.P succeed the Palaeozoic to Mesozoic Karoo Supergroup and its associated dykes dated by Ar-Ar to be Jurassic between ~168 and 179 Ma, broadly within the age range of the Drakensberg basalts of South Africa (Carter & Bennett, 1973; Jacobs et al., 2005). The intrusion of the C.A.P occurs within and outside the rift graben and is approximately 300-400 km in diameter (Fig. 2-5; Garson, 1965; Woolley, 2001). The C.A.P igneous rocks are comprised of the following in order of emplacement.

The earliest emplacement is the intrusions of syenite-quartz syenite and granite and is marked by Mulanje and Zomba-Malosa, and there are also several smaller intrusions (Fig. 2-5). The rocks are generally characterized as peralkaline with Suites of alkali amphiboles and pyroxenes (Woolley & Platt, 1986; Woolley, 1987b). The syenites are also related to the dykes that concentrate around them and some cut the central syenites and microsyenites. The dyke types include microsyenites (Mulanje), phonolite (Mongolowe) trachyte and nephelinite dykes (Salambidwe). There is also an extensive swarm of solvsbergite dykes from Salambidwe to Zomba Mountain (Fig. 2-5) and Bloomfield (1965) suggests these represent the youngest manifestation of the C.A.P. The swarm of alkaline dykes (solvsbergites, trachytes, microfoyaite, phonolites, nephelinites) are grouped in sub-orthogonal systems trending NE-SW and NW-SE, compatible with two extensional directions NW-SE and NE-SW. The NW-SE extension controlled the end of the Karoo sedimentation and the Stormberg volcanism was extended in the Jurassic that controlled the emplacement of the first systems of NE-SW alkaline dykes of the C.A.P. (Fig. 2-5; Castaing, 1991).

The nepheline syenite intrusions, are not abundant and the main occurrence forms the East-West-trending hills (e.g. Chikala Chaone-Mongolowe-Chinduzi hills). However, the major nepheline syenite intrusions are Junguni and Mauze hills (Fig. 2-5), while other smaller intrusions is Salambidwe hill. On the other hand basic rocks are scarce (Woolley, 1987). Although the occurrence of basic rock (dolerite and plugs and sills of gabbro and biotite pyroxenite) was recorded in Salambidwe, it is assumed to be a

product of metamorphism by syenites that were probably part of the earlier Stormberg (Karoo) igneous activity (Woolley, 1987). A similar observation was made on hornfels basic volcanic rocks from Chikala, Chaone and Mongolowe that were identified as nepheline tephrite. These were comparable to nephelinites from the Chilwa Island Carbonatites (Vail & Monkman, 1960; Vail & Mallick, 1965; Woolley & Jones, 1987).

The last to form in the emplacement of the C.A.P was the carbonatite. Detailed geological mapping and field descriptions of the carbonatite centers and volcanic vents rocks, together with the surrounding country rock, was documented by Garson (1962, 1965, 1966) and Garson & Smith Campbell (1965). In general the carbonatites were emplaced as centers of the intrusion. Most of the carbonatite develop extensive fenite aureoles, which occur with and without associated alkaline silicate rocks (Garson, 1966). The Kangankunde and Chilwa Island, carbonatites occurred with only minor plugs, dykes and xenoliths of trachyte, nepheline syenite, alnoite, lamprophyre and nephelinite, while at Tundulu, Carbonatite occurred with associated nepheline syenite and a variable dyke Suite including trachyte, phonolite, nephelinite and ijolite (Garson, 1965).

In addition, common in the C.A.P are numerous volcanic vents that range from few meters to kilometers in diameter (i.e. Lake Malombe vents; Garson, 1965). These events occurred within or around major intrusive centers or isolated from them. They are usually choked with agglomerates comprising nephelinite, carbonatite, fenite and trachyte, as well as fragments of the country rocks. The presence of the vents indicates the abundance of volatiles that must have been released, over and above losses through the principal centers, during the development of the province (Fullgraf et al., 2017).

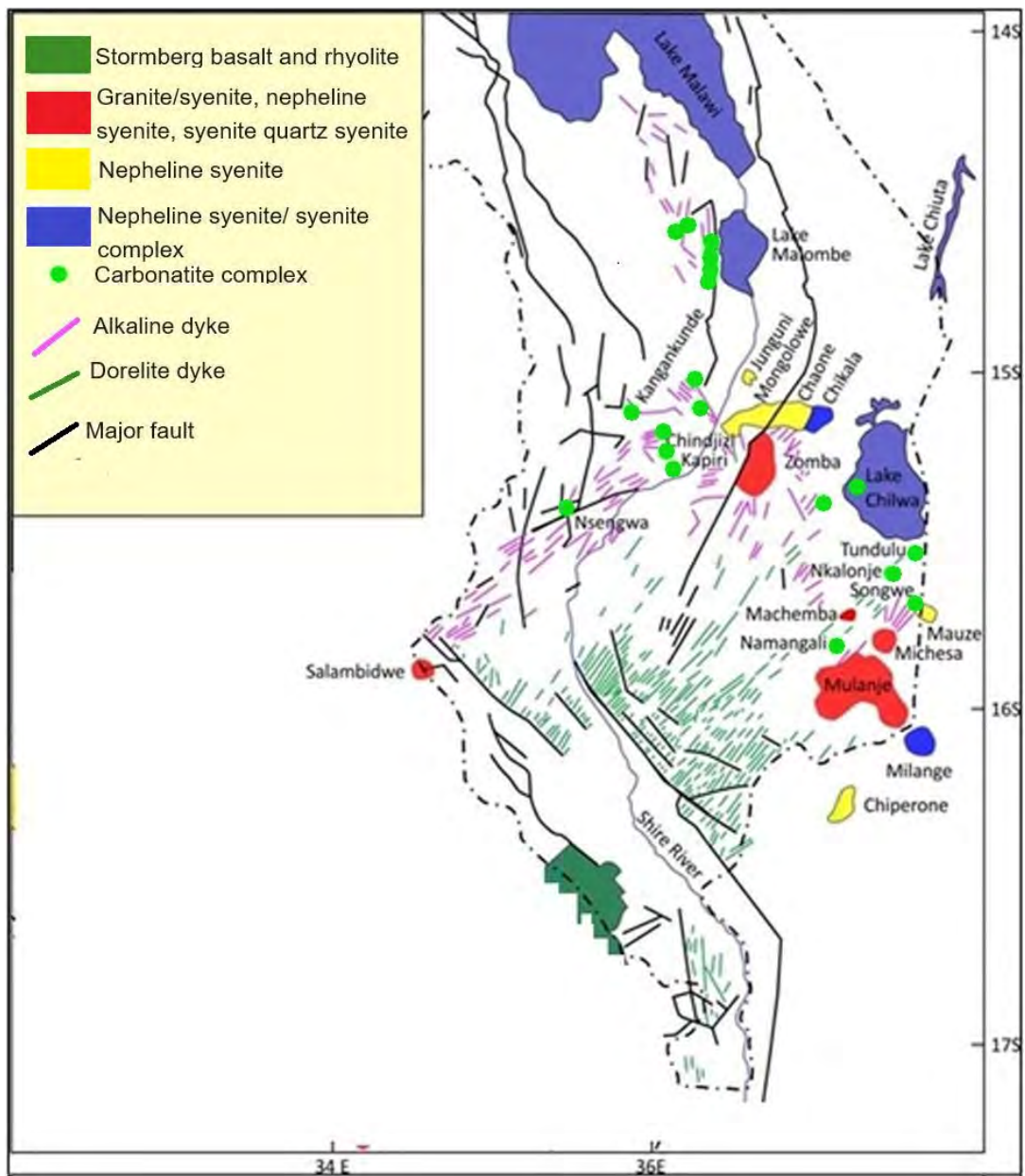


Fig. 2-5: Map of South Malawi showing structural and igneous geology. The major igneous centres of the Chilwa Alkaline Province are shown, as well as the dyke swarm and basaltic and rhyolitic lavas of late Karoo age (modified from Woolley, 1987).

2.3.1 Petrogenesis of the Chilwa Alkaline Province

A petrogenetic model for the C.A.P was proposed by Woolley (1987) on consideration of the following: (i) there is abundant occurrence of felsic rocks (i.e. nepheline syenites, syenites, quartz syenites and granites) and their hypabyssal equivalents but basic rocks are scarce. (ii) intrusive felsic rocks cover large area of the C.A.P ($>1000 \text{ km}^2$), but basic rocks are confined to scarce nephelinite dykes, and the remnant metamorphosed nephelinite lavas in the nepheline syenite complexes north of Zomba. (iii) absence of basic intrusions. and (iv) there are several types of felsic rock (Syenite-quartz syenite-granite, Nepheline syenite-syenite, and Nephelinite-nepheline syenite), although each rock type may occur in isolation. The felsic rock types have different magma compositions (Fig. 2-6; Woolley, 1987). Although the nephelinites and nepheline syenites derived from them, which are found in some of the carbonatite complexes (e.g. Tundulu and Chilwa Island), form a reasonably long evolutionary series, there are no rocks in the province that would constitute acceptable parental compositions for the nepheline syenite-syenite or syenite-quartz syenite-granite groups, if it is assumed that these rocks were generated by crystal fractionation of more basic magma. It is concluded that three contrasting primary magmas must have been involved, namely a nephelinite-carbonatite magma, phonolitic magma and trachytic magma.

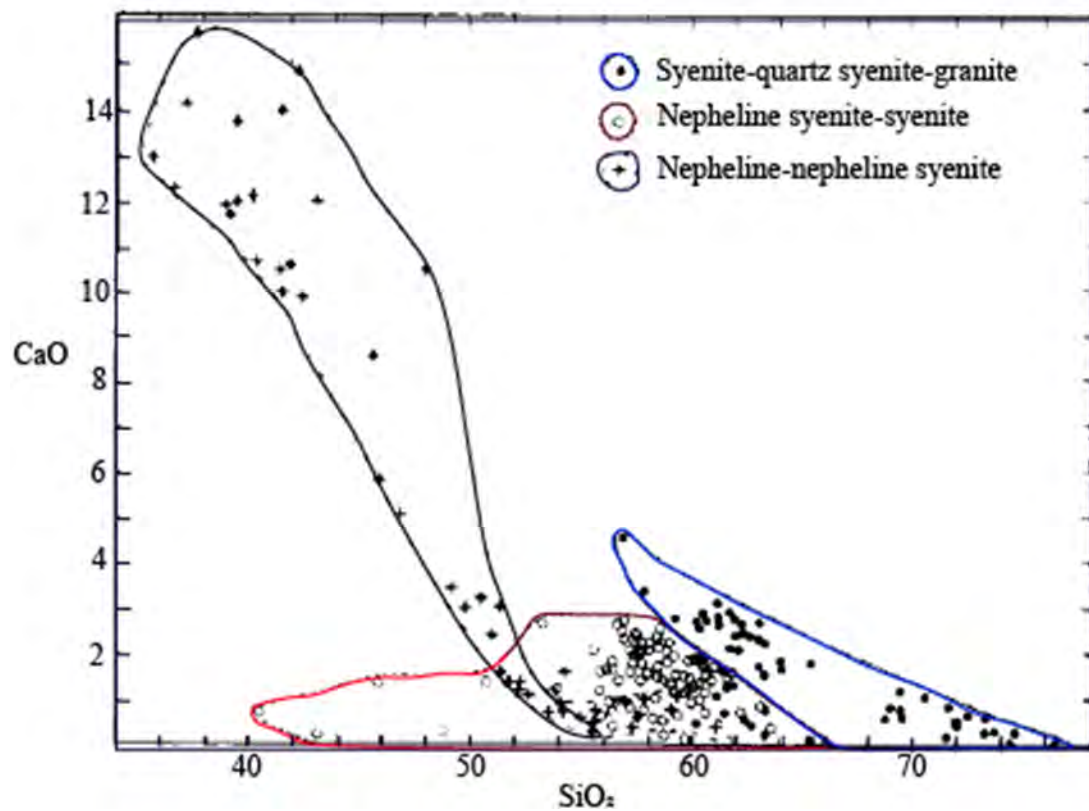


Fig. 2-6. Plot of SiO_2 vs CaO (wt. %) for rocks of the Chilwa Alkaline Province. Most of the data are for the northern part of the province, and a few are for the southern part. The three-magma series of the rock groups (adapted from Woolley, 1987).

References

- Bingen, B., Jacobs, J., Viola, G., Henderson, I. H. C., Skår, Ø., Boyd, R., Thomas, R. J., Solli, A., Key, R. M., and Daudi, E. X. F. (2009). Geochronology of the Precambrian crust in the Mozambique belt in NE Mozambique, and implications for Gondwana assembly. *Precambrian Research*, 170, pp.231–255.
- Bloomfield, K. (1965). The Geology of the Zomba Area, Government Printers, Zomba, Bulletin 16, 193pp.
- Bloomfield, K. (1968). The Pre-Karoo Geology of Malawi. Government Printer, Memoir 5, 166pp.
- Bloomfield, K., and Garson, M. (1965). The Geology of the Kirk Range-Lisungwe valley area. Government Printers, Bulletin 17, 234pp.
- Carter, G., and Bennett, J. D. (1973). The Geology and mineral resources of Malawi. Government Printers, Zomba. 62pp.
- Castaing, C. (1991). Post-Pan-African tectonic evolution of South Malawi in relation to the Karroo and Recent East African Rift Systems. *Tectonophysics*, 191, pp.55–73.
- Eby, G. N., Woolley, A. R., and Platt, V. D. G. (1998). Geochemistry and petrogenesis of nepheline syenites: Kasungu-Chipala, Ilomba, and Ulindi nepheline syenite intrusions, North Nyasa Alkaline Province, Malawi. *Journal of Petrology*, 39(8), pp.1405–1424.
- Engvik, A. K., Tveten, E., Bingen, B., Viola, G., Erambert, M., Feito, P., and Azavedo, S. D. E. (2007). P-T-t evolution and textural evidence for decompression of Pan-African high-pressure granulites, Lurio Belt, north-eastern Mozambique. *Journal of Metamorphic Geology*, 25, pp.935–952.
- Evans, K. R. (1965). The Geology of the Shire Highlands. Government Printers. Bulletin 18, 54pp.
- Fritz, H., Abdelsalam, M., Ali, K. A., Bingen, B., Collins, A. S., Fowler, A. R., Ghebreab, W., Hauzenberger, C. A., Johnson, P. R., Kusky, T. M., Macey, P., Muhongo, S., Stern, R. J., and Viola, G. (2013). Orogen styles in the East African Orogen: A review of the Neoproterozoic to Cambrian tectonic evolution. *Journal of African Earth Sciences*, 86, pp.65–106.
- Fullgraf, T., Bailly, L., Thomas, R. J., Boger, S. D., Hyvönen, E., Zammit, C., and

- Dombola, K. (2022). Kirk Range Lisungwe Valley area 17. In 1:100.000 Geological Map Series, Sheet explanation. Geological Survey Department, Zomba, 76p.
- Fullgraf, T., Thomas, R., Le Bayon, B., Boger, S. D., and Charles, N. (2022a). Tectonics. Memoir Series. Geological Survey Department, Malawi, 132pp.
- Garson, M., and Walshaw, R. (1969). The Geology of the Mlanje Area. Government Printers, Bulletin 21, 157pp.
- Garson, M. S. (1962). The Tundulu carbonatite ring-complex in Southern Nyasaland. Government Printer, Memoir 2. 235p.
- Garson, M. S. (1965). Carbonatites in Southern Malawi. Government Printers, Bulletin 15, 128pp.
- Garson, M. S. (1966). Carbonatites in Malawi. In *Carbonatites* Tuttle, O. Edition, Wiley-Interscience.
- Garson, M. S., and Smith Campbell, W. (1965). Carbonatite and Agglomeratic Vents in the Western Shire Valley. Government Printers, Memoir 3, 161pp.
- Goscombe, B., Foster, D. A., Gray, D., and Wade, B. (2020). Assembly of central Gondwana along the Zambezi Belt: Metamorphic response and basement reactivation during the Kuunga Orogeny. *Gondwana Research*, 80, pp.410–465.
- Jacobs, L. L., Winkler, D. A., Newman, K. D., Gomani, E. M., and Deino, A. (2005). Therapsids from the permian Chiweta Beds and the age of the Karoo Supergroup in Malawi. *Palaeontologia Electronica*, 8(1).pp1-23.
- Thatcher, E., and Walter, M. (1968). The Geology of South Lilongwe Plain and Dzalanyama area. Government Printers, Zomba, Bulletin 23. 77pp.
- Tsunogae, T., Uthup, S., Nyirongo, M. W., Takahashi, K., Rahman, M. S., Liu, Q., Takamura, Y., and Tsutsumi, Y. (2021). Neoproterozoic crustal growth in southern Malawi: New insights from petrology, geochemistry, and U–Pb zircon geochronology, and implications for the Kalahari Craton–Congo Craton amalgamation. *Precambrian Research*, 352, 106007.
- Vail, J. R., and Mallick, D. I. J. (1965). The Mongolowe Hills nepheline-syenite ring-complex, southern Malawi. Record, Geological Survey Malawi 3, pp.49–60.
- Vail, J. R., and Monkman, L. J. (1960). A geological reconnaissance survey of the Chaone Hill ring complex, southern Nyasaland. *South African Journal of Geology*,

- 63(1), pp.119–135.
- Walshaw, R. D. (1965). The Geology of the Ntcheu-Balaka Area Government Printers, Zomba, Bulletin 19, 96pp.
- Walter, M. (1972). The Geology of the Lilongwe-Dowa Area. Government Printers, Zomba. Bulletin 26, 38pp.
- Woolley, A. R. (1987). Lithosphere metasomatism and the petrogenesis of the Chilwa Province of alkaline igneous rocks and carbonatites, Malawi. *Journal of African Earth Sciences*, 6(6), pp.891–898.
- Woolley, A. R. (2001). Alkaline Rocks and Carbonatites of the World Part 3: Africa. The Geological Society of London.
- Woolley, A. R., and Jones, G. C. (1987). The petrochemistry of the northern part of the Chilwa alkaline province, Malawi. Geological Society Special Publication, 30, pp.335–355.
- Woolley, A. R., and Platt, G. (1986). The mineralogy of nepheline syenite complexes from the northern part of the Chilwa Province, Malawi. *Mineralogical Magazine*, 50, pp.597–610.

Chapter 3 Sample description and methodology

3.1 Introduction

Samples for the research were collected during the field campaigns in 2022 and 2023. Samples collected were outcrops for all three study sites including drill core from Kangankunde carbonatite. Samples from all study sites show a colour variation from leucocratic to melanocratic while grain size varies from fine to coarse (Fig. 3-1). Outcrops samples at Kangankunde carbonatite, were collected for lithologies either highly weathered or not observed on the drill core. Purpose sampling technique was used targeting lithological variations, mineralization, and fresh rock, as most of the lithologies were weathered. Methods used includes field observation, petrography, whole-rock geochemistry and isotope geochemistry. All methods were applied to Kangankunde, Tundulu and Nkalonje carbonatites.

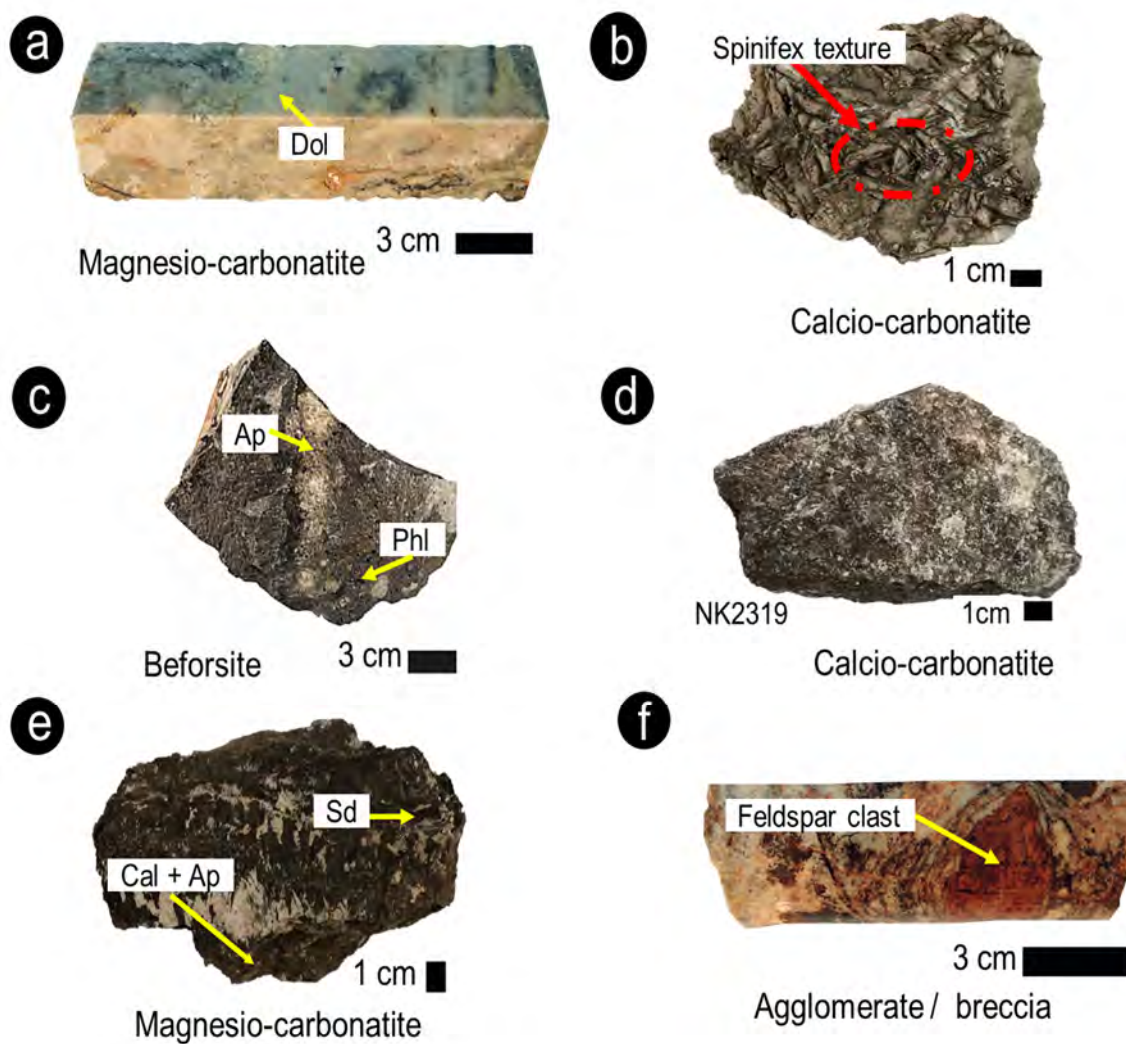


Fig. 3-1 Photographs of representative samples (a) drill core sample of leucocratic, fine to medium grained magnesio-carbonatite from Kangankunde carbonatite, (b) outcrop sample of leucocratic, coarse grained calcio-carbonatite from Tundulu carbonatite, (c) outcrop of mesocratic fine to medium grained beforite from Kangankunde, (d) outcrop sample of mesocratic, fine to medium grained calcio-carbonatite, (e) outcrop of melanocratic, fine to medium grained magnesio-carbonatite, (f) drill core sample of leucocratic agglomerate with feldspar xenocryst.

3.2 Sample preparation

Sample preparations were done at the Geological Survey Department, Malawi and Kyushu University, Japan. Petrographic analysis used thin sections. Thin section preparation steps include cutting samples into blocks of approximately 2.5 cm x 4 cm, grinding and polishing the block, gluing the sample to slide glass, drying the sample on a hot plate, trimming the samples to 3mm, grinding and polishing to 200 μm (Fig. 3-2a).

X-ray diffractometry (XRD) samples were hand crushed using an agate crucible following the manual on sample preparation for XRD of the Economic Geology Laboratory, Kyushu University.

Whole-rock geochemical analysis assessed the major- and trace-element composition. The first step was the separation of carbonates and silicate mineral fragments. Separation of carbonate and silicate mineral fragments was done to improve the chemical composition to that of initial carbonatite magma. The carbonates were pulverized to 50 μm using a tungsten carbide. About 2 grams of pulverized samples were compressed into pellets using a hydraulic press. Hydraulic press was set at 4 tons. Pellet was held by polythene sample ring (Fig. 3-2b). Powder sample mounting was conducted as described in the pellet preparation manual of the Economic Geology Laboratory, Kyushu University.

Glass beads were prepared as described by Zongshou et al. (2003; Fig. 3-2c). and used a sample flux ratio of 1:2. (1.8: 3.6g) as described in the manual for glass beads preparation of the Economic Geology Laboratory of Kyushu University. The flux composition was 80% lithium tetraborate and 20% lithium metaborate ($\text{Li}_2\text{B}_4\text{O}_7$ / LiBO_2). The advantage of using the glass bead method includes its suitability for bulk composition analysis, high degree of internal homogeneity for trace elements, a quick and simple preparation method that attacks resistant phases such as zircon without the need for acid dissolution (Zongshou et al., 2003). In addition, fusion of the sample leads to increased detection limits and either losses or gains from the crucible are realised (Sylvester, 2001; Norman et al., 2003). Although potential drawbacks in terms of contamination are inevitable from the flux. Contamination was considered negligible in this study as the flux and crucible elemental composition were not considered for the analysis.

Furthermore, the combination of XRF and LA-ICP-MS analysis of $\text{Li}_2\text{B}_4\text{O}_7$ / LiBO_2 fused glasses was desirable for the study as it provided high-quality major and trace element data when an appropriate matrix-matched calibration is adopted (Zongshou et al., 2003).

Carbon and oxygen isotope analysis sample preparation includes crushing rock samples to 0.1 to 6.0 mm grits; hand picking of carbonate mineral separates (calcite, strontianite, ankerite, dolomite) using a tweezer with the aid of a micro binocular and confirmed using a Rigaku ultima IV X-ray diffractometer

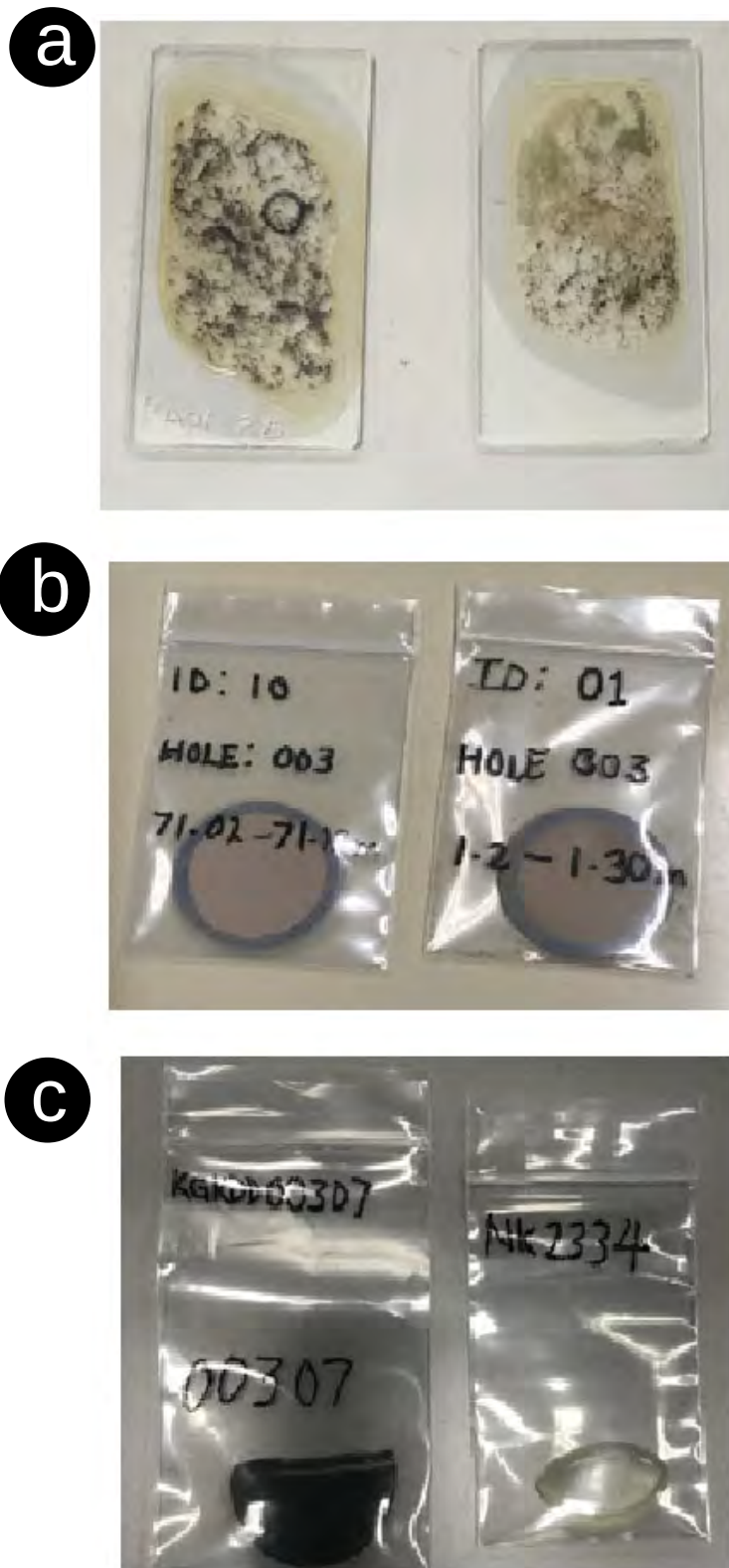


Fig. 3-2 Product of samples prepared. (a) thin section, (b) pellet, (c) glass bead

3.3 Sample analysis

Petrographic analysis and whole-rock geochemistry analysis were done at Kyushu University, Japan, while carbon and oxygen isotope analysis was conducted by Activation laboratories (Actlabs), Canada.

3.3.1 Petrographic analysis

Petrographic analysis helps in determination of the origin, whether igneous, sedimentary, or metamorphic, the mineral content for the classification of rock and evidence of alteration and or deformation by studying fabric, color, grain size, and texture (de Oliveira Frascá, 2018). Samples were analyzed for mineral assemblage and texture identification using a Nikon Eclipse LV100POL optical microscope. Backscattered electron (BSE) images were acquired using a Hitachi SUD3500 scanning electron microscope (SEM) equipped with an energy-dispersive analyzer EDAX Octane Plus energy dispersive X-ray spectrometer (EDS). The samples were coated with a conductive carbon layer and analyzed at high vacuum at an accelerating voltage of 15 kV and working distance of 10 mm. The use of SEM based analysis enables identification primary magmatic signatures from post magmatic signatures (Anenburg, Mavrogenes, & Bennett, 2020).

Mineral assemblage identification was also supplemented by X-ray diffractometry (XRD) using a Rigaku Ultima-IV. The XRD operating conditions included energy of 50 kV and 40 mA current, slit size of 0.8 mm, continuous scan mode speed of $2^\circ/\text{min}$, step width 0.02° , and scan range from 2 to 65° . The advantage of combining XRD, SEM-EDX and optical petrography is the reduction of uncertainty by improved spatial resolution for observation and mineral composition in the case of SEM (Szyrkowska, 2005).

3.3.2 Geochemical analysis

The first step in geochemical sample analysis was the determination of Loss on ignition (LOI). LOI was calculated from total weight loss after igniting the samples at 1000 °C for 1 hours (e.g. Thuy et al., 2014). Major element concentrations including SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₃, SrO, BaO were

determined from the sample pellets using a Rigaku ZSX Primus IV energy dispersive X-ray fluorescence (XRF). Although F contents were determined by XRF, F was not considered in this study due to its accuracy. The analytical error was estimated to be < 2 %.

Trace element compositions of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu, Ti, Ni, Co, Zn, Ga, Rb, Zr, Nb, Mo, Hf, Ta, Pb, Th, and U were determined by Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The LA-ICP-MS system consists of an SS-LB-RAIZIN4500FEMTO laser and an Agilent 7900 ICP-MS. Fused beads for trace element determination were prepared following the Zongshou et al. (2003). The LA-ICP-MS system consists of a SS-LB-RAIZIN4500FEMTO laser and an Agilent 7900 ICP-MS. Each sample batch was bracketed with replicate analyses NIST 612 for the instrumental drift correction. NIST 612 was also used as an external standard for all elements, and Ca^{43} was used as an internal standard using the CaO concentration determined by XRF. The rock standard JB-2 from the Geological Survey of Japan (Imai et al., 1995) was also analyzed to evaluate the sample preparation procedure and the accuracy of the analysis. Chemical alteration of the sample was evaluated by calculating CaO molar weight and weathering index defined by Parker, (1970).

3.3.3 Isotope analysis

Carbon and oxygen isotopic analysis of the carbonates separated from selected carbonatite rocks was conducted using Activation laboratories analytical protocol. Approximately 5 mg of pulverized carbonate separates were analyzed at 550–600 °C following the conventional BrF_5 procedure of Clayton and Mayeda (1963), using the dual inlet Thermo-Finnigan DeltaPlusXP Isotope-ratio mass spectrometer (IRMS). The standard material NBS28 was used. The carbon and oxygen isotope results are reported in the standard $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ notation as permille (‰) deviations from Vienna Pee Dee Belemnite (V-PDB) and Vienna Standard Mean Ocean Water (VSMOW), respectively. Analysis precision was 0.5‰.

References

- Anenburg, M., Mavrogenes, J. A., and Bennett, V. C. (2020). The fluorapatite P-REE-Th vein deposit at Nolans Bore: Genesis by carbonatite metasomatism. *Journal of Petrology*, 61(1), pp.1–42.
- Clayton, R. N., and Mayeda, T. K. (1963). The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochimica et Cosmochimica Acta*, 27(1), pp.43–52.
- de Oliveira Frascá, M. H. B. (2018). Petrographic Analysis. In Bobrowsky P. T. and Marker B. (Eds.), *Encyclopedia of Engineering Geology*. Encyclopedia of Earth Sciences Series. Springer, Cham. pp. 705–713.
- Imai, N., Terashima, S., Itoh, S., and Ando, A. (1995). Compilation of analytical data for minor and trace elements in seventeen GSJ geochemical reference samples, “igneous rock series. *Geostandards Newsletter*, 19(2), pp.135–213.
- Norman, M., Robinson, P., and Clark, D. (2003). Major- and trace-element analysis of sulfide ores by laser-ablation ICP–MS, solution ICP–MS, and XRF: new data on international reference materials. *The Canadian Mineralogist*, 41(2), pp.293–305.
- Parker, A. (1970). An index of weathering for silicate rocks. *Geological Magazine*, 107(6), pp.501–504.
- Sylvester, P. (2001). Trace element analysis of fused whole rock glasses by laser-ablation ICPMS. In Sylvester P. (Ed.), *Laser-Ablation-ICPMS in the Earth Sciences: Principles and Applications (Short Course)*. *Mineralogical Association of Canada*. , pp. 147–162.
- Szynkowska, M. (2005). Scanning Electron Microscopy. *Encyclopedia of Analytical Science Second Edition*, pp.134–143.
- Thuy, T. N., Wada, H., And, I., and Taketo, S. (2014). Geochemistry and petrogenesis of carbonatites from South Nam Xe, Lai Chau area, northwest Vietnam. *Mineralogy and Petrology*, 108(3), pp.371–390.
- Zongshou, Y., Norman, M. D., and Robinson, P. (2003). Major and trace element analysis of silicate rocks by XRF and laser ablation ICP-MS using lithium borate fused glasses: Matrix effects, instrument response and results for international reference materials. *The Journal of Geostandards and Geoanalysis*, 27, pp.67–89.

Chapter 4 : Petrochemistry of the Kangankunde carbonatite

4.1 Introduction

The Kangankunde carbonatite in the Chilwa Alkaline Province (C.A.P) in southern Malawi has been studied previously in terms of its origin, fluid evolution, and REEs mineralization (Garson, 1965; Holt, 1965; Cressey et al., 1999; Duraiswami & Shaikh, 2014; Broom-Fendley et al., 2016a, 2017c; Chikanda et al., 2019). These studies proposed that primary REEs mineralization occurred in a magmatic stage and was later overprinted by hydrothermal activities. Mitchell (2005) suggested that fluid-wall rock interaction from several sources contributed to the enrichment of REEs in Kangankunde carbonatite, which is enriched in light rare earth elements (LREEs). Although the magmatic nature of primary REEs mineralization has been reported on the Kangankunde carbonatite, the evolution path and which magmatic process(es) influenced the REE enrichment are yet to be well understood. Furthermore, there is limited information on the conditions of the Malawi basement complex (MBC) architect for the emplacement of the Kangankunde carbonatite.

The Kangankunde carbonatite is located in SW Malawi, within the Lilongwe subdomain, a few kilometers from the western border of the East African Rift System (EARS) (Garson & Smith Campbell, 1965, Fullgraf et al., 2022b; Fig. 2-2). The Kangankunde carbonatite forms a low hill of about 800 m above the surrounding plain (Fullgraf, et al., 2022b). Garson (1962, 1965) gave detailed geology. The bulk $^{147}\text{Sm}/^{143}\text{Nd}$ isotopic age from quartz-apatite in the Kangankunde carbonatite was dated at approximately 136 ± 11 Ma (Wall, 1994).

The MBC rock in the Kangankunde area are gneisses assigned to Lilongwe subdomain, formed by regional metamorphism of arkose or feldspathic sandstone within intercalations of more argillaceous sediments. The grade of metamorphism is preferable to the transitional stage between the amphibolite and granulite's facies (Bloomfield and Garson 1965). The gneisses underwent several stages of intrusion and deformation, including the placement of a much earlier episode of late Precambrian

alkaline magmatism (Bloomfield, 1968). Regional Pan-African deformation manifested through metamorphic overprinting (Woolley et al., 1991).

The Kangankunde carbonatite was emplaced as a circular ring complex (Fig. 4-1). The emplacement sequence from the contact with MBC rocks (hornblende biotite gneiss) started with orthoclase fenite, characterized by brecciation and agglomeration consisting mainly of albite toward the carbonatite breccia. The carbonatite breccia and agglomerate contain feldspar and carbonatite clasts. The abundance of feldspar clasts decreases in carbonatite breccia and agglomerate toward the main carbonatite. Main carbonatite includes magnesio-carbonatite (carbonatized feldspathic), ferruginous calcio-carbonatite (intrusive and remobilized carbonatite), and ferro-carbonatite (manganiferous carbonatite). However, apatite-rich dolomite carbonatite (beforsite), which is also magnesio-carbonatite, is the earliest-formed carbonatite (Garson, 1965; Garson & Smith Campbell, 1965;). What makes the Kangankunde carbonatite different from other carbonatites within the C.A.P and the carbonatite of the world is the absence of associated alkaline silicate rocks within the complex (Garson, 1965). The Kangankunde carbonatite is exposed now as isolated inselbergs within a Cenozoic lacustrine peneplain (Eby et al., 2004).

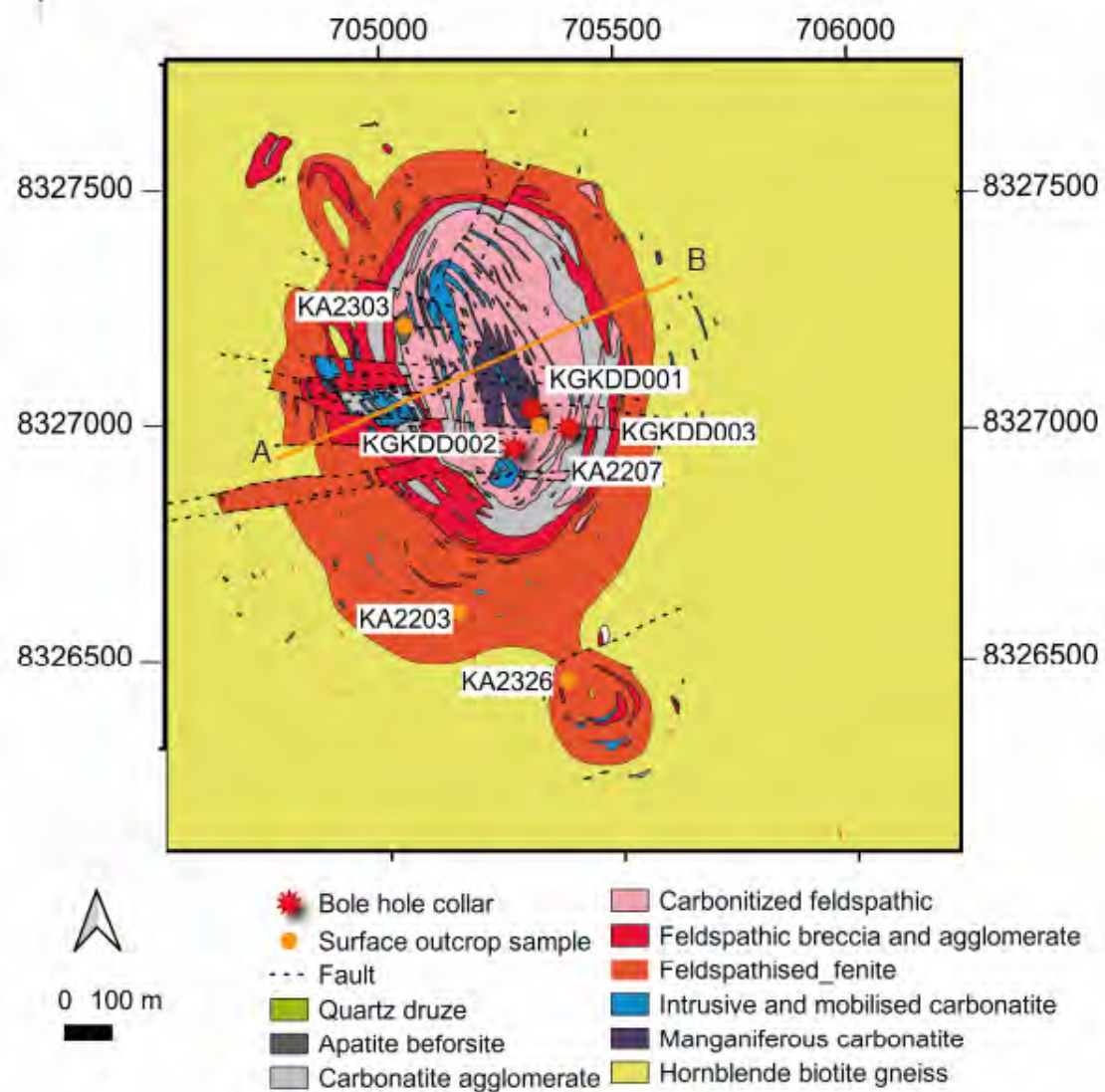


Fig. 4-1. Map of Kangankunde carbonatite showing local geology, drilled hole collar and sampling point (modified after Garson 1965). Drill collar coordinates from Lindian Resources Limited.

4.2 Samples description

Samples were collected from drill cores KGKDD003, KGKDD002, and KGKDD001, drilled up to 145, 188, and 300 m depths, respectively. In addition, surface rock chips from surface outcrops were also collected for lithology either not observed on drill core or heavy weathered. The three drill cores selected for this study were obtained in the 2023 drilling campaign conducted by Lindian Resources Limited. The boreholes were drilled obliquely and intersected several lithologies along the Kangankunde carbonatite. Sampling points on drilled core are shown in Figure 4-2 while samples location for outcrops are shown in Figure 4-1. Each sample was a quarter of the drilled core approximately 10 cm long. Representative sample photographs are shown in Figure 4-3.

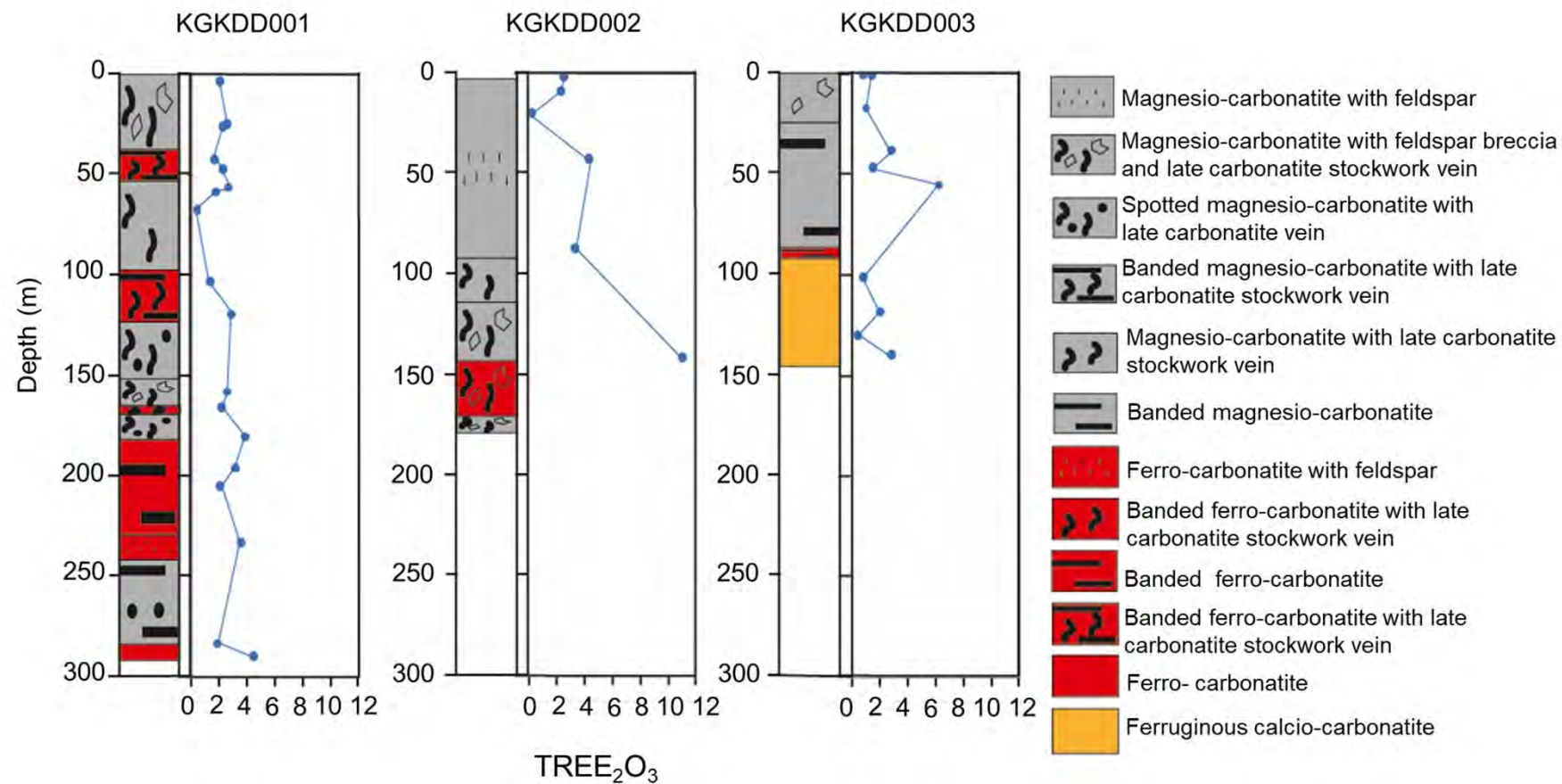


Fig. 4-2 Section of exploration drilled cores showing lithological variation, total rare earth element (TREE₂O₃) distribution at depth and sampling locations.

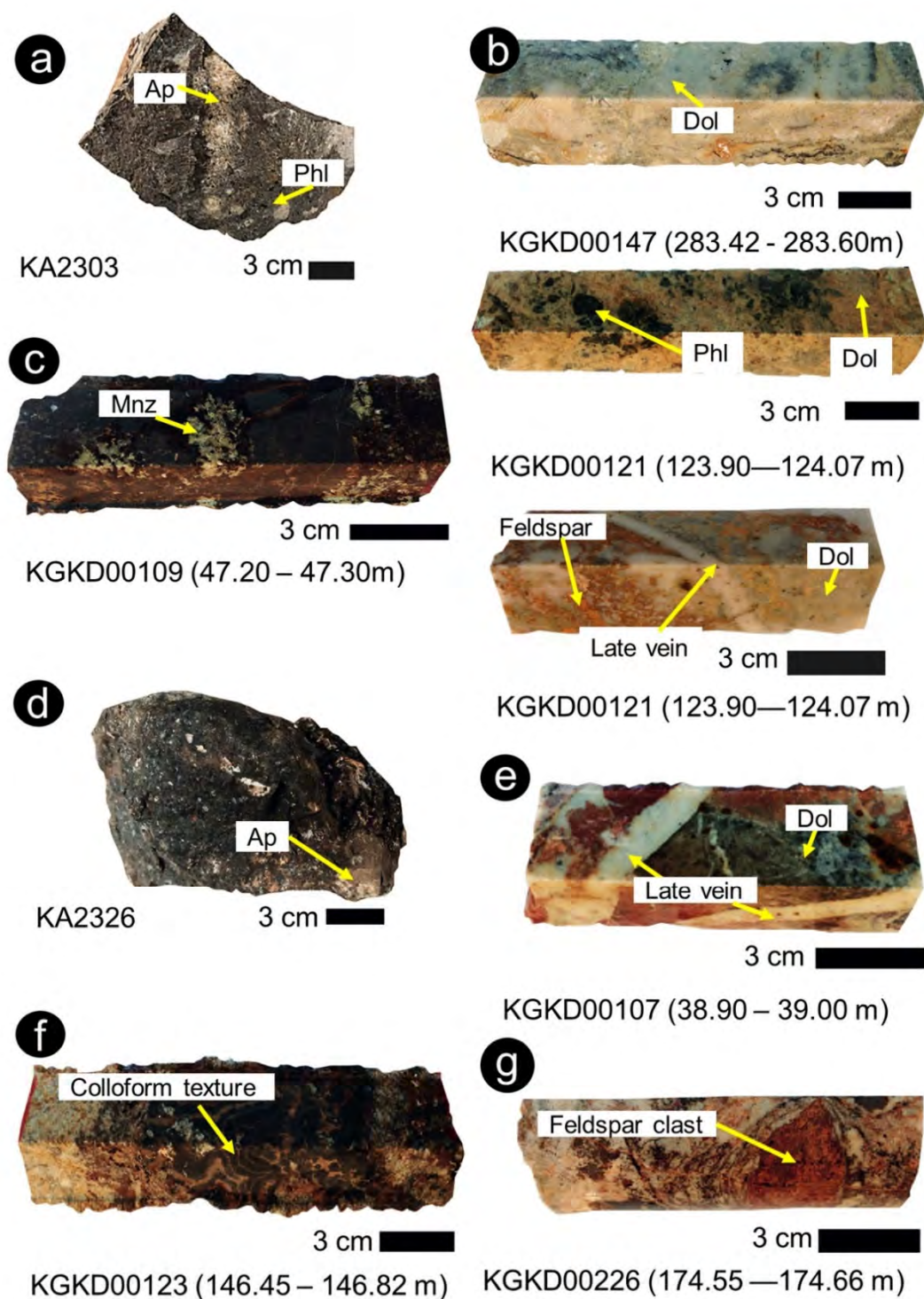


Fig. 4-3 Representative photos of drill core and rock chip samples. (a) beforosite, the earliest carbonatite rock, (b) magnesio-carbonatite in whitish to light grey color, and magnesio-carbonatite with greenish spots of weathered phlogopite and magnesio-carbonatite with highly resorbed feldspar xenolith, (c) ferro-carbonatite, (d) ferruginous calcio-carbonatite that formed at a later stage of emplacement, (e) late carbonatite dyke that cut early carbonatite, (f) colloform texture on ferro-carbonatite indicating hydrothermal activity, (g) agglomerate/breccia with carbonatite and feldspar clast. Abbreviation: Ap - apatite, Phl— phlogopite, Dol — dolomite, Mnz — monazite

4.3 Results

4.3.1 Drill core and outcrop observations

4.3.1.1 Lithological variation

A summary of drill core logs that illustrates the lithological variations at holes KGKDD001, KGKDD002, and KGKDD003 are shown in Figure 4-2. In general, the carbonatites were weathered to brown to dark brown in color. Based on the field observation and core logging, identified rocks in the Kangankunde carbonatite, including beforsite, magnesio-carbonatite, ferro-carbonatite, ferruginous calcio-carbonatite, and agglomerate/breccia of carbonatite and fenite rocks.

Beforsite is an apatite-rich dolomite carbonatite that occurs as a small outcrop within the Kangankunde carbonatite (Fig. 4-1). Beforsite is fine-grained, characterized by a grayish-greenish color (Fig. 4-3a). Beforsite at Kangankunde shows evidence of alteration, manifested by brown-colored stain.

Magnesio-carbonatite shows different textural and mineralogical variations over a centimetre distance; based on these variations, this rock unit was further classified into three types including the spotted magnesio-carbonatite, banded magnesio-carbonatite, and feldspar-bearing magnesio-carbonatite. The spotted magnesio-carbonatite is whitish gray to brown in color, fine to medium-grained and contains greenish spots of phlogopite resulting from weathering (Fig. 4-3b). It is observed mainly on drilled core KGKDD001 at 124.0-150.6 m, 170.0-175.7 m and 240.4-286.6 m depth intervals and is occasionally cut by carbonate vein. The banded magnesio-carbonatite is dark-whitish grey and dark-brown in color, and fine to medium-grained. Pink to reddish feldspar is commonly observed in banded magnesio-carbonatite, which occurs at 17.0-91.8 m depth interval along the KGKDD003 drill core. Magnesio-carbonatite with feldspar breccia is dark to light gray and pink color, fine to medium-grained with a granular texture. Feldspar in this rock occurs as an altered xenocryst. The magnesio-carbonatite with feldspar was observed at 56.1–98.2 m and 90.0–111.6 m depth intervals along the KGKDD001 and KGKDD002 drill core, respectively, and contains 2–60 mm thick carbonate veins

Ferro-carbonatite is whitish to dark reddish-brown in color and is fine to medium-grained with granular to equigranular texture and altered (Fig. 4-3c). The ferro-carbonatite variation includes; fine to medium-grained ferro-carbonatite and banded ferro-carbonatite. The fine to medium-grained ferro-carbonatite is dark-brown to reddish-brown in color and was observed on KGKDD001 drill core at 230.9–240.1 m depth interval. The banded ferro-carbonatite although is also fine to medium-grained, commonly has interbedding structure, characterized by layers of different colors, along the drill hole KGKDD001 and KGKDD003, at 175.7–230.9 m and 86.4–91.1m depth intervals. At shallower depth of the KGKDD001 drill core (i.e., 39.5–56.1 and 98.2–124.0 m), the banded ferro-carbonatite is also observed, crosscut by carbonate stockwork veining. Mineralization occurred sporadically in the margin between dark and light-coloured carbonatite.

Ferruginous calcio-carbonatite occurs with occasional pink patches of apatite and is fine to coarse-grained (Fig. 4-3d). This is associated with later carbonatite dykes, with approximately 2-60 mm thickness that cut almost all carbonatites (Fig. 4-3e). The dark areas in ferro-carbonatite and ferruginous calcio-carbonatite exhibit colloform texture represented by Fe-oxides (Fig. 4-3f). This was observed on KGKDD003 at 98.6-144.0 m depth interval. Carbonatite agglomerate/breccia consists of angular silicate clasts (i.e. feldspars) cemented mainly by pyrolusite matrix (Fig. 4-3g).

Furthermore, feldspathic breccia make contact between magnesio-carbonatite and fenite represents the initial intrusion of the carbonatite magma into the country rock (Fig. 4-1).

Fenite is reddish to pink in color and fine to medium-grained with a granular texture. It is characterized by orthoclase, carbonates, and amphiboles.

4.3.1.2 Mode of occurrence of REEs mineralization

From the drill core observations, monazite appears to be the main REEs-bearing mineral in Kangankunde carbonatite. On drill cores, monazite is green in color. The REEs mineralization in this deposit occurred in different forms. These forms include dissemination of mainly monazite in almost all carbonatites (Fig. 4-4a-b); acicular mineralization of mainly monazite within magnesio-carbonatite (Fig. 4-4c-d); and

patchy mineralization, clusters of mainly monazite associated with miarolitic cavities in magnesio-carbonatite (Fig. 4-4e-f).

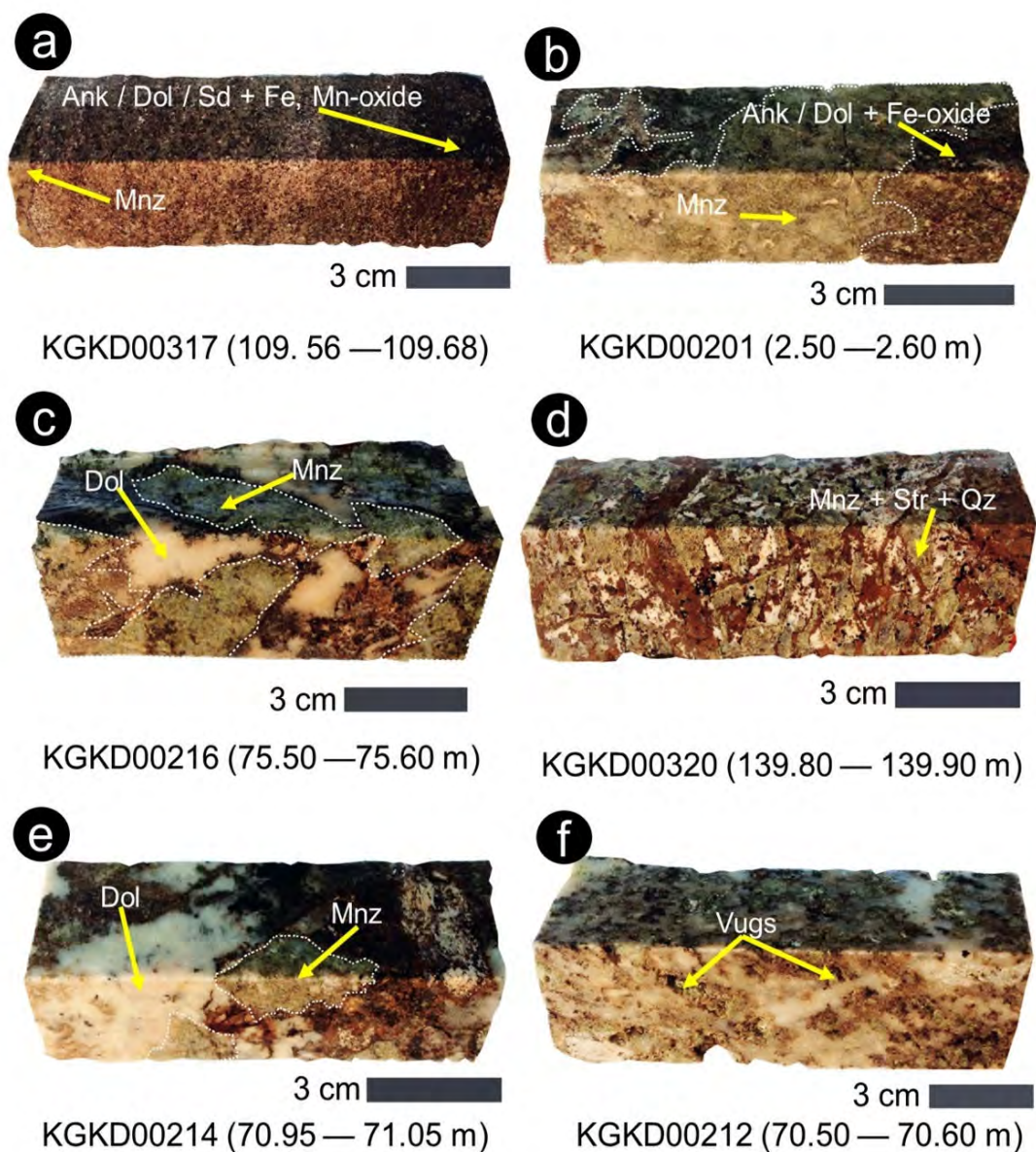


Fig. 4-4 Photographs of representative samples showing the mode of occurrence of the mineralization in Kangankunde. (a-b) monazite disseminated in ferro-carbonatite, (c-d) acicular monazite in magnesio-carbonatite, (e-f) magnesio-carbonatite showing patchy mineralization and miarolitic cavities indicating the presence of the magmatic-hydrothermal fluid phase. Abbreviation: Ank—ankerite, Brt—barite, Dol—dolomite, Fe-oxide — iron oxide, Mnz—monazite, Str—strontianite.

4.3.2 Petrography

4.3.2.1 Beforsite

The beforsite is composed mainly of apatite, dolomite, phlogopite, and magnetite. Monticellite, calcite, and perovskite are present as accessory minerals (Fig. 4-5a-b). Apatite is dominant and has an elongated oval in shape, displaying oscillatory zoning and reaction rim on its edges. In addition, apatite appeared to have replaced calcite and dolomite. Calcite is anhedral. Dolomite is abundant and forms the main groundmass. Dolomite is fine-grained and occurs as both subhedral and anhedral. Magnetite is subhedral and replaced dolomite and monticellite (Fig. 4-5b). Most of the silicate minerals were altered.

4.3.2.2 Magnesio-carbonatite

The magnesio-carbonatite is composed mainly of Fe-bearing dolomite, calcite, monazite and strontianite. Pyrochlore, apatite, goyazite and quartz are also present in magnesio-carbonatite. Fe-bearing dolomite is dominant and occurred as subhedral to anhedral. Monazite is interstitial or intergranular between Fe-bearing dolomite (Fig. 4-5c). as inclusion in Fe-bearing dolomite and quartz (Fig. 4-5d-e). Additionally, monazite replaced Fe-bearing dolomite or strontianite (Fig. 4-5f-g). Strontianite overprinted Fe-bearing dolomite and quartz and enveloped monazite (Fig. 4-5e). Pyrochlore occurs as an accessory mineral that is euhedral to subhedral overprints phlogopite (weathered green spots) and goyazite (Fig. 4-5g-h). Quartz occurred from euhedral to anhedral, zoned with monazite inclusions (Fig. 4-5e). These characteristics were observed in samples from drill cores KGKDD001 at 123.50–150.60 m, 170.00–175.70 m and 244.40–286.60 m depth intervals, and KGKDD002 at 110.80–143.40 m depth intervals. XRD representative pattern are given in Appendix A1.

4.3.2.3 Ferro-carbonatite

The mineral assemblage of the ferro-carbonatite includes Fe-bearing dolomite, Mg-bearing siderite, hematite, apatite, monazite, strontianite, goyazite, daquingshanite, and pyrolusite. Mg-bearing siderite is dominant with a dissolution texture. Monazite is euhedral forms spherulitic texture. Mg-bearing siderite is overprinted Fe-dolomite and

has a dissolution texture. Monazite overprints Fe-dolomite and Mg-siderite. Strontianite overprints monazite (Fig. 4-5i). Pyrolusite occurs as veinlets and sometimes as dissemination (Fig. 4-5j). Both pyrolusite and Fe-bearing dolomite were altered to Mn- and Fe-oxides, respectively. These characteristics were observed in samples from drill cores KGKDD001 (at 0.0–47.20 m and 180.73–232.48 m depth intervals), KGKDD002 (at 174.55 m depth), and KGKDD003 (at 23.30 m and 86.45 m depths). XRD representative pattern are given in Appendix A1.

4.3.2.4 Ferruginous calcio-carbonatite

Under the microscope, the mineral assemblage of the ferruginous calcio-carbonatite includes Fe-bearing dolomite, fluorapatite, ankerite, calcite, strontianite, monazite, fluorite, hematite, synchysite and Fe-oxides (Fig. 4-5k-l). Ankerite and Fe-bearing dolomite are dominant; ankerite appears to have replaced Fe-bearing dolomite and coexists with fluorite (Fig. 4-5k). Fluorite and strontianite occurred with consertal texture. Synchysite has a dissolution texture being replaced by fluorite (Fig. 4-5k). Monazite is replaced by fluorite. Hematite overprinted Fe-bearing dolomite (Fig. 4-5l). In addition, fluorapatite shows a dissolution texture and is replaced by dolomite and quartz (Fig. 4-5m). The ferruginous calcio-carbonatite is also associated with sporadic ankerite vein cutting the older carbonatites. XRD representative pattern is given in Appendix A1.

4.3.2.5 Fenite

Under the microscope, the mineral assemblage in fenite includes orthoclase, biotite, calcite, dolomite, quartz, and hematite. Fenite is altered and comprised of turbid orthoclase, quartz, biotite, dolomite, and apatite (Fig. 4-5p). Orthoclase is dominant but plagioclase is also present. Quartz occurred subhedral to anhedral in association with orthoclase. Biotite occurred anhedral as shreds were replaced by orthoclase. Dolomite occurred anhedral interstitial to orthoclase. Hematite overprinted orthoclase.

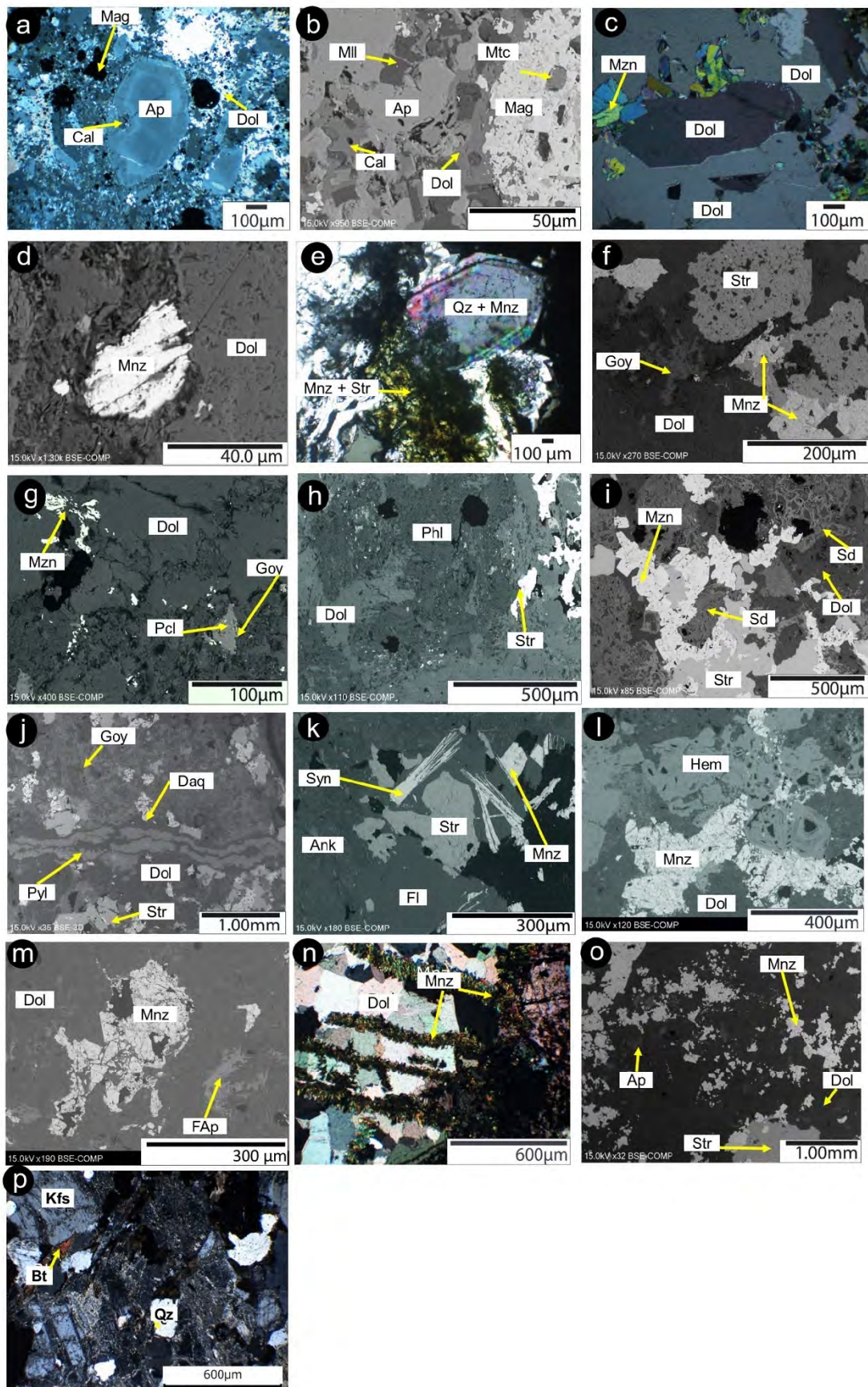


Fig. 4-5 Backscattered electron images and photomicrographs of mineral assemblages of samples studied. (a-b) before site— earliest-formed apatite-rich carbonatite with associated accessory silicate minerals, (c) magnesio-carbonatite with monazite occurring interstitial between Fe-bearing dolomite, (d) magmatic magnesio-carbonatite with corroded monazite inclusion, (e) magnesio-carbonatite having zoned quartz with monazite inclusion, overprinted by strontianite that enveloped monazite (f) magnesio-carbonatite with monazite replacing strontianite, (g) magnesio-carbonatite with pyrochlore associated with goyazite and Fe-bearing dolomite, (h) magnesio-carbonatite with greenish spots of weathered phlogopite associated with pyrochlore, (i) ferro-carbonatite with Mg-bearing siderite with dissolution texture and strontianite replacing monazite. (j) ferro-carbonatite with pyrolusite vein, goyazite replacing Fe-bearing dolomite, (k) ferruginous calcio-carbonatite showing ankerite with amorphous texture replacing dolomite and dissolution of synchysite, and formation of fluorite and strontianite, (l) ferruginous calcio-carbonatite with hematite in association with monazite overprinting Fe-bearing dolomite occurring together with ankerite in ferruginous calcio-carbonatite, (m) ferruginous calcio-carbonatite with quartz having apatite inclusions and overprinted by strontianite enveloped monazite, (n) ferruginous calcio-carbonatite with monazite wisp veining, and (o) magnesio-carbonatite with disseminated monazite overprinting dolomite, (p) fenite with biotite occurring as shred and turbid orthoclase and Abbreviation: Ap - apatite, Ank— ankerite. Brt—Baryte, Cal— calcite, Daq—daqingshanite, Dol—dolomite, Fe— iron, Fl— fluorite, Goy— goyazite, Hem- hematite, Mag— magnetite, Mnz—monazite, Mll— melilite, Mtc— monticellite, Pcl— pyrochlore, Pyl—pyrolusite, Phl— phlogopite, Qz— quartz, Str—strontianite. Kfs— orthoclase, Bt— biotite.

4.3.2.6 Mineralization

As mentioned in section 4.3.1.2, the REEs mineralization in the Kangankunde carbonatite occurred as dissemination, acicular, patchy forms within carbonatite (Fig. 4-4a-f) as well as wispy veinlets. Acicular mineralization was formed by euhedral monazite, strontianite and quartz together forming a hexagonal pseudomorph or strontianite enveloping monazite (Fig. 4-5e). This is common in magnesio-carbonatite. Disseminated mineralization was formed by monazite that occurred randomly but covering larger surface areas in carbonatite, occasionally occurring as inclusions in or overgrowing dolomite (Fig. 4-5c-d-o). Patchy mineralization was formed by clusters of monazite, which overgrew or overprinted dolomite in association with strontianite and apatite (Fig. 4-5i). Wispy veinlets were formed by monazite that occasionally exhibits a spherulitic texture, and these veinlets overprinted dolomite (Fig. 4-5n).

4.3.3 Whole-rock geochemistry

4.3.3.1 Major element geochemistry

Major element compositions of carbonatite samples are presented in Appendix A4. Classification of carbonatites used the molar proportion of MgO, CaO, FeO and MnO proposed by Gittins and Harmer (1997; Fig. 4-6a). This classification is preferable in evaluating the carbonatite differentiation as it removes the ambiguity that comes with

iron proportion in classification of carbonatite as ferro-carbonatite by restricting ferro-carbonatite to much Fe-rich rock (Gittins & Harmer, 1997). The Kangankunde carbonatite is dominated by magnesio-carbonatite, ferro-carbonatite and ferruginous calcio-carbonatite. The silica component was assessed using a tetrahedral plot from Mitchell and Gittins (2022) (Fig. 4-6b). The geochemical data (Fig. 4-6a; Appendix A4) shows a continuous trend of compositional evolution between beforosite through magnesio-carbonatite and ferro-carbonatite, while ferruginous calcio-carbonatite has a compositional gap with magnesio-carbonatite and ferro-carbonatite. The SiO₂ content of the Kangankunde carbonatite ranges from 0.6 to 19.9 wt. %. The Na₂O content ranges from 0.07 to 2.0 wt % in beforosite and magnesio-carbonatite. The SrO contents decrease from magnesio-carbonatite (0.7-8.8 wt.%), ferro-carbonatite (0.8-6.9 wt.%), and ferruginous calcio-carbonatite (0.5-2.0 wt.%). The MnO content increases from magnesio-carbonatite (2.0-6.0 wt.%), ferro-carbonatite (5.0–10.0 wt.%) and lower in ferruginous calcio-carbonatite (2.0–4.0 wt.%). The FeO content increases from magnesio-carbonatite (4.5–20.0 wt. %), ferruginous calcio-carbonatite (15.0-17.4 wt. %) to ferro-carbonatite (7.8-38.2 wt. %; Appendix A4).

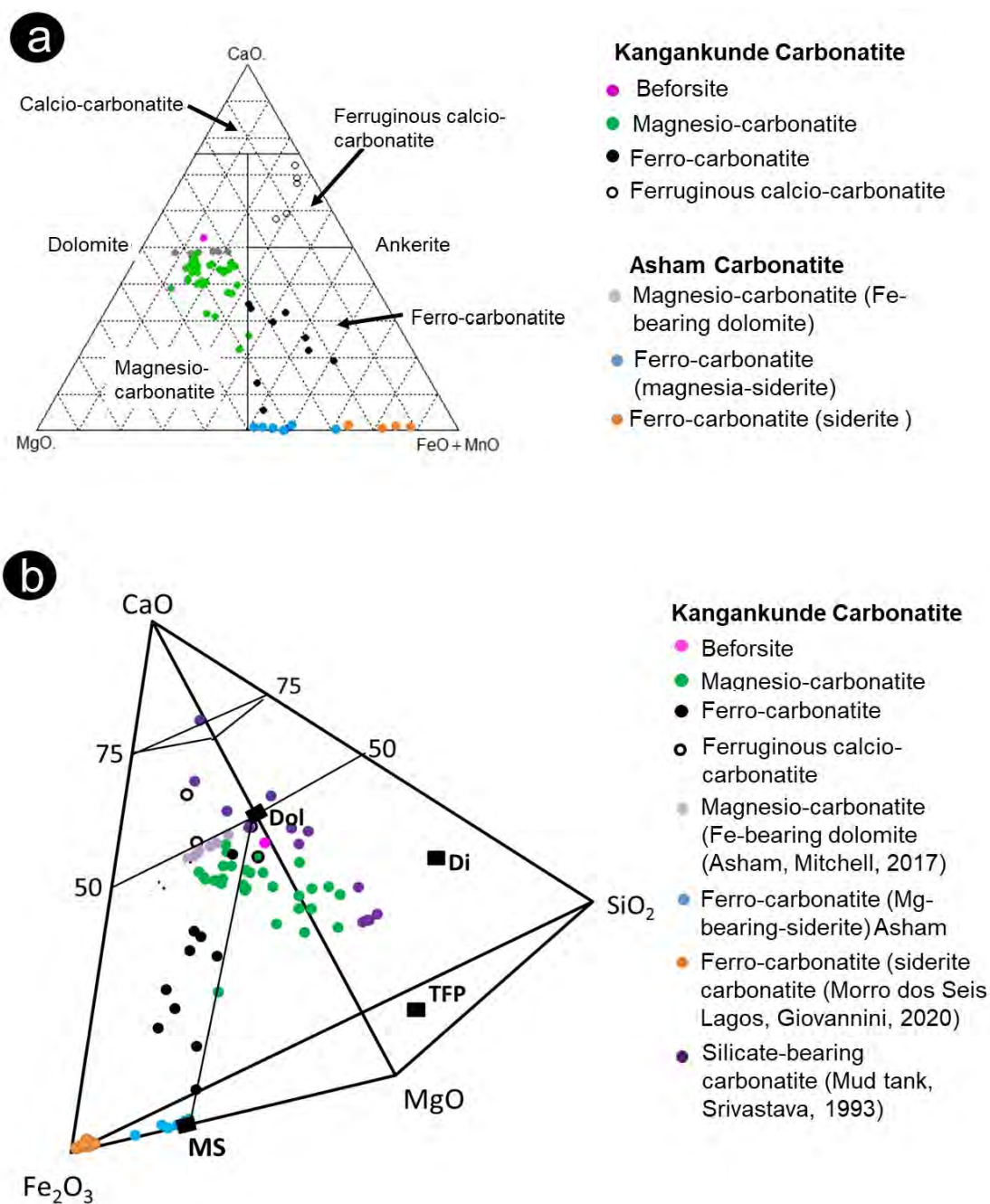


Fig. 4-6. Carbonatite classification using major oxides. (a) classification using molar proportion defined by Gittins and Hammer (1997), (b) tetrad plot using weight percent defined by Mitchel (2022) in comparison with silicate-bearing carbonatite, magnesio-carbonatite with Fe-bearing dolomite and ferro-carbonatite with Mg-bearing siderite, where Di and TFP are the ideal compositions (quaternary wt. %) of diopside and tetraferriphlogopite, respectively. Dol - dolomite; MS - magnesian siderite.

4.3.3.2 Trace-element geochemistry

The trace element compositions of carbonatite samples are presented in Appendix A4. Lithophile (Ta, REEs, Nb, Zr, Hf, Th, U, Ti, Rb) and chalcophile (Pb) elements were used to assess REEs mineralization and magma evolution as these are commonly associated with carbonatite related REEs deposits (e.g., Hou et al., 2015; Jia & Liu, 2020; Slezak & Spandler, 2020; Benkó et al., 2021). The chondrite-normalized ratio of lanthanum and ytterbium $(La/Yb)_N$ ranges from 123 to 2306, 280 to 678 and 101 to 212 in magnesio-carbonatite, ferro-carbonatite and ferruginous calcio-carbonatite respectively Appendix A4). However, LREEs are more enriched in magnesio-carbonatite followed by ferro-carbonatite, ferruginous calcio-carbonatite, and beforsite, with averages of $(La/Yb)_N$ of 681, 488, 248 and 53, respectively (Fig. 4-7a).

The primitive-mantle-normalized patterns reveal similarities among the carbonatites (Fig. 4-7b). Ferruginous calcio-carbonatite is enriched in Th among high field strength elements (HFSE) and depleted in large-ion lithophile elements (LILE; Rb) and other HFSE such as Zr, Hf, Ti and Pb, while Nb, Ta and U are variable. The magnesio-carbonatite variable enrichment of Nb and depleted in Rb, Zr, Ti and Pb, while Th, Hf and U are variable. Ferro-carbonatite is enriched in Th, Mo and depleted in Rb, Hf, Zr, Pb, and Ti, while Nb is variable. Beforsite is enriched in Nb and depleted in Hf, Pb, Ta, Ti and Rb. Y/Ho ratio ranges from 15 to 30, 21 to 26, 16 to 26 and 24 in magnesio-carbonatite, ferro-carbonatite, ferruginous calcio-carbonatite and beforsite, respectively (Appendix A4). These Y/Ho ratios vary less from primitive mantle value (Sun & McDonough, 1989). The observed element enrichment and depletion in the Kangankunde carbonatite are almost similar to a general chemical feature of carbonatites elsewhere (e.g. Shaxiongdong Complex, China, Su et al., 2022; Dicker Willem, Namibia, Cooper & Reid, 1998).

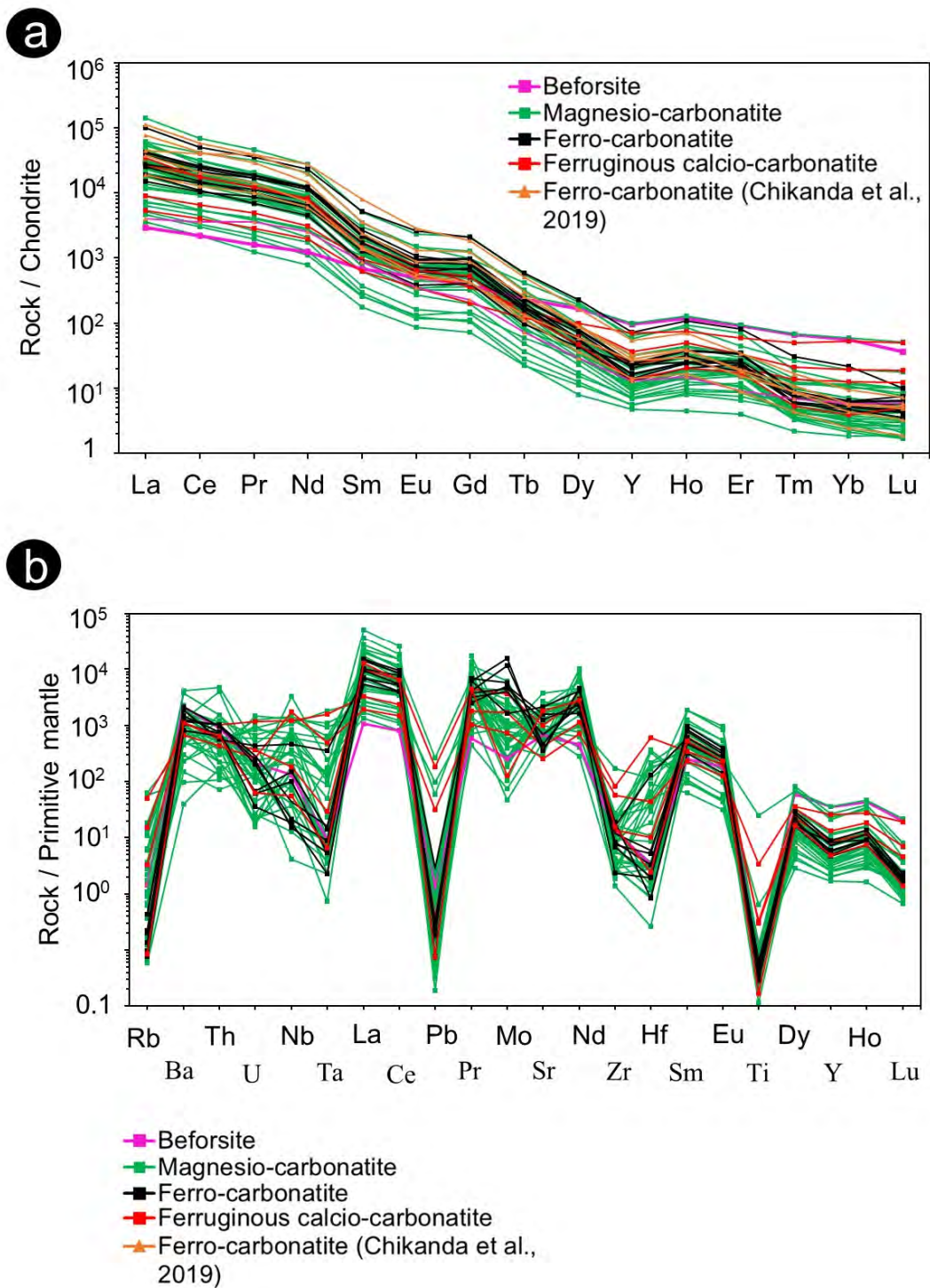


Fig. 4-7 Whole-rock REEs and trace element patterns for magnesio-carbonatite, ferro-carbonatite and ferruginous calcio-carbonatite. (a) chondrite-normalized REEs patterns, (b) primitive mantle normalized LILE and HFSE elements. Chondrite and primitive mantle values from McDonough and Sun (1995).

4.3.3.3 Correlation between REE and major and trace elements

The total REEs oxides (TREE_2O_3) and P_2O_5 contents are strongly positively correlated in the ferruginous calcio-carbonatite and ferro-carbonatite while weakly correlated in the magnesio-carbonatite (Fig. 4-8a). The TREE_2O_3 and SrO contents are strongly positively correlated in the ferruginous calcio-carbonatite and weakly correlated in the ferro-carbonatite and magnesio-carbonatite (Fig. 4-8b). The TREE_2O_3 and BaO contents are strongly positively correlated in the ferro-carbonatite and magnesio-carbonatite, while weakly correlated in the ferruginous calcio-carbonatite (Fig. 4-8c). The TREE_2O_3 and (FeO+MnO) contents are weakly correlated in the ferro-carbonatite, magnesio-carbonatite, and ferruginous calcio-carbonatite (Fig. 4-8d). There are no correlations between TREE_2O_3 and Nb contents in magnesio-carbonatite, ferro-carbonatite and ferruginous calcio-carbonatite (Fig. 4-8e).

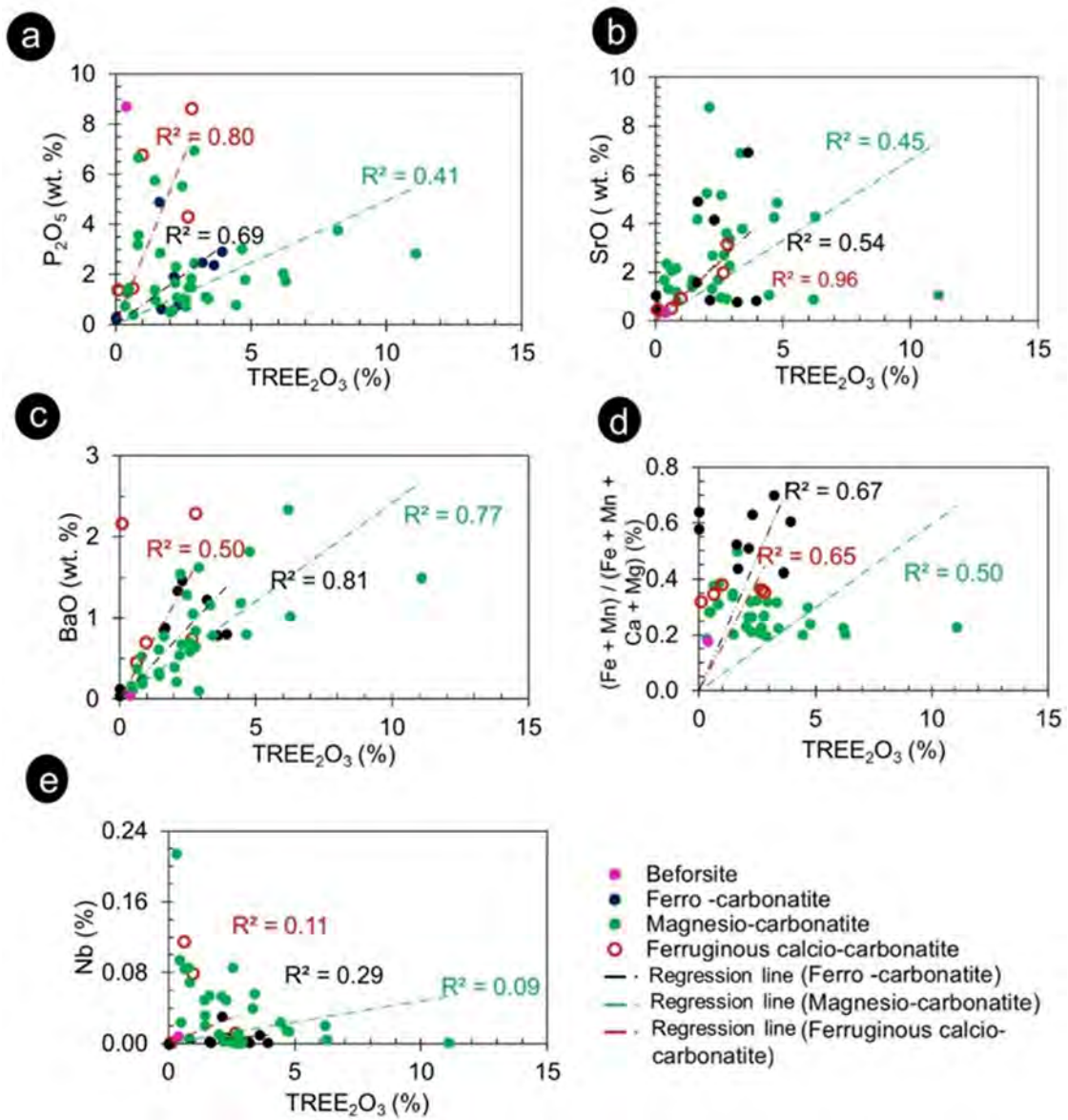


Fig. 4-8 Bivariate plots of major and trace element oxides against total rare earth elements oxides. (a) P₂O₅ vs. TREE₂O₃, (b) SrO vs. TREE₂O₃, (c) Ba vs. TREE₂O₃, (d) (Fe+Mn)/(Fe+Mn+Ca+Mg) vs. TREE₂O₃, and (e) Nb vs. TREE₂O₃. R² means the linear correlation coefficient.

4.3.3.4 Carbon and Oxygen isotope

The carbon and oxygen isotopic compositions of the Kangankunde carbonatites are given in Appendix A7. Four samples were analyzed: two samples of ankerite and one sample of calcite from the ferruginous-carbonatite, and one sample of strontianite from the magnesio-carbonatite. The ankerite samples yielded a wide range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, from -3.5 to -0.5 ‰ and from +14.8 to +16.2 ‰, respectively (Fig. 4-9a; Appendix A7). The calcite sample yielded $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of -4.0 ‰ and +26.7 ‰, while the strontianite sample yielded $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of -4.3 ‰ and +12.0 ‰, respectively (Fig. 4-9b; Appendix A7). These samples were supplemented with data from Broom-Fendley et al. (2017) (Appendix A7).

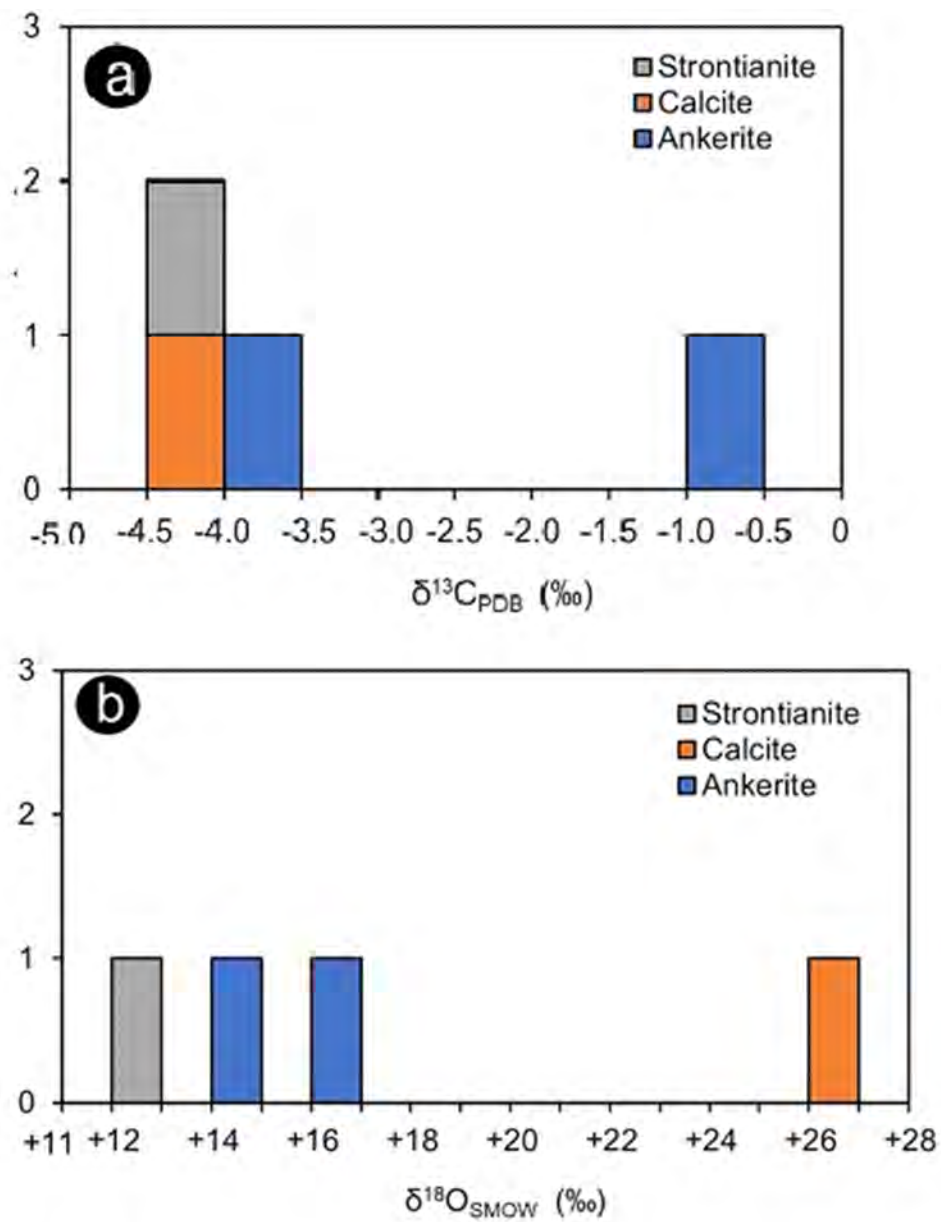


Fig. 4-9 Histogram of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope analysis of ankerite and calcite from the ferruginous-carbonatite, and strontianite from the magnesio-carbonatite.

4.4 Discussion

4.4.1 Origin of carbonatite magma

Although petrogenesis of the carbonatite is still debatable, there is a consensus that most carbonatites are derived from carbonate-silicate magma via liquid immiscibility or fractional crystallization (Wyllie & Lee, 1998; Veksler et al., 1998; Mitchell, 2005; Martin et al., 2013). In general one of the main evidence of liquid immiscibility in carbonatite complexes is the spatial and temporal association of carbonatite and alkaline silicate rocks (e.g. Woolley & Kempe, 1989; Tappe et al., 2017).

Based on field observation, there are no silicate rocks within the Kangankunde carbonatite Complex, but a swarm of alkaline dikes are present to the south of the complex, which have been interpreted as the initial emplacement of the C.A.P (Bloomfield & Garson, 1965). Although the alkaline rocks are at a distance (Fig. 2-5), the timing of emplacement of the dykes is similar to that of the Kangankunde carbonatite and may suggest a genetic relationship. However, there are very limited geochemical data supporting genetic relationship between carbonatite and silicate rocks in the area. In general, the carbonatite samples investigated in this study show variable negative anomaly of Nb and Zr, and contain high of SiO₂ and P₂O₅ contents (Fig. 4-6b, Appendix A4). The high SiO₂ contents of the beforosite and the magnesio-carbonatite are attributed to the presence of phlogopite, while those of ferruginous calcio-carbonatite and the ferro-carbonatite are attributed to the presence of quartz (Fig. 4-6b). These geochemical signatures are consistent with carbonatite magma formed from liquid immiscibility (e.g. Hornig-Kjarsgaard, 1998; Martin et al., 2012; Veksler et al., 2012; Yaxley et al., 2022). The beforosite in the Kangankunde Complex was previously classified as carbonatized nephelinite (Garson & Campbell Smith, 1965; Woolley, 1982; Broom-Fendley et al., 2017c) due to the presence of phlogopite, perovskite, and magnetite also observed in the studied samples (Fig. 4-5a-b).

A plot of $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ given in figure 4-10 (Ray & Ramesh, 2006) show considerable isotopic variation for the Kangankunde carbonatite, with $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ spanning from of -7.7 ‰ to -0.7 ‰, and from +4.4 ‰ to +26.7 ‰, respectively. The lowest range was observed in magnesio-carbonatite, which plot within the primary

igneous carbonatite (P.I.C) field. Previous study reported much lower $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of apatite bearing dolomite (beforsite) which plot within the P.I.C, closer to the mantle field (Fig. 4-10; Broom-Fendley et al., 2017c).

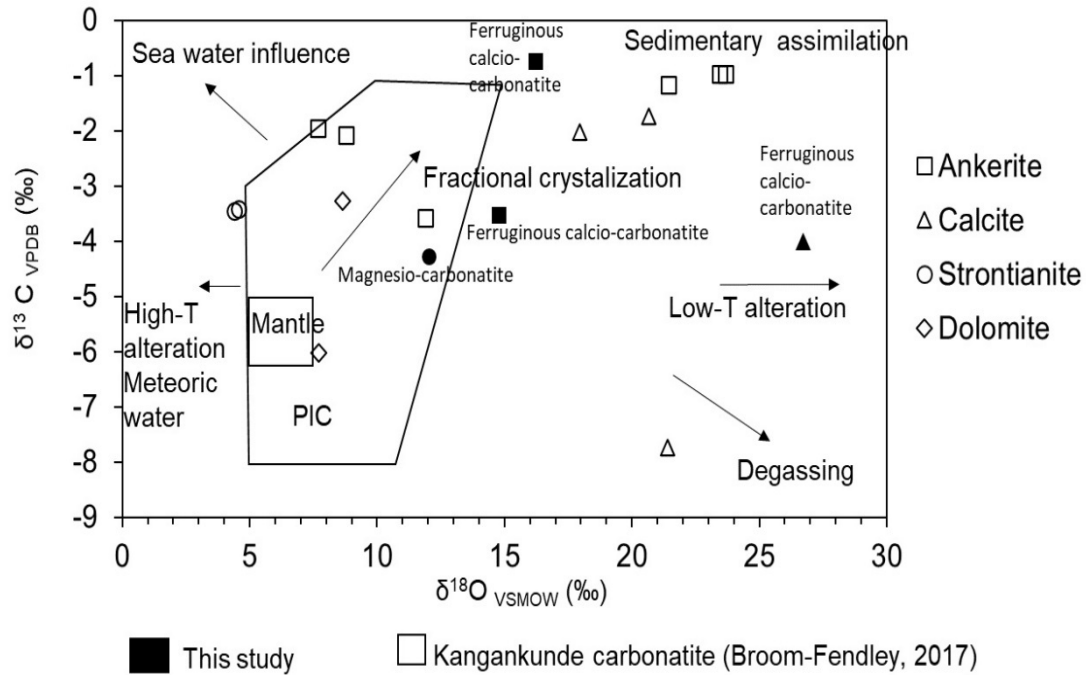


Fig. 4-10 The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions of the Kangankunde carbonatites. The filled symbols are from this study. The open symbols are supplement composition data from Broom-Fendley et al. (2017c). Arrows indicate possible principal controls on carbonatite O and C isotope ratio after Deines (1989) and Demény et al. (2004). The mantle field is adapted from Kyser (1990), Deines (1992), and Cartigny et al. (1998). Primary igneous carbonatite (P.I.C) field from Ray & Ramesh (2006).

Based on these observations, the Kangankunde carbonatite possibly formed from liquid immiscibility of a mantle derived silicate-carbonate magma. This is also supported by the bulk Y/Ho ratios of carbonatite samples, which vary less from the primitive mantle value (Sun & McDonough, 1989). The absence of silicate rocks within Kangankunde carbonatite can be attributed to a non-surface exposure of these rocks which could be present at deeper parts of the complex as a parental plutonic body (e.g., Mitchell, 2005).

In nature, carbonatite melts are a solution of a wide range of chemical components including Ca, Mg, Fe, Na, K, P, F, Cl, H₂O, and others (Yaxley et al., 2022). The crystallization of either dolomite or calcite phases would depend on the temperature of the melts, as well as the previous evolution crystallization history of the magma. Thus, potentially, calcio-carbonatite, magnesio-carbonatite and mafic silicate-calcite carbonatites can form from the same parental carbonatite magma, depending on the evolutionary paths taken by a primary magnesian-carbonatite melt or by a calcic-carbonatite melt from the upper mantle (Djeddi et al., 2021).

Anenburg, et al. (2020a) and Wei et al. (2020) suggested that in carbonatite fractionation Mg would preferentially be incorporated into early-formed calc-silicate minerals. The observed dominance of Fe-bearing dolomite and the presence of phlogopite from petrography of the studied carbonatites samples indicates the abundance of Mg and Si in the initial carbonate melt. This is also supported by the tetrahedral plots of major components of studied carbonatite samples as they plots in the field of silicate-rich carbonatite derived from tetraferriphlogopite-bearing (Srivastava & Rajesh, 1993; Mitchell & Gittins, 2022) and are similar to silicate-bearing carbonatite from the Mud Tank Carbonatite (Fig. 4-6b).

4.4.2 Evolution of carbonatite magma

The isotope composition plots show a broad fractional crystallization trend for the Kangankunde carbonatite, from the beforosite to ferruginous calcio-carbonatite (Fig. 4-10) and may be inferred that the initial magma of the Kangankunde carbonatite evolved from a Mg- and P-rich melt to a relatively Mg- and P-poor melt through magma differentiation. Furthermore, the emplacement of Kangankunde complex as a ring structure with ferro-carbonatite and ferruginous calcio-carbonatite at the center support

magmatic differentiation (e.g. Anenburg et al., 2021; Fig. 4-1). In addition, the total REEs oxides (REE_2O_3) and P_2O_5 contents are positively correlated in the ferruginous calcio-carbonatite and ferro-carbonatite, respectively, and weakly correlated in the magnesio-carbonatite, which supports concomitant enrichment of REEs and P as the carbonatite magma evolved (Fig. 4-8a). The low alkali contents, Na_2O (0.0-2.0 wt. %) and K_2O (0.0-2.7 wt.%) for all units, regardless of their degree of differentiation, can be interpreted as an evidence of alkali loss that could be caused by late-stage metasomatic activity which is consistent with previous studies (e.g. Woolley, 1982).

The four carbonatite lithotypes are identified at the Kangankunde carbonatite (Fig. 4-6a). Petrographic observation suggests beforite to have formed earlier and fractionated calcite, magnetite and apatite. A mineral assemblage of apatite, magnetite and calcite commonly form early in the carbonatite magma fractionation (e.g. Anenburg et al., 2021). Additionally, apatite characteristics including elongated subhedral form, oscillatory zoning and partially altered areas (Fig. 4-5a) suggest the magmatic nature of beforite (e.g. Chakhmouradian et al., 2017). Early formation of beforite is also supported by the observed preference of heavy rare earth elements (HREEs; Gd-Lu) to beforite compared to magnesio-carbonatite, ferro-carbonatite, and ferruginous calcio-carbonatite which are more enriched in LREE (La-Pr; Fig. 4-7a; e.g. Rollinson, 1993).

The magnesio-carbonatite that fractionated Fe-bearing dolomite, strontianite, monazite, and the ferro-carbonatite fractionated Mg-bearing siderite, strontianite, and monazite and goyazite. Apatite is scarce in more evolved magnesio-carbonatite, but common in less evolved beforite. Monazite, apatite and minor goyazite are the main REEs- and P-bearing minerals in magnesio-carbonatite. Monazite occurred as inclusions or filling interstices within Fe-bearing dolomite suggesting earlier formation compared to Fe-bearing dolomite (Fig. 4-5b-c) (e.g. Heinrich, 1980; Kim et al., 2005). In addition, monazite occurred in dolomite interstitially. These textures of monazite indicate early formation. Heinrich (1980) and Kim et al. (2005) Some P in the studied samples is hosted by goyazite. However, goyazite in magnesio-carbonatite occurs as a replacement product of dolomite and likely primary P-bearing minerals such as apatite and monazite, suggesting that goyazite is secondary in origin (Fig. 4-5g). Moore et al. (2015) and Andersen et al. (2017) reported the breakdown of primary REEs-bearing reported the minerals such as apatite to liberate REE-hydrated alumino-phosphate

(plumbogummite series e.g. goyazite). Furthermore, formation of goyazite in carbonatite has been reported to occur at temperatures $>500\text{ }^{\circ}\text{C}$ (McKie, 1962). Experimental studies on carbonatite magma differentiation indicated that the magmatic phase of carbonatite in the earth's crust ranges from $650\text{--}400\text{ }^{\circ}\text{C}$ (Prokopyevsk et al. 2016).

The ferro-carbonatite fractionated Mg-bearing siderite, strontianite, monazite, goyazite daqingshanite and pyrolusite. Daqingshanite occurred as replacement mineral for goyazite, while pyrolusite seem to replace both goyazite and daqingshanite suggesting late formation. This is also supported by presence of pyrolusite veins (Fig. 4-5j). In carbonatite magmatic differentiation Mn proportion increase on passing from early formed carbonatite to the later carbonatite (Le Bas, 1981). These observations suggest ferro-carbonatite precedes formation of magnesio-carbonatite.

The ferruginous calcio-carbonatite fractionated ankerite, monazite, strontianite, synchysite. Ankerite occurred with an amorphous texture replacing Fe-bearing dolomite (Fig. 4-5k). Ankerite is considered to have formed a consequence of the incomplete solid solution between dolomite and Fe-rich dolomite (e.g. Davidson et al., 1994) and can form within a magmatic framework as a low temperature ($400\text{--}460\text{ }^{\circ}\text{C}$) product (e.g. Cooper & Reid, 1998; Thompson et al., 2002). Alteration of dolomite to ankerite might result in formation of hematite (Fig. 4-5l). In addition, fluorapatite dissolution (Fig. 6m) might have resulted to the release of P and Ca to form monazite and calcite during remobilization. Furthermore, synchysite is dissolved (Fig. 4-5k), thereby releasing REE, Ca, and F, which would be available to precipitate monazite fluorite and calcite. From observed mineral paragenetic ferruginous calcio-carbonatite formed last and was altered by hydrothermal fluids. This is also supported by stable isotope data that shows low temperature alteration signature (Fig. 4-10).

Geochemical evidence in magnesio carbonatite, ferro-carbonatite and ferruginous calcio-carbonatite identified variations of SrO and MnO contents across the lithotypes. The SrO contents decrease from magnesio-carbonatite (0.7-8.8wt.%) to ferro-carbonatite (0.8-6.9wt.%) and ferruginous calcio-carbonatite (0.5-2.0wt.%). The MnO contents increases from magnesio-carbonatite (2.0-6.0wt.%) to ferro-carbonatite (5.0–10.0wt.%) while lower in ferruginous calcio-carbonatite (2.0–4.0 wt.%). The variable concentrations of SrO and Mn in the same rock unit, as well as among rock units, has

been also interpreted to be a result of element enrichment due to magmatic differentiation (Le Bas, 1981, Woolley & Kempe 1989; Cooper & Reid, 1998) or contamination by hydrothermal processes. In addition, the mineralogy of the rocks could also account for the observed variable element concentration. For example, Sr and Ba contents of beforsite are lower than those of magnesio-carbonatite and ferro-carbonatite (Fig. 4-8b-c; Appendix A4). Compared to beforsite, magnesio-carbonatite contains xenocrysts of feldspar. Strontium and Ba are easily incorporated in feldspar by substituting Ca and K in crystal structure, respectively. Similarly, there is no correlation between Nb and $TREE_2O_3$ suggesting that pyrochlore might fractionate late during differentiation (Fig. 4-8e; e.g. Anenburg et al. 2020). This is also supported with petrography where pyrochlore was observed to overprint goyazites. In addition, Fe content, increases towards ferro-carbonatite due to the presence of Mg-bearing siderite. However, there is no correlation between Fe and $TREE_2O_3$ (Fig. 4-8d).

Furthermore, the observed lower Mn content (2.0–4.0 wt.%) in ferruginous calcio-carbonatite might be attributed from low Mn content in beforsite. Mn concentration is expected to increase in later carbonatite as carbonatite magma differentiation progress (e.g. Le Bas, 1981; Woolley & Kempe, 1989). Beforsite formed earlier and has lower Mn content (0.6 wt.%). Ferruginous calcio-carbonatite probably evolved from beforsite. This is also supported by narrow range of Y/Ho (21-26) in ferruginous calcio-carbonatite that is close to chondrite values of 28.

From the above observations, it suggests that the magma possibly differentiated from the beforsite to the ferruginous calcio-carbonatite and through the magnesio-carbonatite to ferro-carbonatite had two pathways. The first path differentiated the carbonate magma from a carbonate-silicate melt as an immiscible liquid to the beforsite, magnesio-carbonatite and ferro-carbonatite by crystalizing apatite, dolomite, calcite, monazite, strontianite, pyrolusite (Figs. 4-5a-h, 4-6a). The second path differentiated the magma from the Beforsite to the ferruginous calcio-carbonatite by fractionating ankerite, monazite and synchysite (Fig. 4-5k-l). The presence of ankerite dykes crosscutting other carbonatites implies that unevolved melts, in some instances, were still present in the complex after the formation of ferro-carbonatite. Garson, 1965 named the calcio-carbonatite as remobilised intrusive carbonatites (Fig 4-1). In addition, post-magmatic emplacement activities such as the replacement of magnetite by hematite and the

formation of fluorapatite and calcite from reworked beforosite (Fig. 4-5l) also affected the carbonatites.

4.4.3 Implications to REEs mineralization

The mineralization of REEs in the Kangankunde carbonatite is represented by the presence of monazite, goyazite and apatite in the magnesio-carbonatite and ferro-carbonatite, and monazite, daqingshanite and synchysite in the ferruginous calcio-carbonatite. The REEs mineralization in Kangankunde carbonatite can be classified into early magmatic mineralization and late-magmatic-hydrothermal mineralization stages. The early-magmatic mineralization stage is characterized by monazite which occur as inclusions in dolomite, as well as filling up interstices in dolomite (Fig. 4-5c-d). The late magmatic-hydrothermal mineralization stage is dominant and characterized by monazite replacing strontianite (Fig. 4-5f), strontianite replacing goyazite (Fig. 4-5i), strontianite enveloping early formed monazite, (Fig. 4-5e) and monazite veins with occasional spherulitic texture overprinting Fe-bearing dolomite (Fig. 4-5n), as well as the occurrence of late REE-bearing minerals such as synchysite in association with fluorite and fluorapatite (Fig. 4-5k). A proposed paragenetic sequence is shown Figure 4-11.

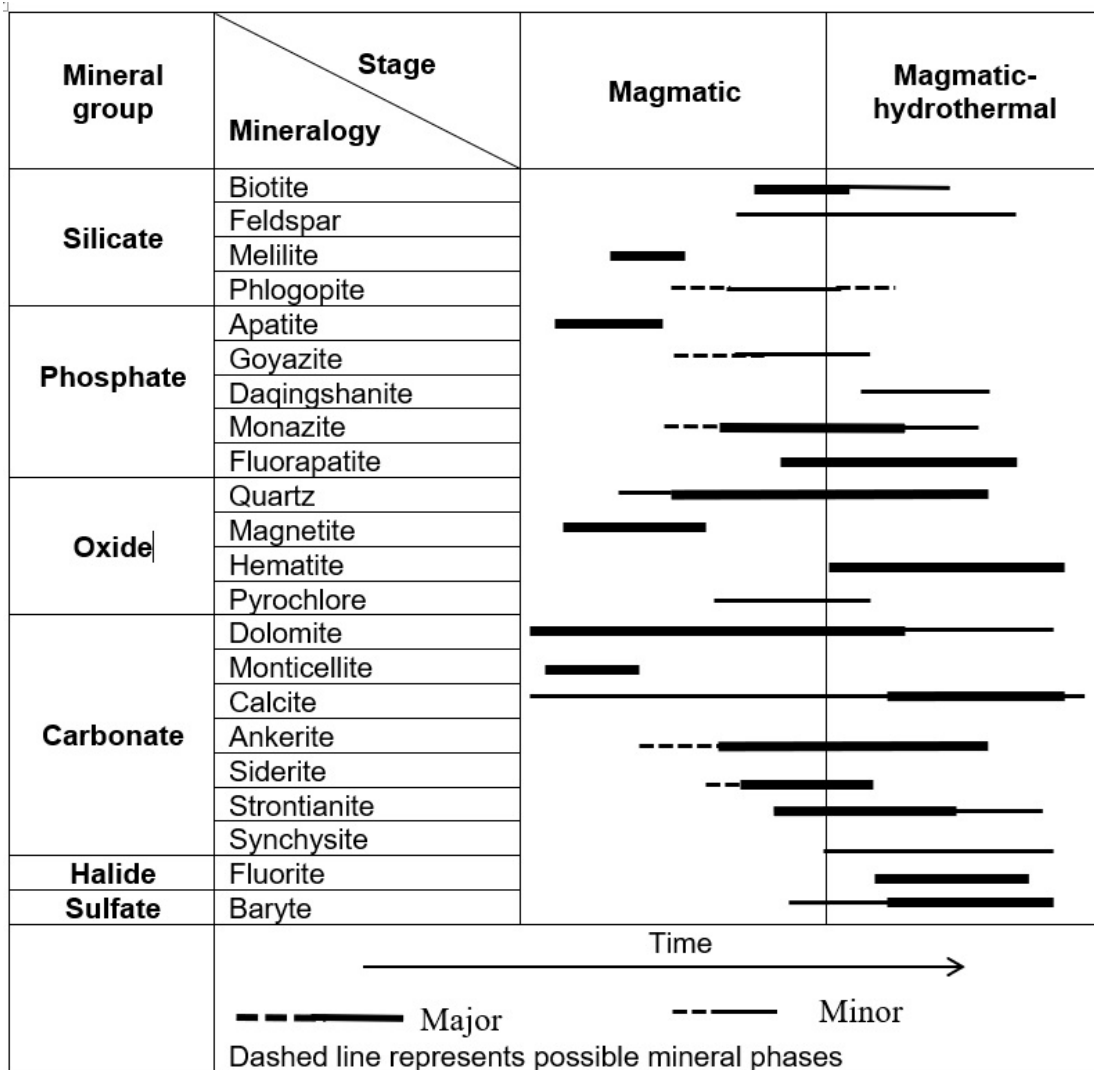


Fig. 4-11 Paragenetic sequence for the Kangankunde carbonatite

The average ratios $(La/Yb)_N$ increases from beforite (53), through the ferruginous calcio-carbonatite (248), and the ferro-carbonatite (488), to the magnesio-carbonatite (681) indicating that LREEs were more compatible in magnesio-carbonatite and ferro-carbonatite probably due to concentration through magmatic differentiation and later local redistribution by hydrothermal processes as carbonatites are concentrated with REEs during the magmatic intrusion event and do not accumulate additional REEs over time via metamorphic or hydrothermal processes (Fig. 4-7a; e.g. Chakhmouradian & Zaitsev, 2012; Smith et al., 2016). The observed $(La/Yb)_N$ trend is consistent with REE distribution along the drill core, where REE_2O_3 decreases from magnesio-carbonatite, which is characterized by dark-brown bands which indicate possible high hydrothermal fluid activity or feldspar brecciated, to ferro-carbonatite with similar characteristics, to ferruginous calcio-carbonatite (Fig. 4-2; e.g. Broom-Fendley et al., 2021). In addition, the occurrence of monazite in miarolitic cavities in the magnesio-carbonatite and ferro-carbonatite (Fig. 4-4f) indicates the crystallization from orthomagmatic fluid phase (Duraishwami & Shaikh, 2014).

The observed Y/Ho ratios in the beforite (Y/Ho of 23) and the ferruginous calcio-carbonatite (Y/Ho of 21–26) are similar to mantle's chondritic Y/Ho value of 28, while those of the magnesio-carbonatite (Y/Ho of 15–30), and the ferro-carbonatite (Y/Ho 16–26) differ from the mantle value. These features further confirm less evolved nature of the beforite and ferruginous calcio carbonatite. This is supported by the gentle sloping REEs pattern of the beforite (Fig. 4-7a), indicating the early formation and the incipient mineralization (e.g. Broom-Fendley et al., 2017c). At the same time the surrounding silicate rocks contaminated the magnesio-carbonatite and ferro-carbonatite. Contamination is evident by C and O isotopic signature that show the system to have involved both magmatic and hydrothermal component (Fig. 4-10). Furthermore, the observed abundance of highly resorbed feldspar xenocryst in magnesio-carbonatite compared to ferro-carbonatite also suggest a possible carbonatite magma contamination by feldspar-bearing silicate rocks at depth. (Anenburg et al., 2018; Giebel et al., 2019; Walter et al., 2021). This is also supported by $^{87}Sr/^{86}Sr$ isotopic studies on apatite from the Kangankunde carbonatite by Wall (1994) who suggested that only the outermost mineralization close to and within the fenite experienced interaction with the country rocks.

The transportation and mineralization of REEs in carbonatites are thought to be commonly associated with CO₂, H₂O, F, P, and S (e.g., Haas et al., 1995; Samson et al., 1995; Williams-Jones & Palmer, 2002; Trofanenko et al., 2016; Strzelecki et al., 2022). In the Kangankunde carbonatite, CO₂ and P were the main transporting ligands. This is supported by the association of strontianite and apatite with monazite. However, petrographic observations indicate that F budget was introduced at a later stage, probably during the stage of hydrothermal activities (Fig. 4-5k). Furthermore, monazite and other calcic REE fluor-carbonates are typically insoluble in carbonatite-associated hydrothermal systems (Migdisov et al., 2016; Ying et al., 2020). Therefore, its role in transporting the REEs was insignificant.

4.4.4 Implication of tectonic controls of the carbonatite evolution.

The Lilongwe sub domain is characterised by high deformation and intermediate granulite metamorphism due to compression forces during the closure of Kuunga ocean as well as W-E and NW-SE compressions of the Pan-African orogeny. These compression episode results in the transposing the early alkaline intrusion characterized by enriched LREE within the gneisses and as well as transporting Unango subdomain over Lilongwe subdomain along the Ntcheu Shear Zone. These tectonic episodes may have facilitated enrichment of REE within the Lilongwe subdomain. The proposed thick crust possibly enabled magma underplating as reported by Njinju et al. (2019) within the Malawi rift. Magma underplating may have resulted in REE enrichment through assimilation as observed in magnesio-carbonatite (Fig. 4-3b). A model section of target lithology for exploration and mining is shown in Figure 4-12.

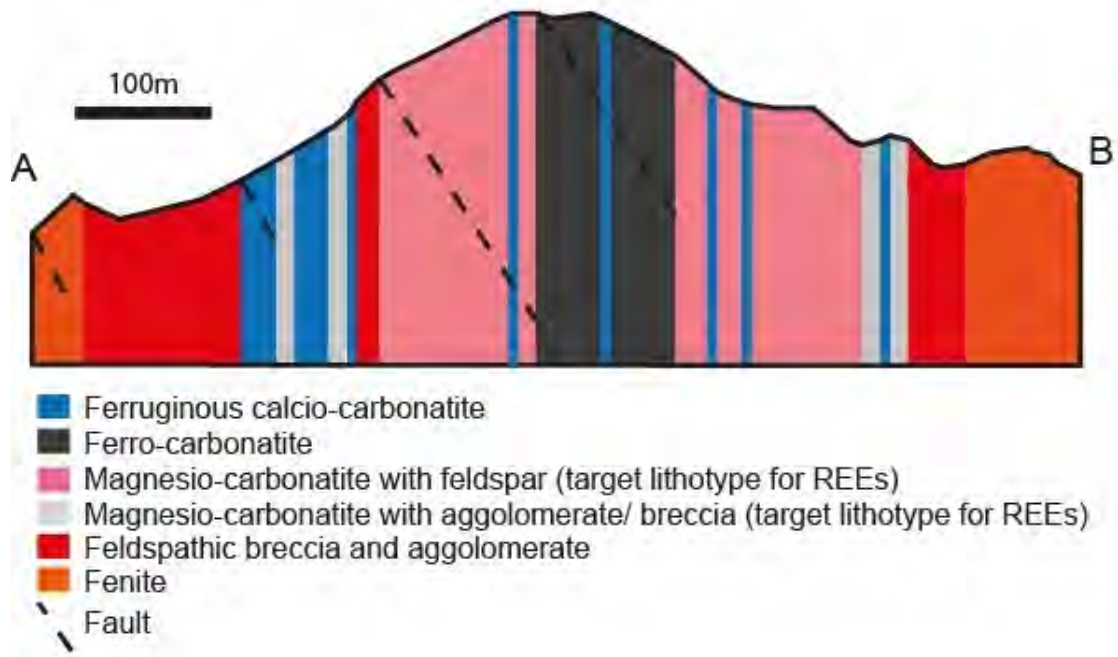


Fig. 4-12 A cross section of the Kangankunde carbonatite facing NW. Cross section line A-B on Fig. 4-1 highlighting the magnesio-carbonatite. Section inferred from Fig 4-1 and carbonatite emplacement model by Garson 1965.

4.5 Summary

Integration of drill core observations, petrography, and whole-rock geochemistry including C and O stable isotope analysis on the late Cretaceous Kangankunde carbonatite in the western belt of the Chilwa Alkaline Province, East African Rift System was employed to understand the magmatic evolution and to discuss its significance in the rare earth elements (REEs) mineralization. The Kangankunde carbonatite Complex was emplaced as a ring structure. Five lithotypes of carbonatite were identified in Kangankunde; beforite, magnesio-carbonatite, ferro-carbonatite, ferruginous calcio-carbonatite and carbonatite agglomerate/breccia. Geochemical analysis of the carbonatite samples shows depletion of Nb and Zr contents and an increase in SiO_2 and P_2O_5 contents. Observed possible associated alkaline silicate rocks were at south of the Kangankunde carbonatite. These factors potentially indicate carbonatite melt to have formed from liquid immiscibility of a mantle derived silicate-carbonate magma. The abundance of dolomite and apatite in the Kangankunde carbonatite suggests that the initial magma was Mg- and P-rich. The bulk SrO contents decrease from magnesio-carbonatite (0.7–8.8 wt.%), ferro-carbonatite (0.7–6.9wt.%), to ferruginous calcio-carbonatite (0.5–2.0wt.%). On the other hand, the MnO contents increase from magnesio-carbonatite (1.0-6.0wt.%) to ferro-carbonatite (5.0-10.0wt.%), while in ferruginous calcio-carbonatite it ranges from 2.0 to 4.0wt.%. Two trends of differentiation of carbonatite magma are proposed. The first differentiation trend was from beforite through magnesio-carbonatite to ferro-carbonatite. The second trend was possibly from beforite to ferruginous calcio-carbonatite. The two identified differentiation trends are consistence with observed mineral paragenetic sequency. The main REE bearing mineral in Kangankunde is monazite. Minor REE-bearing minerals include apatite, synchysite, goyazite, and daqingshanite. The REEs mineralization in the Kangankunde carbonatite occurs as dissemination, wispy veinlets, and patchy forms within almost all identified carbonatite rocks, as well as acicular form in magnesio-carbonatite, and is classified into primary magmatic and late-magmatic-hydrothermal stages. The primary REEs mineralization occurred during magmatic differentiation, evidenced by the occurrence of monazite interstitial between spaces of subhedral dolomite and as inclusion in dolomite. The late-magmatic-hydrothermal mineralization

is considered localised and is characterized by wispy veins of monazite with spherulitic texture, monazite overprinting dolomite or quartz and strontianite enveloping primary monazite. Geochemical data average show decreasing chondrite-normalized La/Yb ratios from magnesio-carbonatite (681), ferro-carbonatite (488), to ferruginous calcio-carbonatite (248). The total REE contents decrease from deeper, more evolved magnesio-carbonatite, which appears to be relatively hydrothermally altered, to ferro-carbonatite with similar characteristics, to the less evolved ferruginous calcio-carbonatite. These observations from petrography and geochemical data suggest that magmatic processes played a significant role in REE mineralization at Kangankunde carbonatite while hydrothermal processes were possibly localized evidenced by dark bands of Fe-bearing dolomite with higher Fe contents

Reference

- Andersen, A. K., Clark, J. G., Larson, P. B., and Donovan, J. J. (2017). REE fractionation, mineral speciation, and supergene enrichment of the. *Ore Geology Reviews*, 89, pp.780–807.
- Anenburg, M., Burnham, A. D., and Mavrogenes, J. A. (2018). REE redistribution textures in altered fluorapatite: Symplectites, veins, and phosphate-silicate-carbonate assemblages from the Nolans Bore P-REE-Th deposit, Northern Territory, Australia. *The Canadian Mineralogist*, 56, 331–354.
- Anenburg, M., Mavrogenes, J. A., and Bennett, V. C. (2020a). The fluorapatite P-REE-Th vein deposit at Nolans Bore: Genesis by carbonatite metasomatism. *Journal of Petrology*, 61(1), 1-42.
- Anenburg, M., Mavrogenes, J. A., Frigo, C., and Wall, F. (2020b). Rare earth element mobility in and around carbonatites controlled by sodium, potassium, and silica. *Advances Science Magazine*, 6, 1–10.
- Anenburg, M., Broom-Fendley, S., and Chen, W. (2021). Formation of rare earth deposits in carbonatites. *Elements*, 17(5), 327–332.
- Bell, K., and Simonetti, A. (2010). Source of parental melts to carbonatites-critical isotopic constraints. *Mineralogy and Petrology*, 98(1–2), 77–89.
- Bell, K., and Tilton, G. R. (2001). Nd, Pb and Sr isotopic compositions of East African carbonatites: Evidence for mantle mixing and plume inhomogeneity. *Petrology*,

42(10), 1927–1945.

- Benkó, Z., Molnár, K., Magna, T., et al. (2021). Combined petrography, noble gas, stable isotope and fluid inclusion chemistry of carbonatites from Uganda: Implications for the origin of the carbonatite melt in continental rift setting. *Chemical Geology*, 578, 1–19.
- Bernhard, P. (2015). The ore minerals under the microscope: An optical guide (second). Elsevier. Amsterdam, Netherlands. pp 9-18.
- Broom-Fendley, S., Styles, M. T., Appleton, J. D., Gunn, G., and Wall, F. (2016). Evidence for dissolution-reprecipitation of apatite and preferential LREE mobility in carbonatite-derived late-stage hydrothermal processes. *American Mineralogist*, 101(3), 596–611
- Broom-Fendley, S., Brady, A. E., Horstwood, M. S. A., et al. (2017a). Geology, geochemistry and geochronology of the Songwe Hill carbonatite, Malawi. *Journal of African Earth Sciences*, 134, 10–23.
- Broom-Fendley, S., Brady, A. E., Wall, F., Gunn, G., and Dawes, W. (2017b). REE minerals at the Songwe Hill carbonatite, Malawi: HREE-enrichment in late-stage apatite. *Ore Geology Reviews*, 81, 23–41.
- Broom-Fendley, S., Wall, F., Spiro, B., and Ullmann, C. V. (2017c). Deducing the source and composition of rare earth mineralizing fluids in carbonatites: Insights from isotopic (C, O, $^{87}\text{Sr}/^{86}\text{Sr}$) data from Kangankunde, Malawi. *Contribution to Mineralogy and Petrology*, 172, 1–18.
- Broom-Fendley, S., Elliott, H. A. L., Beard, C. D., Wall, F., Armitage, P. E. B., Brady, A. E., Deady, E., and Dawes, W. (2021). Enrichment of heavy ree and Th in carbonatite-derived fenite breccia. *Geological Magazine*., pp. 2025-2041.
- Bühn, B., Wall, F., and Le Bas, M. J. (2001). Rare-earth element systematics of carbonatitic fluorapatites and their significance for carbonatite magma evolution. *Contributions to Mineralogy and Petrology*, 141(5), 572–591.
- Cangelosi, D., Broom-Fendley, S., Banks, D., Morgan, D., and Yardley, B. (2020). Light rare earth element redistribution during hydrothermal alteration at the Okorusu carbonatite complex, Namibia. *Mineralogical Magazine*, 84(1), 49–64.
- Castor, S. B. (2008). The Mountain Pass rare-earth carbonatite and associated ultrapotassic rocks, California. *Canadian Mineralogist*, 46, 779–806.

- Chakhmouradian, A. R., and Zaitsev, A. N. (2012). Rare earth mineralization in igneous rocks: Sources and processes. *Elements*, 8(5), 347–353.
- Chakhmouradian, A. R., Reguir, E. P., and Zaitsev, A. N. (2016a). Calcite and dolomite in intrusive carbonatites. I. Textural variations. *Mineralogy and Petrology*, 110(2–3), 333–360.
- Chakhmouradian, A. R., Reguir, E. P., Zaitsev, A. N., Couëslan, C., Xu, C., Kynický, J., Mumin, A. H., and Yang, P. (2017). Apatite in carbonatitic rocks: Compositional variation, zoning, element partitioning and petrogenetic significance. *Lithos*, 274–275, pp.188–213.
- Chen, W., Honghui, H., Bai, T., and Jiang, S. (2017). Geochemistry of monazite within carbonatite related REE deposits. *Resources*, 6(4), 51.
- Chikanda, F., Otake, T., Ohtomo, Y., Ito, A., Yokoyama, T. D., and Sato, T. (2019). Magmatic-hydrothermal processes associated with rare earth element enrichment in the Kangankunde carbonatite Complex, Malawi. *Minerals*, 9(7), 1–22.
- Cooper, A. F., and Reid, D. L. (1998). Nepheline sovites as parental magmas in Carbonatite Complexes: Evidence from Dicker Willem, Southwest Namibia. *Journal of Petrology*, 39(11), 2123–2136.
- Cressey, G., Wall, F., and Cressey, B. A. (1999). Differential REE uptake by sector growth of monazite. *Mineralogical Magazine*, 63(6), 813–828.
- Djeddi, A., Parat, F., Bodinier, J., Ouzegane, K., and Dautria, J. (2021). The syenite - carbonatite complex of Ihouhaouene (Western Hoggar, Algeria): Interplay between alkaline magma differentiation and hybridization of cumulus crystal mushes. *Frontiers in Earth Science*, 8(2), 1–23.
- Duraiswami, R. A., and Shaikh, T. N. (2014). Fluid-rock interaction in the Kangankunde carbonatite Complex, Malawi: SEM based evidence for late-stage pervasive hydrothermal mineralization. *Central European Journal of Geosciences*, 6(4), 476–491.
- Eby, G. N., Roden-Tice, M., Krueger, H. L., Ewing, W., Faxon, E. H., and Woolley, A. R. (1995). Geochronology and cooling history of the northern part of the Chilwa Alkaline Province, Malawi. *Journal of African Earth Sciences*, 20, 275–288.
- Fullgraf, T., Bailly, L., Thomas, R. J., Bo (2022a) Kirk Range Lisungwe valley area 17, 1:100.000 Geological Map Series, Sheet explanation. Geological survey

- Department , Zomba Malawi, 76p
- Fullgraf, T., Thomas, R. ., Le Bayon, B., Boger, S. D., and Charles, N. (2022b). Tectonics. Memoir Series.
- Garson, M. S. (1962). The Tundulu carbonatite Ring-Complex in Southern Nyasaland. Government Printers, Memoir Number 2, 235p.
- Garson, M. S. (1965). Carbonatites in Southern Malawi. Government Printers, Bulletin 15, pp.1-128.
- Garson, M. S., and Smith Campbell, W. (1965). Carbonatite and Agglomeratic Vents in the Western Shire Valley. Government Printers, Memoir 3, 161p.
- Giebel, R. J., Parsapoor, A., Walter, B. F., Braunger, S., Marks, M. A. W., Wenzel, T., and Markl, G. (2019). Evidence for magma-wall rock interaction in carbonatites from the Kaiserstuhl Volcanic Complex (Southwest Germany). *Journal of Petrology*, 60(6), 1163–1194.
- Gittins, J., and Harmer, R. E. (1997). What is ferrocarbonatite? A revised classification. *Journal of African Earth Sciences*, 25(1), 159–168.
- Haas, J. R., Shock, E. L., and Sassani, D. C. (1995). Rare earth elements in hydrothermal systems: Estimates of standard partial molal thermodynamic properties of aqueous complexes of the rare earth elements at high pressures and temperatures. *Geochimica et Cosmochimica Acta*, 59(21), 4329–4350.
- Heinrich, E. W. M. (1980). The Geology of Carbonatite. Robert E. Krieger Publishing CompanyHuntington, Newyork. 585 pp.
- Holt, D. N. (1965). The Kangankunde Hill rare earth prospect. Government Printers, Bulletin 20. pp,1-130.
- Hornig-Kjarsgaard, I. (1998). Rare earth elements in sövitic carbonatites and their mineral phases. *Journal of Petrology*, 39, 2105–2121.
- Hou, Z., Liu, Y., Tian, S., Yang, Z., and Xie, Y. (2015). Formation of carbonatite-related giant rare-earth-element deposits by the recycling of marine sediments. *Nature*, 5(1), 1–10.
- Imai, N., Terashima, S., Itoh, S., and Ando, A. (1995). Compilation of analytical data for minor and trace elements in seventeen GSJ geochemical reference samples, “igneous rock series.” *Geostandards Newsletter*, 19(2), 135–213.
- Jaireth, S., Hoatson, D. M., and Mieizitis, Y. (2014). Geological setting and resources of

- the major rare-earth-element deposits in Australia. *Ore Geology Reviews*, 62, 72–128.
- Jia, Y. H., and Liu, Y. (2020). REE enrichment during magmatic–hydrothermal processes in carbonatite-related REE deposits: A case study of the weishan REE deposit, China. *Minerals*, 10(1), 1–30.
- Jones, A. P., Genge, M., and Carmody, L. (2013). Carbonate melts and carbonatites. *Reviews in Mineralogy and Geochemistry*, 75(1), 289–322.
- Kachingwe, M., Nyblade, A., and Julià, J. (2015). Crustal structure of Precambrian terranes in the southern African subcontinent with implications for secular variation in crustal genesis. *Geophysical Journal International*, 202(1), 533–547.
- Kim, S. J., Lee, H. K., Yin, J., and Park, J. K. (2005). Chemistry and origin of monazites from carbonatite dikes in the Hongcheon-Jaeun district, Korea. *Journal of Asian Earth Sciences*, 25(1), pp.57–67.
- Kjarsgaard, B. A., Hamilton, D. L., and Peterson, T. D. (1995). Peralkaline nephelinite/carbonatite liquid immiscibility: Comparison of phase compositions in experiments and natural lavas from Oldoinyo Lengai. In K. Bell and J. Keller (Eds.), *Carbonatite Volcanism* (4th ed.), Springer, Berlin Heidelberg, pp. 163–190.
- Kogarko, L. N., and Veselovskiy, R. V. (2019). Geodynamic origin of carbonatites from the absolute paleotectonic reconstructions. *Journal of Geodynamics*, 125, 13–21.
- Kono, Y., Kenney-benson, C., Hummer, D., Ohfuji, H., Park, C., Shen, G., Wang, Y., Kavner, A., and Manning, C. E. (2014). Ultralow viscosity of carbonate melts at high pressures. *Nature Communications*, 5(5091), pp.2–5.
- Le Bas, M. J. (1981). Carbonatite magmas. *Mineralogical Magazine*, 44(334), 133–140.
- Lewis, A., Mdelein, P., Schmitz, M., and Kevin, B. (2016). Isotopic evidence for a lithospheric origin of alkaline rocks and carbonatites: an example from southern Africa. *Canadian Journal of Earth Sciences*, 53(11), 1–50.
- Liu, D., Zhao, Z., Zhu, D. C., et al. (2015). Identifying mantle carbonatite metasomatism through Os-Sr-Mg isotopes in Tibetan ultrapotassic rocks. *Earth and Planetary Science Letters*, 430, 458–469.
- Marien, C., Dijkstra, A. H., and Wilkins, C. (2018). The hydrothermal alteration of carbonatite in the Fen Complex, Norway: mineralogy, geochemistry, and implications for rare-earth element resource formation. *Mineralogical Magazine*,

- 82(SI), pp.S115–S131.
- Martin, L. H. J., Schmidt, M. W., Mattsson, H. B., Ulmer, P., Hametner, K., and Günther, D. (2012). Element partitioning between immiscible carbonatite – kamafugite melts with application to the Italian ultrapotassic Suite. *Chemical Geology*, 320–321, 96–112.
- McDonough, W. F., and Sun, S. S. (1995). The composition of the Earth. *Chemical Geology*, 120(4), pp.223–253.
- McKie, D. (1962). Goyazite and florencite from two African carbonatites. *Mineralogical Magazine and Journal of the Mineralogical Society*, 33(259), pp.281–297.
- Migdisov, A., Williams-jones, A.E., Brugger, J., and C.A.Poruscio, A.F. (2016) Hydrothermal transport, deposition, and fractionation of the REE: Experimental data and thermodynamic calculations. *Chemical. Geology.*, 439, 13–42.
- Mitchell, R. H. (2005). Carbonatites and carbonatites and carbonatites. *Canadian Mineralogist*, 43(6), 2049–2068.
- Mitchell, R. H., and Smith, D. L. (2017). Geology and mineralogy of the Ashram Zone carbonatite, Eldor Complex, Québec. *Ore Geology Reviews*, 86, 784–806.
- Mitchell, R. H., and Gittins, J. (2022). Carbonatites and carbothermalites: A revised classification. *Lithos*, 430–431, 1–11.
- Moore, M., Chakhmouradian, A. R., Mariano, A. N., and Sidhu, R. (2015). Evolution of rare-earth mineralization in the Bear Lodge carbonatite, Wyoming: Mineralogical and isotopic evidence. *Ore Geology Reviews*, 64, 499–521.
- Ngwenya, B. T., and Bailey, D. K. (1990). Kaluwe carbonatite, Zambia: an alternative to natrocarbonatite. *Journal of Geological Society (London)*, 147(2), 213–216.
- Njinju, E. A., Atekwana, E. A., Stamps, D. S., et al. (2019). Lithospheric structure of the Malawi Rift: Implications for magma-poor rifting processes. *Tectonics*, 38(11), 3835–3853.
- Parker, A. (1970). An index of weathering for silicate rocks. *Geological Magazine*, 107(6), pp.501–504.
- Pirajno, F. (2015). Intracontinental anorogenic alkaline magmatism and carbonatites, associated mineral systems and the mantle plume connection. *Gondwana Research*,

- 27(3), 1181–1216.
- Prokopyev, I. R., Borisenko, A. S., Borovikov, A. A., and Pavlova, G. G. (2016). Origin of REE-rich ferrocarbonatites in southern Siberia (Russia): Implications based on melt and fluid inclusions. *Mineralogy and Petrology*, 110(6), 845–859.
- Ray, J. S., and Ramesh, R. (2006). Stable Carbon and Oxygen Isotopic Compositions of Indian Carbonatites Stable Carbon and Oxygen Isotopic Compositions. *International Geological Review*, 48, pp.17–45
- Samson, I. M., Liu, W., and Williams-Jones, A. E. (1995). The nature of orthomagmatic hydrothermal fluids in the Oka carbonatite, Quebec, Canada: Evidence from fluid inclusions. *Geochimica et Cosmochimica Acta*, 59(10), 1963–1977.
- Sano, S., Oberha, R., and Vinx, R. (2002). Petrological, geochemical and isotopic constraints on the origin of the Harzburg Intrusion, Germany. *Journal of Petrology*, 43(8), 1529–1549.
- Slezak, P., and Spandler, C. (2020). Petrogenesis of the Gifford Creek Carbonatite Complex, Western Australia. *Contributions to Mineralogy and Petrology*, 175(3), 1–23.
- Smith, M. P., and Henderson, P. (2000). Preliminary fluid inclusion constraints on fluid evolution in the Bayan Obo Fe-REE-Nb deposit, inner Mongolia, China. *Economic Geology*, 95(7), 1371–1388.
- Snelling, N. (1965). Age determination of three African carbonatites. *Nature*, 205, pp.491
- Srivastava, R. K., and Rajesh, K. (1993). Chemical classification of silica rich carbonatites. *Indian Journal of Geochemistry*, 8(12), 15–24.
- Strzelecki, A. C., Migdisov, A., Boukhalfa, H., Sauer, K., McIntosh, K. G., Currier, R. P., Williams-Jones, A. E., and Guo, X. (2022). Fluocerite as a precursor to rare earth element fractionation in ore-forming systems. *Nature Geoscience*, 15(4), 327–333.
- Su, J. H., Zhao, X. F., Li, X. C., Hu, W., Chen, W., and Slezak, P. (2022). Unmixing of REE-Nb enriched carbonatites after incremental fractionation of alkaline magmas in the Shaxiongdong complex, Central China. *Lithos*, 416–417(12), 10665.
- Tappe, S., Romer, R. L., Stracke, A., et al. (2017). Sources and mobility of carbonate melts beneath cratons, with implications for deep carbon cycling, metasomatism and rift initiation. *Earth and Planetary Science Letters*, 466, 152–167.

- Thompson, R. N., Smith, P. M., Gibson, S. A., Matthey, D. P., and Dickin, A. P. (2002). Ankerite carbonatite from Swartbooisdrif, Namibia: The first evidence for magmatic ferrocarbonatite. *Contributions to Mineralogy and Petrology*, 143, 377–395.
- Trofanenko, J., Williams-Jones, A. E., Simandl, G. J., and Migdisov, A. A. (2016). The nature and origin of the REE mineralization in the Wicheeda Carbonatite, British Columbia, Canada. *Economic Geology*, 111(1), 199–223.
- Veksler, I. V., Dorfman, A. M., Dulski, P., Kamenetsky, V. S., et al. (2012). Partitioning of elements between silicate melt and immiscible fluoride, chloride, carbonate, phosphate and sulfate melts, with implications to the origin of natrocarbonatite. *Geochimica et Cosmochimica Acta*, 79, 20–40.
- Wall, F. (1994). Isotopic evidence for late-stage processes in carbonatites: Rare earth mineralization in carbonatites and quartz rocks at Kangankunde, Malawi. *Mineralogical Magazine*, 58A(2), 951–952.
- Wall, F., and Mariano, A. N. (1996). Rare earth minerals in carbonatites: A discussion centred on the Kangankunde carbonatite, Malawi. In Jones, A. P., Wall, F., and William, C. T. (Eds.), *Rare Earth Minerals: Chemistry Origin and Ore deposits*. Chapman and Hall, pp.193–225.
- Wall, F., and Zaitsev, A. N. (2004). Rare earth minerals in Kola carbonatites. In Wall, F., and Zaitsev, A. (Eds.), *Phoscorite and Carbonatite from the Mantle to Mine: The Key Example of the Kola Alkaline Province*. Mineralogical Society of Great Britain and Ireland, pp. 341–373.
- Walter, B. F., Giebel, R. J., Siegfried, P. R., Gudelius, D., and Kolb, J. (2023). The eruption interface between carbonatitic dykes and diatremes – The Gross Brukkaros volcanic field Namibia. *Chemical Geology*, 621, 121344.
- Walter, B. F., Giebel, R. J., Steele-MacInnis, M., Marks, M. A. W., Kolb, J., and Markl, G. (2021). Fluids associated with carbonatitic magmatism: A critical review and implications for carbonatite magma ascent. *Earth-Science Reviews*, 215, 103509.
- Wang, Z. Y., Fan, H. R., Zhou, L., Yang, K. F., and She, H. D. (2020). Carbonatite-related REE deposits: An overview. *Minerals*, 10(11), 1–26.
- Wei, C., Xu, C., Chakhmouradian, A. R., Brenna, M., Kynicky, J., and Song, W. (2020). Carbon – strontium isotope decoupling in carbonatites from Caotan (Qinling,

- China): Implications for the origin of calcite carbonatite in orogenic settings. *Journal of Petrology*, 61(2), 1–26.
- Williams-Jones, A. E., and Palmer, D. A. S. (2002). The evolution of aqueous-carbonic fluids in the Amba Dongar carbonatite, India: Implications for fenitisation. *Chemical Geology*, 185(3–4), 283–301.
- Woolley, A. R. (1982). A discussion of carbonatite evolution and nomenclature, and the generation of sodic and potassic fenites. *Mineralogical Magazine*, 46(338), 13–17.
- Woolley, A. R. (1987). Lithosphere metasomatism and the petrogenesis of the Chilwa Province of alkaline igneous rocks and carbonatites, Malawi. *Journal of African Earth Sciences*, 6(6), 891–898.
- Woolley, A. R., and Bailey, D. K. (2012). The crucial role of lithospheric structure in the generation and release of carbonatites: Geological evidence. *Mineralogical Magazine*, 76(2), 259–270.
- Woolley, A. R., and Kempe, D. R. C. (1989). Carbonatites: Nomenclature, average chemical compositions, and element distribution. In Bell, K. (Ed.), *Carbonatite: Genesis and Evolution*, 1Ed., UnwinHyman, London, pp. 1–13.
- Woolley, A. R., and Kjarsgaard, B. A. (2008). Carbonatite Occurrences of the World: Map and Database. Geological Survey of Canada. 22p.
- Woolley, A. R. (2001). Alkaline Rocks and Carbonatites of the World Part 3: Africa. The Geological Society of London. 372pp
- Wyllie, P. J., and Lee, W. (1998). Model system controls on conditions for formation of magnesiocarbonatite and calciocarbonatite magmas from the mantle. *Journal of Petrology*, 39(11), 1885–1893.
- Xu, C., Wang, L., Song, W., and Wu, M. (2010). Carbonatites in China: A review for genesis and mineralization. *Geoscience Frontiers*, 1(1), 105–114.
- Yang, K. F., Fan, H. R., Santosh, M., Hu, F. F., and Wang, K. Y. (2011). Mesoproterozoic carbonatitic magmatism in the Bayan Obo deposit, Inner Mongolia, North China: Constraints for the mechanism of super accumulation of rare earth elements. *Ore Geology Reviews*, 40(1), 122–131.
- Yang, K., Fan, H., Pirajno, F., and Li, X. (2019). The Bayan Obo (China) giant REE accumulation conundrum elucidated by intense magmatic differentiation of carbonatite. *Geological Society of America*, 47(12), 1198–1202.

- Yaxley, G. M., Anenburg, M., Tappe, S., Decree, S., and Guzmics, T. (2022). Carbonatites: Classification, sources, evolution, and emplacement. *Annual Reviews Earth and Planetary Sciences*, 50, 261–293.
- Ying, Y., Chen, W., Simonetti, A., and Jiang, S. (2020) Significance of hydrothermal reworking for REE mineralization associated with carbonatite: Constraints from in situ trace element and C-Sr isotope study of calcite and apatite from the Miaoya carbonatite complex, China. *Geochimica et Cosmochimica Acta*, 280, 340–359
- Zongshou, Y., Norman, M. D., and Robinson, P. (2003). Major and trace element analysis of silicate rocks by XRF and laser ablation ICP-MS using lithium borate fused glasses: Matrix effects, instrument response and results for international reference materials. *Geostandards News Letter*, 27, 67–89

Chapter 5 : Petrochemistry of the Tundulu carbonatite

5.1 Introduction

The Tundulu carbonatite is located approximately 50 km east-south-east of Zomba and 25 km north-north-east of Phalombe, close to Lake Chirwa (Fig. 1-1). The carbonatite has been mined before for phosphate production by Optichem Limited and production stalled since 1996. However, preliminary resource calculation of the Nathache hill estimates 4.5 Mt at 1 % TREE₂O₃, with a cut-off grade of 0.5 % TREE₂O₃, and 1.8 Mt at 10 wt. % P₂O₅, with a cut-off grade of 5 wt. % P₂O₅ (Broom-Fendley, 2016). Malawi updated legislation in 2019 and now provides for the extraction of all available economic minerals during mine operations to promote sustainable mining (Mines and Mineral Act, 2019). Prior to this study, research on REEs mineralization at Tundulu carbonatite focused on the hydrothermal processes and carbonatite composition (Woolley, 1982; Ngwenya, 1994; Broom-Fendley et al., 2016). This study re-evaluated the Tundulu carbonatite REE mineralization, focusing on the magmatic processes and their implications on REE mineralization. This was achieved through a detailed description of the composition of the host rock, ore minerals, and stable isotope geochemistry.

Garson (1962, 1965) reported the geology of the Tundulu carbonatite. The Tundulu carbonatite was emplaced as a ring structure composed of three igneous centers with a diameter of about 1.6 kilometres (Fig. 5-1). The first center (Tundulu Hill) is related to the initial intrusion on the Malawi basement complex (MBC). Its initial emplacement is characterized by feldspathic breccia, while its final emplacement is characterized by calcio-carbonatite (soviet) with siderite affinity. The second center, Nathache Hill, is inside the first structure on the southwest of the first center and invades the calcio-carbonatite and feldspathic breccia of the first center. The Nathache Hill is characterized by feldspathic breccia, pyroclastic agglomerate, and dykes of ferruginous calcio-carbonatite (apatite-rich carbonatite), magnesio-carbonatite (bastnaesite carbonatite) and calcio-carbonatite (sovite). The third center occurs as dykes of melanephelinite, olivine-melanephelinite and beforite and beforitic

lamprophyres. K-Ar dating of the biotite from the syenite gave an age of 133 ± 7 Ma (Snelling, 1965).

Garson (1965) proposed the following sequence of events: (i) formation of a dome of contact breccia that formed above a carbonatite pluton due to intense stress whose cracks were filled with fenitic material while the contact breccia is recrystallized and ramified and partly replaced by carbonatite magma; (ii) a pattern of radial/ spiral cracks which were produced by an outward pressure from a pipe like-pluton which had two orthogonal tension cracks. A renewed magmatic pressure influenced these cracks; (iii) cone sheet formation from the ring dykes and sills which were earlier injected with carbonatite and associated magmatic material in the shear cracks; (iv) cauldron subsidence within steep zones of crack lubricated by magma that resulted in the widening of the ring dykes at the time of formation of composite ring dykes. and (vi) consolidation of the rocks renewed pressure from the active underlying part of the carbonatite pluton and repeating the circle at different levels or centers.

On the surface, late Pre-Cambrian to early Cambrian rocks of gneisses and syenite are distributed in the southern and western parts (Nathache Hill), (Makhanga Hill and the north-western part (Namuka Hill); these gneisses are biotite and granitic gneisses. (Fig. 5-1). Furthermore, dolerite dykes are distributed in the Namilemba Hill and intrude the basement gneisses.

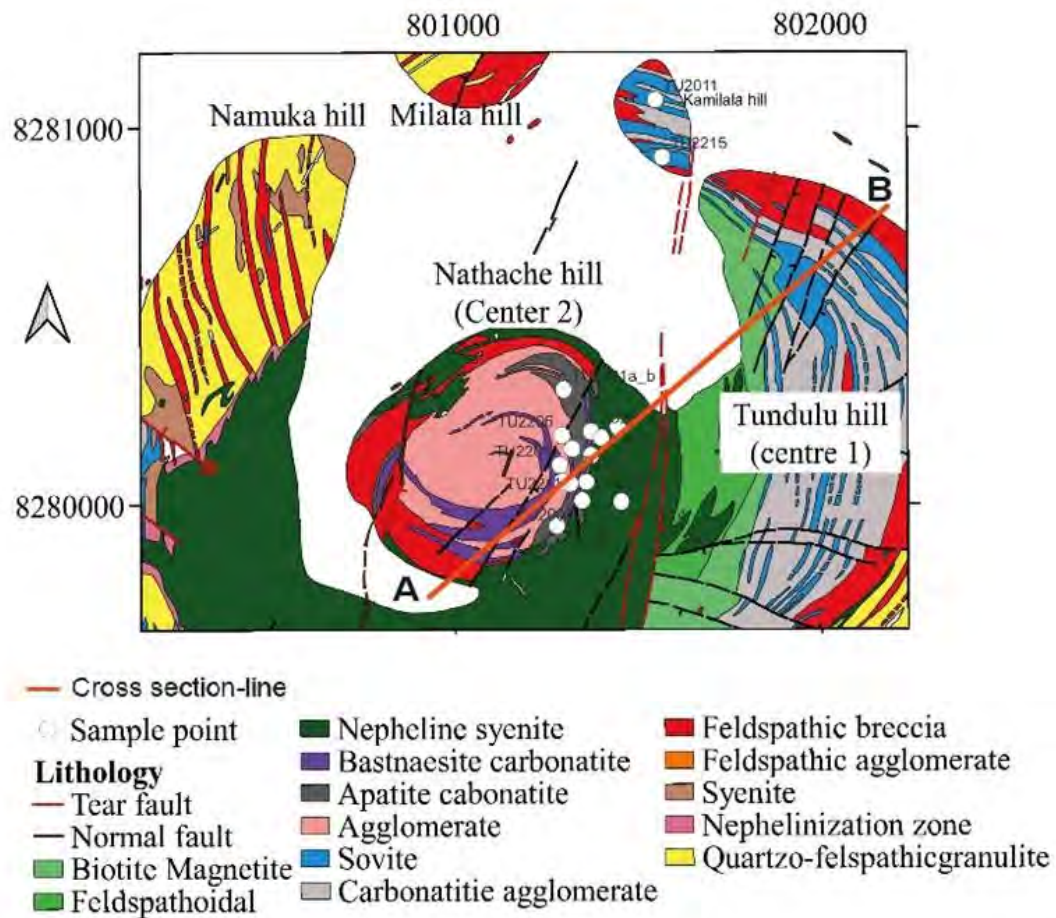


Fig. 5-1 Map of the Tundulu carbonatite showing the geology and sampling points (adapted from Garson, 1962).

5.2 Results

5.2.1 Field observation

5.2.1.1 Lithological observation

Based on field observation, six lithotypes in the Tundulu carbonatite were identified, including calcio-carbonatite, ferruginous calcio-carbonatite, magnesio-carbonatite, agglomerate, feldspathic breccia, and syenite. Calcio-carbonatite is a calcite-rich rock. At Tundulu Hill, the calcio-carbonatite occurred as ring dykes interspaced with carbonatite agglomerate and feldspar agglomerate. Calcio-carbonatite is characterized by a dark grayish color, fine to medium-grained, and flow banding with foliated feldspar (Figs. 5-1, 5-2a). Nathache Hill, calcio-carbonatite occurred as dyke intruding ferruginous calcio-carbonatite. Calcio-carbonatite is characterized by a whitish color, coarse-grained spinifex texture, and occasionally, it is cut by a barite vein (Figs. 5-1, 5-2b-c).

Ferruginous calcio-carbonatite is characterized by light pink to light-brown color, fine to medium-grained with porphyritic texture. Siderite and ankerite occasionally form spots and bands. Apatite gives the pink color. In addition, ankerite forms a lens-like appearance when weathered (Fig. 5-2d-e-f).

Magnesio-carbonatite showed variable apatite concentration and is further classified as apatite-rich magnesio-carbonatite and apatite-poor magnesio-carbonatite. Apatite-rich magnesio-carbonatite is dark brown with random light-pinkish patches of apatite and fine to medium-grained. The apatite and carbonates form comb and porphyritic textures. (Fig. 5-2g-h). Apatite-poor magnesio-carbonatite is dark brown and whitish in color, fine to medium-grained. It also has sporadic occurrence of thin calcite veins (Fig. 5-2i). Occasionally, biotite inclusions were observed in apatite-poor magnesio-carbonatite at the bottom of the old mine pit (Fig. 5-2j). Furthermore, hematite dykes intrude the apatite-poor magnesio-carbonatite (Fig. 5-2k).

Agglomerate has xenocryst of feldspar cemented by carbonate and quartz. Quartz and calcite also form veins. Quartz also occurs crystalline in miotic cavities (Fig. 5-2l). Syenite is light gray in color, coarse-grained and composed of nepheline, biotite, magnetite, and calcite (Fig. 5-2m).

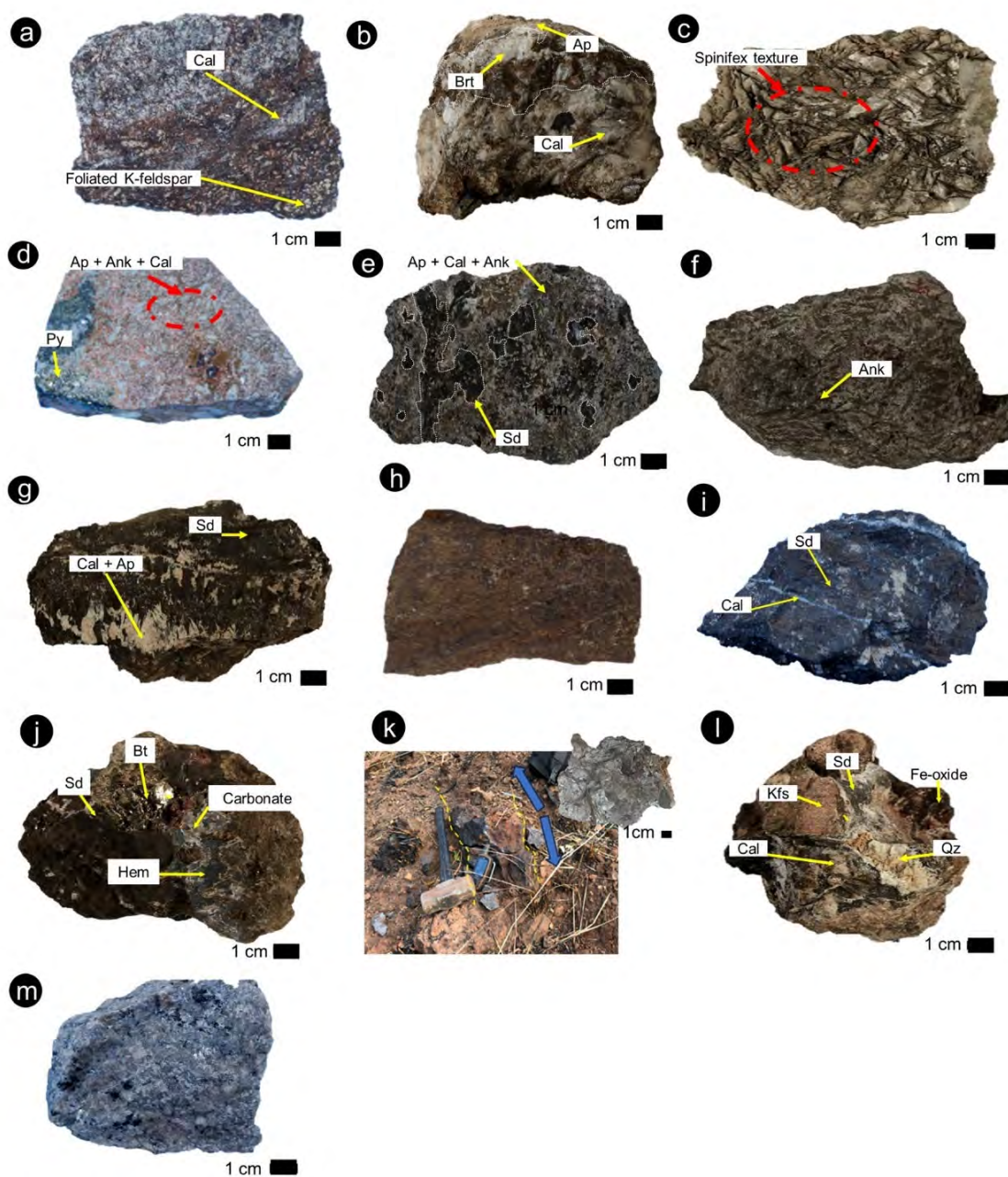


Fig. 5-2 Representative photos of rock samples. (a-c) calcio-carbonatite with foliated feldspar, barite vein, spinifex texture, (d-f) ferruginous calcio-carbonatite with pyrite, and siderite, (g-h) apatite-rich magnesio-carbonatite with comb and porphyritic texture, (i-j) apatite-poor magnesio-carbonatite with veins composed of calcite, hematite, biotite, (k) hematite dyke in apatite-poor carbonatite, (l) agglomerate crystalline quartz, (m) syenite. Abbreviation: Ap - apatite, Cal— calcite, Kfs —K-feldspar., Sd- Siderite, Bt- biotite, Hem- hematite, Ank- ankerite, Brt- barite, Py- pyrite.

5.2.2 Petrography

5.3.2.1 Calcio-carbonatite

Calcio-carbonatite is composed of calcite, orthoclase, ankerite, siderite, apatite, synchysite, strontianite, magnetite and quartz (Fig. 5-3a-e). In the Tundulu Hill calcite, ankerite and feldspar are dominant. Orthoclase formed trachytoid texture of semi-elongated blebs ranging from 50 μm to 300 μm in length with a prismatic termination. Calcite occurred anhedral with elevated Fe, overprinted orthoclase. Ankerite occurred euhedral and zoned. Ankerite and calcite form an interlocking mosaic (Fig. 5.3a). Apatite occurred subhedral elongated replaced calcite and orthoclase. Synchysite is zoned, and the outer rim has elevated Ti content and formed an intergrowth texture in association with strontianite and apatite (fig. 5-3b). Strontianite is Ca-rich and anhedral, replacing synchysite (Fig. 5-3b). Pyrochlore occurred euhedral as an accessory mineral.

Nathache Hill calcio-carbonatite composed of calcite, apatite, magnetite synchysite. Calcite dominant, which occurs euhedral to anhedral with and without Fe. Magnetite occurred as anhedral overprinted by calcite and apatite. Apatite has an idiomorphic texture (Fig. 5-3c). In addition, magnetite occurred as an anhedral with a corroded texture and had shown to form in an immiscible environment. (Fig. 5-3d). Strontianite occurred anhedral overprinting calcite and apatite. Synchysite occurred as inclusion in calcite (Fig. 5-3e). XRD representative pattern are given in Appendix A2.

5.3.2.2 Ferruginous calcio-carbonatite

Ferruginous calcio-carbonatite is composed of fluorapatite, ankerite, calcite, synchysite, barite, strontianite, pyrite, celestine and quartz (Fig. 5-3f-n). Ankerite and apatite are dominant. Ankerite occurs euhedral to subhedral, with hexagonal pseudomorphs that are filled with synchysite strontianite barite and quartz that make glomeroporphyritic texture (Fig. 5-3f). Ankerite is brecciated and overprinted by fluorapatite. Celestine overprints quartz filling spaces between ankerite and apatite (Fig. 5-3g-h). Fluorapatite occurred euhedral to anhedral with overgrowth and dissolution textures. The core of the fluorapatite is contaminated by Fe (Fig. 5-3i). Pyrochlore is brecciated overprinting quartz filling spaces of brecciated ankerite and fluorapatite (Fig.

5-3i). Synchronite occurred with intergrowth texture overprinting quartz filling spaces of fluorapatite or overprinting recrystallized fluorapatite and calcite (Fig. 5-3i-j). Calcite occurred euhedral to anhedral contaminated with REE and Fe (Fig. 5-3k). Pyrite is euhedral to subhedral with unwelded texture, replacing apatite with graphitic texture (Fig. 5-3l). XRD representative pattern are given in Appendix A2

5.3.2.3 Magnesio-carbonatite

Magnesio-carbonatite is composed of siderite, ankerite, dolomite, calcite, barite, pyrolusite, quartz, hematite and synchronite. Apatite-rich magnesio-carbonatite has siderite that occurs subhedral with an exsolution texture and is altered to ankerite and dolomite. Siderite shows zoning in the early stages and skeletal texture in the late stage. Dolomite is anhedral, replacing siderite and ankerite (Fig. 5-3m-n). Barite and strontianite are consertal and overprint synchronite and quartz (Fig. 5-3o). Synchronite overprints quartz (Fig. 5-3o) and also occurred corroded. Furthermore, rhodochrosite precipitated on synchronite and calcite (Fig. 5-3p).

Apatite-poor magnesio-carbonatite has siderite that occurred euhedrally and is replaced by dolomite. Synchronite overprints dolomite. Barites overprints synchronite (Fig. 5-3q). XRD representative pattern are given in Appendix A2.

5.3.2.4 Agglomerate-carbonatite

Agglomerate is composed of subhedral quartz, calcite orthoclase, ankerite, feldspar, and Fe-oxide. Calcite and quartz also formed veins. Orthoclase occurred turbid (Fig. 5-3r-s).

5.3.2.5 Syenite

Syenite is composed of nepheline, magnetite, biotite, and orthoclase. Nepheline is abundant and altered biotite that forms skeletal shreds replaced by magnetite. Calcite is anhedral with reaction rims (Fig. 5-3t).

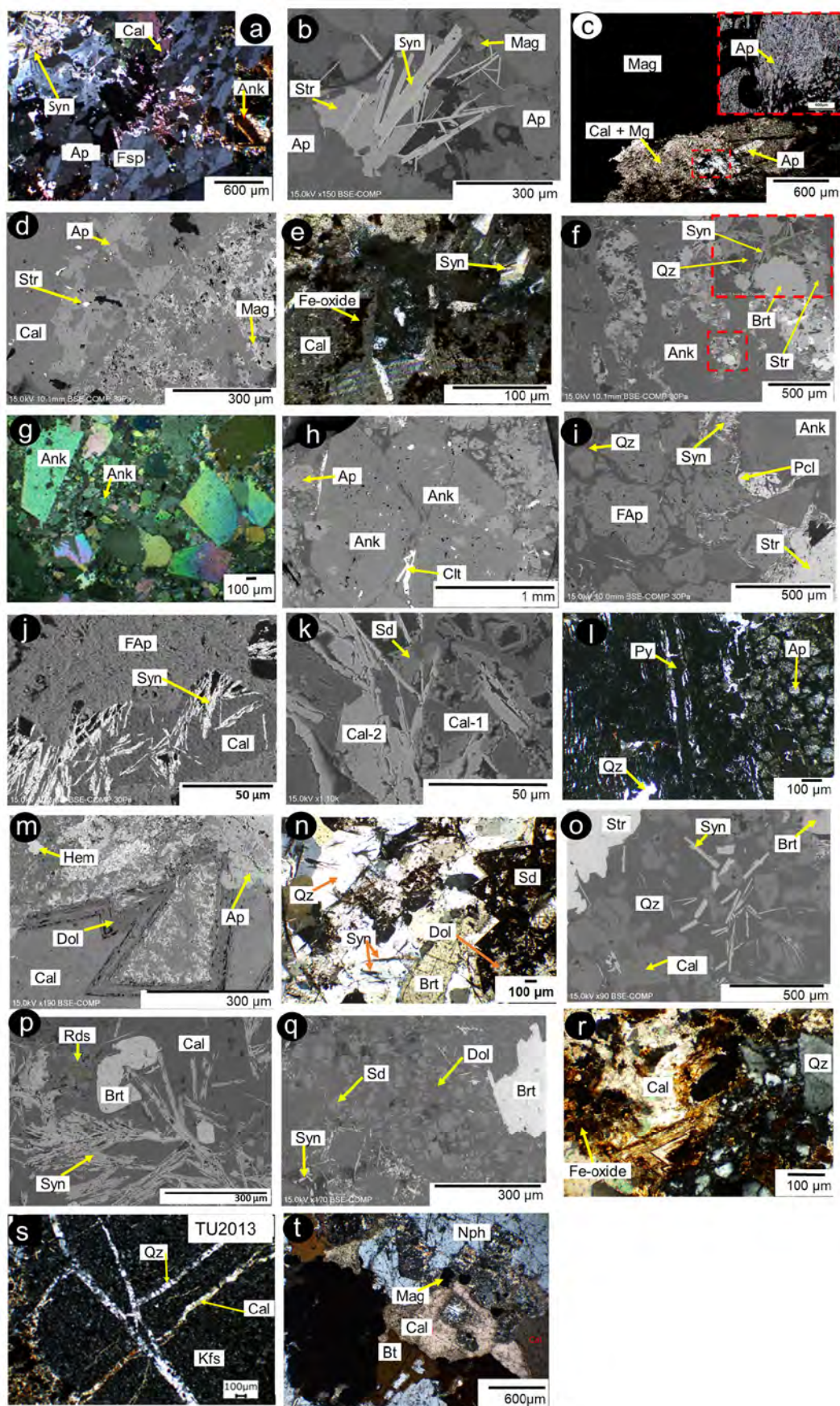


Fig. 5-3 Backscattered electron images and photomicrographs of mineral assemblages of samples studied. (a-b) calcio-carbonatite from Tundulu Hill first igneous center with foliated feldspar blebs, and synchysite with glomeroporphyritic texture. (c) calcio-carbonatite with calcite and idiomorphic texture of apatite overprinting magnetite, (d) calcio-carbonatite with differentiation between Fe and P₂O₅ rich melt, (e) synchysite inclusion in calcio-carbonatite, (f). ferruginous calcio-carbonatite with hexagonal pseudomorph indicating magmatic REE mineralization, (g) ferruginous calcio-carbonatite with brecciated ankerite, (h) ferruginous calcio-carbonatite with apatite overprinting brecciated ankerite, and celestine interstitial between ankerite and apatite, (i) ferruginous calcio-carbonatite with apatite overgrowth and dissolution textures, quartz filling spaces between apatite and ankerite, synchysite and barite overprinting quartz, and brecciated pyrochlore overprinting quartz (j) ferruginous calcio-carbonatite with recrystallized calcite overprinted by synchysite, (k) ferruginous calcio-carbonatite with calcite contaminated with REE, (l) ferruginous calcio-carbonatite with pyrite unwedged texture, (m) Apatite-rich magnesio-carbonatite with dolomite replacing siderite, (n) apatite-rich magnesio-carbonatite with synchysite overprinting quartz, (o) apatite-rich magnesio-carbonatite with skeletal texture of siderite alteration, (p) apatite-poor magnesio-carbonatite with fibrous texture of synchysite having rhodochrosite on rim and calcite, (q) apatite-poor magnesio-carbonatite with dolomite replacing siderite, (r) agglomerate with Fe-oxides filling calcite (s) agglomerate with quartz and calcite veins, (t) syenite with consertal texture. Abbreviation: Ap - apatite, Ank— ankerite, Brt—Baryte, Cal— calcite, Str—Strontianite, Py— Pyrite, Dol—dolomite, Fe-oxide — iron, Syn— Synchysite, Qz— Quartz, Mag— magnetite, Clt—Celestine, Bt— Biotite, Kfs—Orthoclase, Pcl— pyrochlore, Pyl—pyrolusite. All photomicrographs are crossed polarized.

5.3.2.6 Mineralization

REE mineralization in the Tundulu carbonatite occurred as disseminated and synchysite is the main REE mineral. Synchysite occurs in various forms and mineral assemblages, including zone synchysite with intergrowth texture associated with apatite (Fig. 5-3b) and as inclusion in calcite (Fig. 5-3e) and is common in calcio-carbonatite. Hexagonal pseudomorphs where synchysite occurred with glomeroporphyritic texture associated with strontianite, barite, and quartz (Fig. 5-3f). This was observed in ferruginous calcio-carbonatite and apatite-rich magnesio-carbonatite. Synchysite with glomeroporphyritic texture overprinting fluorapatite, calcite, and quartz (Fig. 5-3i-j-o) is common in ferruginous calcio-carbonatite and magnesio-carbonatite.

5.2.3 Whole-rock geochemistry

5.2.3.1 Major-element geochemistry

The major element composition of the studied carbonatites is given in Appendix A5. Using the classification of Gittins & Harmer (1997), Tundulu carbonatite is dominated by calcio-carbonatite, ferruginous calcio-carbonatite and magnesio-carbonatite. The ferruginous calcio-carbonatite also plot in the field of calcio-carbonatite and magnesio-carbonatite (Fig. 5-4). The geochemical data shows a continuous trend from calcio-carbonatite through ferruginous calcio-carbonatite to

magnesio-carbonatite. The SiO_2 content ranges from 0.6 to 19 wt. %. The FeO and MnO contents increase from calcio-carbonatite (0.6-12.3 wt. % and 0.3-2.2 wt. %), ferruginous calcio-carbonatite (5.2-15.4 wt. % and 0.1-2.3 wt. %) and magnesio-carbonatite (11.2-30.3 wt. % and 2.0-6.0 wt. %) respectively. The SrO and BaO contents increase from calcio-carbonatite (1,050-20151 ppm and 58-22290 ppm), ferruginous calcio-carbonatite (1,370-30821 ppm and 857-25468 ppm) and magnesio-carbonatite (1898-43507 ppm and 3129-95412 ppm). Furthermore, P_2O_5 content ranges in carbonatite (0.13-13.5 wt. %) while in syenite (0.1-0.5 wt. %).

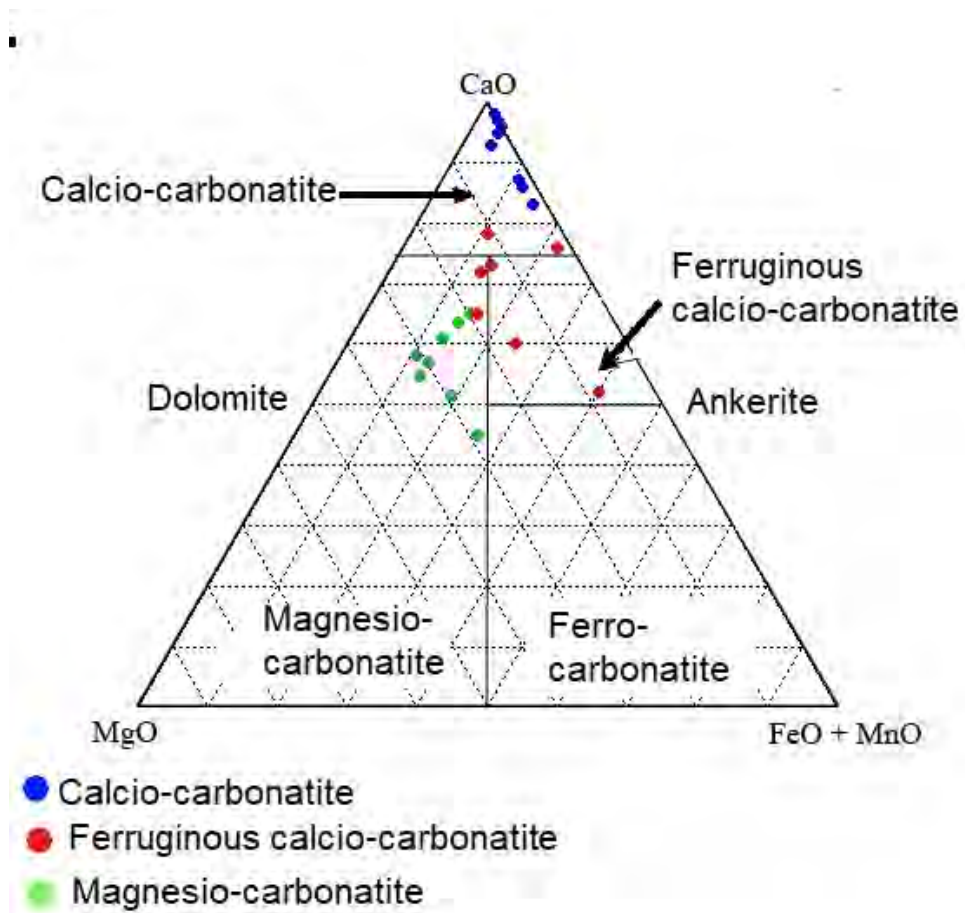


Fig. 5-4 Carbonatite classification using major oxide molar proportion defined by Gittins and Hammer (1997).

5.2.3.2 Trace element geochemistry

The trace element composition of the carbonatite samples studied is given in Appendix A5. Similar to the Kangankunde carbonatite, (Ta, REEs, Nb, Zr, Hf, Th, U, Ti, Rb) and chalcophile (Pb) elements were used to assess REEs mineralization and magma evolution (e.g. Hou et al., 2015; Benkó et al., 2021). The chondrite-normalized ratio of lanthanum and ytterbium $(La/Yb)_N$ ranges from 33 to 289, 122 to 3034 and 30 to 56 in calcio-carbonatite, magnesio-carbonatite and ferruginous calcio-carbonatite respectively (Appendix A5). LREEs (La-Nd) are more enriched in magnesio-carbonatite followed by calcio-carbonatite and ferruginous calcio-carbonatite with averages of $(La/Yb)_N$ of 1265, 110 and 44, respectively Middle rare earth elements (MREEs; Sm-Y) are more enriched in ferruginous calcio-carbonatite. Magnesio-carbonatite shows a negative Y anomaly (Fig. 5-5a).

The primitive-mantle-normalized patterns reveal similarities to the carbonatites of the worlds (Fig. 5-5b; e.g. Woolley & Kempe, 1989). All carbonatites show a negative anomaly for Ti, Zr, and Pb, while Th and Nb are variable. Magnesio-carbonatite showed variability in Hf relative to mantle values. Carbonatite Zr and Nb contents range from 1.3–321.0 ppm and 5.3-3600 ppm respectively, while in syenite, Zr and Nb contents range from 230.6-524 ppm and 99.3-4864.7 ppm, respectively.

Y/Ho ratio ranges from 26 to 33, 21 to 35 and 24-38 in calcio-carbonatite, magnesio-carbonatite and ferruginous calcio-carbonatite, respectively and are similar to other carbonatites elsewhere (Fig. 5-6; Appendix A5).

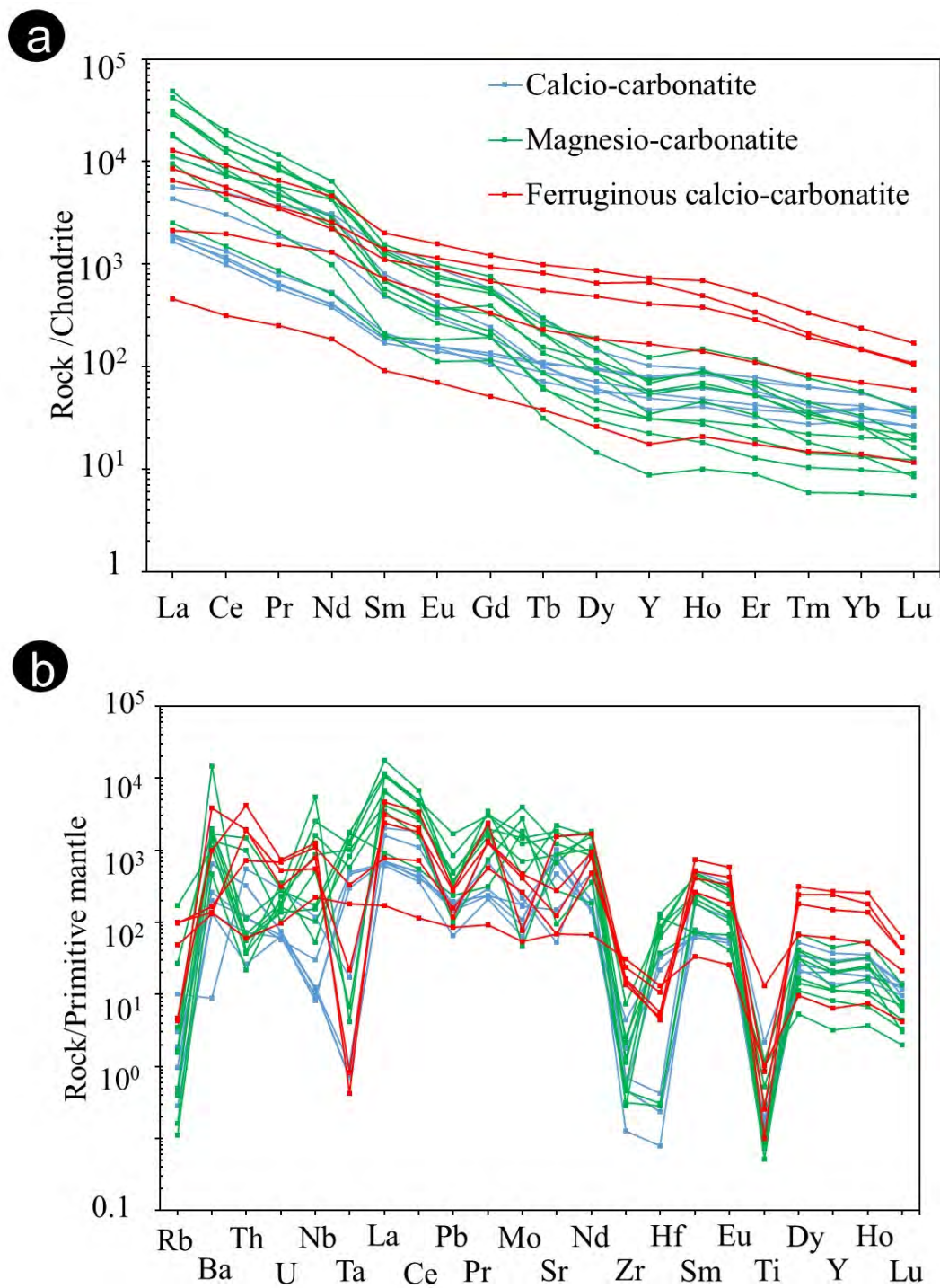


Fig. 5-5 Whole-rock REE and trace element patterns for magnesio-carbonatite, calcio-carbonatite and ferruginous calcio-carbonatite. (a) Chondrite-normalized REE patterns. (b) Primitive mantle normalized LILE and HFSE elements. Chondrite and primitive mantle values from McDonough and Sun (1995).

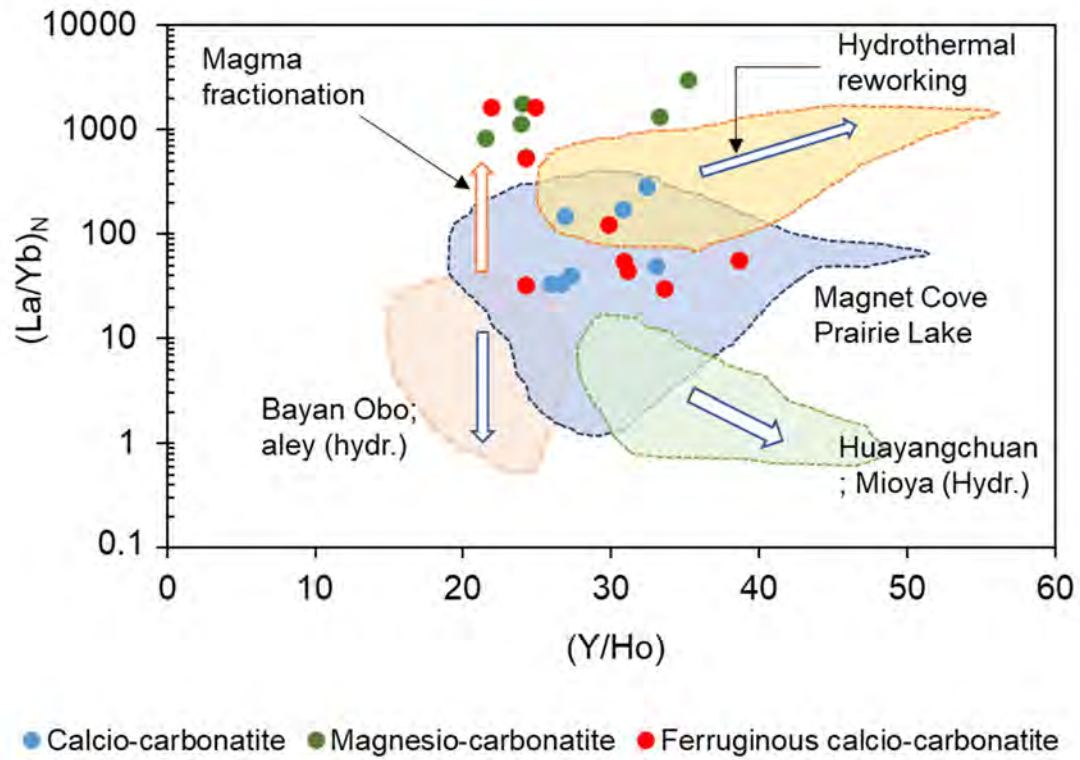


Fig. 5-6 Chondrite-normalized diagrams of REE ratios $(La/Yb)_N$ versus Y/Ho (chondrite values from McDonough & Sun, (1995). Adapted from Bau (1996) (primary and alteration fields from Zheng et al., 2023)

5.2.3.3 Correlation between REEs and major and trace REE elements

The TREE_2O_3 and P_2O_3 contents are strongly positively correlated in the ferruginous calcio-carbonatite and moderately correlated in the magnesio-carbonatite and calcio-carbonatite (Fig. 5-7a). The TREE_2O_3 and SrO contents are strongly positively correlated in the ferruginous calcio-carbonatite, moderately correlated in the magnesio-carbonatite and not correlated in calcio-carbonatite (Fig. 5-7b). The TREE_2O_3 and BaO contents are moderately positively correlated in the calcio-carbonatite, weakly correlated in ferruginous calcio-carbonatite, and not correlated in the magnesio-carbonatite (Fig. 5-7c). The TREE_2O_3 and (FeO+MnO) contents are strongly positively correlated in the calcio-carbonatite, moderately correlated in the magnesio-carbonatite and weakly correlated in ferruginous calcio-carbonatite (Fig. 5-7d). The TREE_2O_3 and Nb contents are strongly positively correlated in the ferruginous calcio-carbonatite and calcio-carbonatite while weakly correlated in magnesio-carbonatite (Fig. 5-7e).

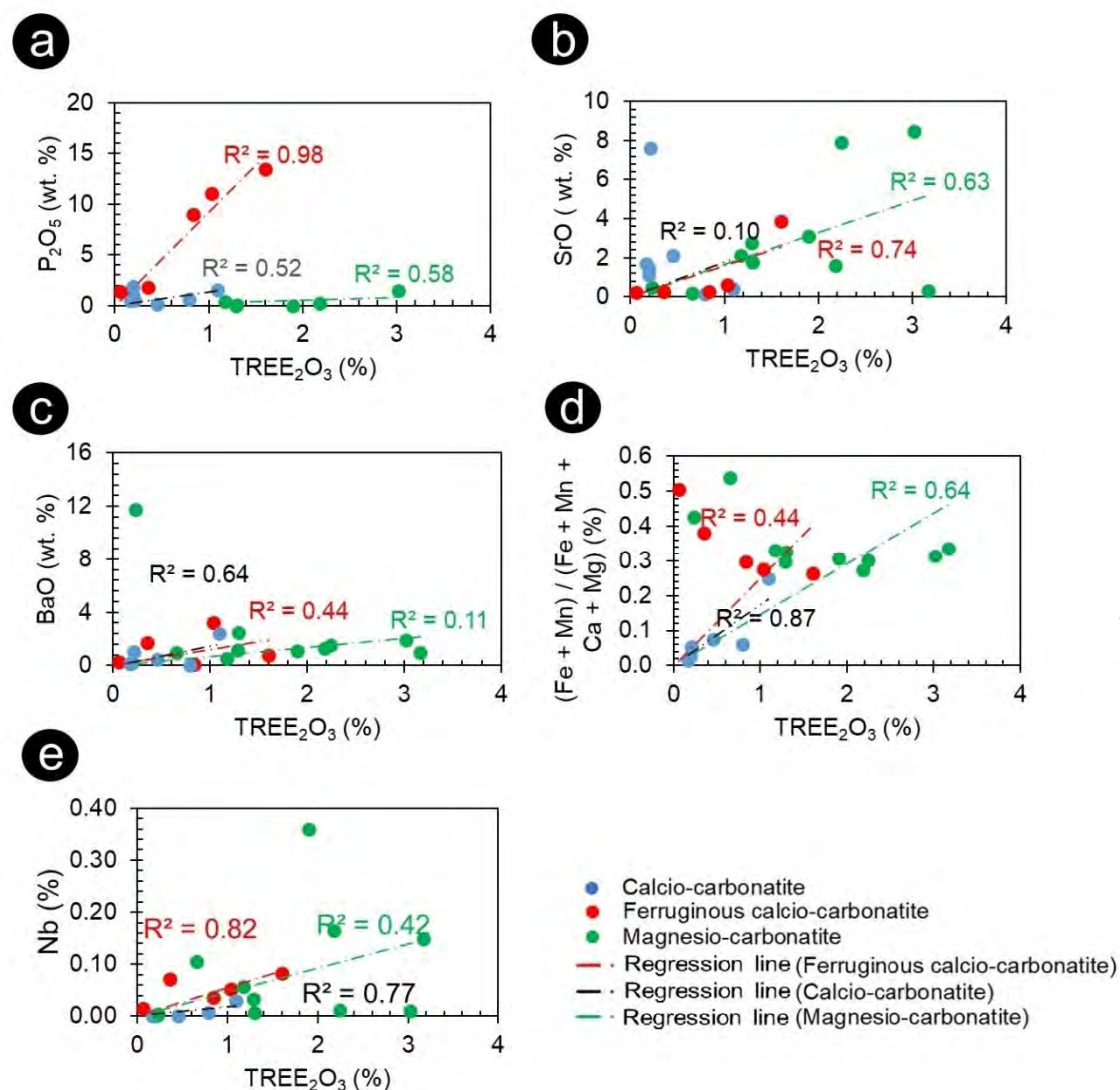


Fig. 5-7 Bivariate plots of major oxides and trace elements against total rare earth elements oxides. (a) P₂O₃ vs. TREE₂O₃, (b) SrO vs. TREE₂O₃, (c) Ba vs. TREE₂O₃, (d) (Fe+Mn)/(Fe+Mn+Ca+Mg) vs. TREE₂O₃, (e) Nb vs. TREE₂O₃. R² means the linear correlation coefficient.

5.2.3.4 Carbon and Oxygen isotope

The carbon and oxygen isotopic compositions of Tundulu carbonatites are given in Appendix A7. Five samples were analyzed: two calcite samples from calcio-carbonatite, one sample of ankerite, and one sample of strontianite from ferruginous calcio-carbonatite, and one sample of quartz from magnesio-carbonatite. The calcite samples yielded a narrow range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, from -3.24 to -3.74 ‰ and +6.39 to 6.39 ‰, respectively. The ankerite sample yielded $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of -2.92 ‰ and +7.75 ‰, while the strontianite sample yielded $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of -3.6 ‰ and +3.59 ‰, respectively. The quartz sample yielded $\delta^{18}\text{O}$ value +13.9 ‰ (Fig. 5-8; Appendix A7).

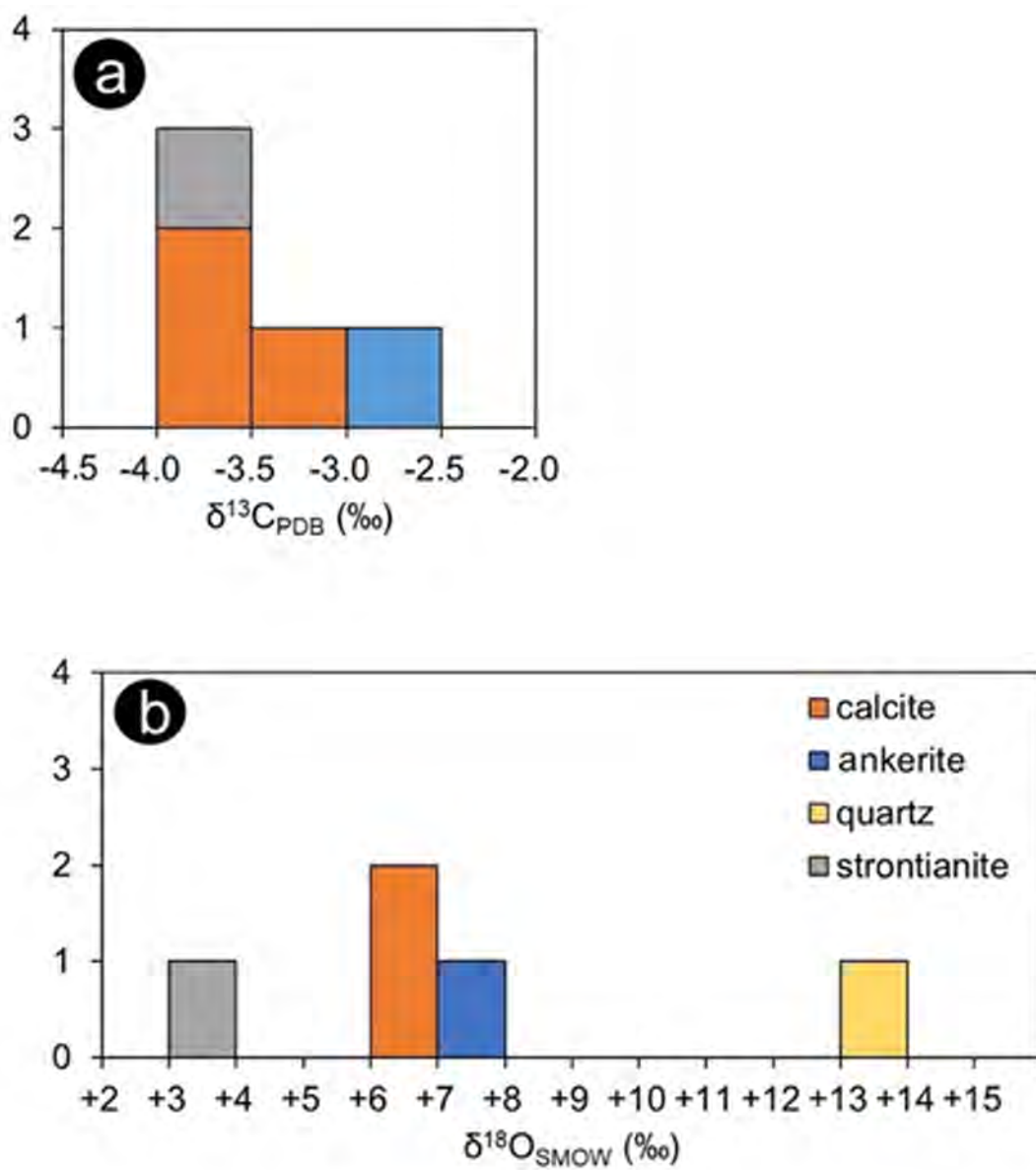


Fig. 5-8 Histogram of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope analysis of calcite from calcio-carbonatite, ankerite and strontianite from ferruginous-carbonatite.

5.3 Discussion

5.3.1 Origin of the carbonatite magma

Based on field observation, Tundulu carbonatite occurred with associated alkaline rock (nepheline syenite) (Fig. 5-1). Carbonatite samples studied showed depleted contents of Nb (1.3–321.0 ppm), Zr (5.3–3600 ppm) and enriched P_2O_5 (0.13–13.5 wt. %), while syenite showed enriched content of Nb (230.6–524 ppm), Zr (99.3–4864.7 ppm) and depleted P_2O_5 (0.1–0.5 wt. %). The observed enrichment and depletion, as Veksler et al. (1998b, 2012) reported, could be produced by fractionation during liquid immiscibility.

A plot of $\delta^{18}O$ versus $\delta^{13}C$ given in figure 5-9 (Ray & Ramesh, 2006) shows narrow isotopic variation for the Tundulu carbonatite, with $\delta^{13}C$ and $\delta^{18}O$ spanning from -3.6 ‰ to -2.92 ‰, and from +3.59 ‰ to +13.9 ‰, respectively. The lowest range was observed in calcio-carbonatite, which plots within the primary igneous carbonatite (P.I.C) field (Fig. 5-9). Based on these observations, Tundulu carbonatite formed from the liquid immiscibility of a mantle-derived silicate-carbonate magma

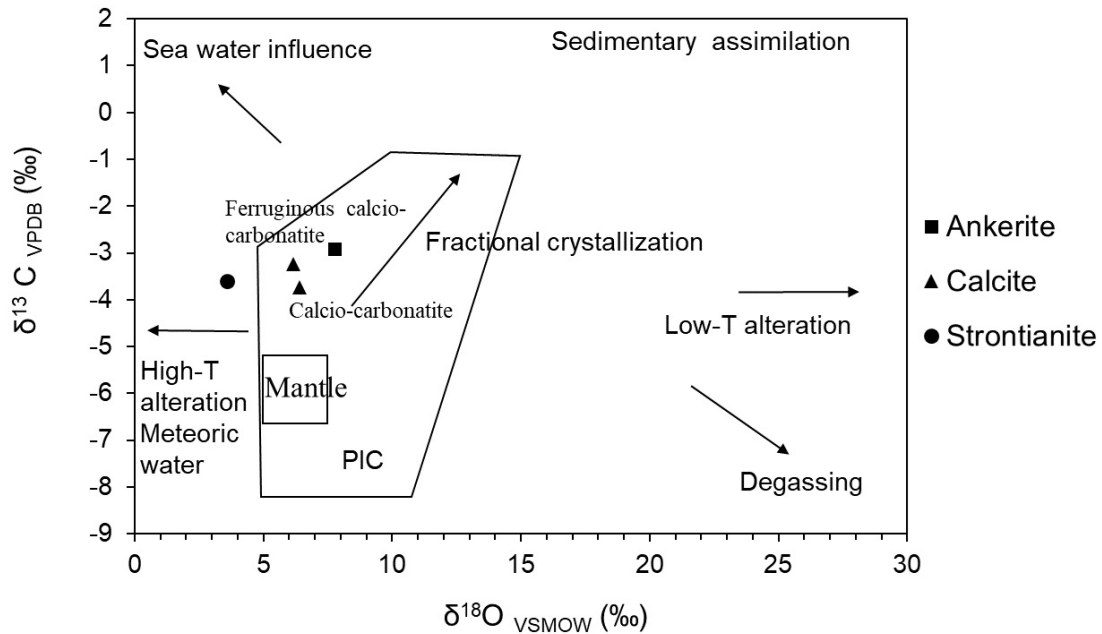


Fig. 5-9. The $\delta^{13}C$ and $\delta^{18}O$ compositions of the Tundulu carbonatites. Arrows indicate possible principal controls on carbonatite O and C isotope ratio after Deines (1989) and Demény et al. (2004). The mantle field is adapted from Kyser (1990), Deines (1992), and Cartigny et al. (1998). Primary igneous carbonatite (PIC) field from Ray & Ramesh (2006).

Geochemical composition of the analysed syenite samples has the SiO₂, Na₂O, K₂O, Al₂O₃ and CaO contents ranges of 40.9–60.4 wt.%, 2.1–8.9 wt.%, 7.8–12.0 wt.%, 14.6–20.8 wt.% and 1.3–6.4 wt.% respectively. These compositions are generally consistent with the compositions favourably generating the immiscible REE-rich carbonate melts (e.g. Zhao et al., 2023). However, the composition is more acidic. The above inference can be supported by the widespread orthoclase in calcio-carbonatite and observed biotite in the field that occurred at the bottom of the old mine pit (Fig. 5-3a, j). The observed acidic composition suggests that the separation of carbonate melts from the silicate melts probably occurred lately at shallow depth during the magmatic evolution. Sodic metasomatism is commonly considered to form earlier, at higher temperatures and deeper levels than potassic metasomatism due to the higher mobility of K than Na at lower temperatures (e.g. Le Bas, 2008; Elliott et al., 2018).

5.3.2 Evolution of the carbonatite magma

The isotope composition plots show a narrow fractional crystallization trend for the Tundulu carbonatite, from the calcio-carbonatite to magnesio-carbonatite (Fig. 5-4), and it may be inferred that the initial magma of the Tundulu carbonatite evolved from a Ca- and P-rich melt to a relatively Ca- and P-poor melt through magma differentiation. Furthermore, the emplacement of the Tundulu carbonatite complex as a ring structure from the contact with fenite, calcio-carbonatite, ferruginous calcio-carbonatite and magnesio-carbonatite at the center supports magmatic differentiation (e.g. Anenburg et al., 2021; Fig. 5-1).

The three lithotypes identified at the Tundulu complex (Fig. 5-4) and petrographic observation indicates that calcio-carbonatite fractionated calcite, magnetite and apatite, an assemblage that forms early in carbonatite crystallization (e.g. Anenburg et al., 2021). The calcio-carbonatite has flow banding and spinifex texture, indicating a magmatic nature (Figs. 5-2a-c, 5-3a). Furthermore, calcite is rich in Fe and forms an interlocking mosaic texture with ankerite, suggesting comagmatic phases (Fig. 5-3a). Apatite formed an idiomorphic texture (Fig. 5-3c), indicating early crystallization at high temperatures (e.g. Sartori et al. 2022). In addition, apatite occurred elongated and associated with

zoned synchysite rich in Ti (Fig. 5-3b). These observations suggest the early formation of calcio-carbonatite during carbonatite magma differentiation.

The ferruginous calcio-carbonatite fractionated ankerite and fluorapatite. Ankerite is characterized by hexagonal pseudomorph filled with synchysite and, barite and quartz (Fig. 5-3f), which probably indicates a late stage of magmatic differentiation as Prokopyev et al. (2016) and Anenburg et al. (2021) reported to occur in temperature between 650-400 °C. In addition, ankerite has been observed to occur in other carbonatites as a low-temperature product (400-460 °C) in the magmatic framework (e.g. Swartbooisdrif, Namibia, Thompson et al., 2002). In addition, a plot of $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ ankerite isotope falls in the P.I.C field, suggesting a primary magmatic nature (Fig. 5-9). Fluorapatite overprinted ankerite and has dissolution and overgrown texture, suggesting formation due to hydrothermal processes (Fig. 5-3i) (e.g. Broom-Fendley et al. 2016; Chakhmouradian et al., 2017). Fluorapatite is contaminated with Fe, probably caused by the dissolution of ankerite. Quartz fill spaces of brecciated ankerite and fluorapatite suggest late formation (Fig. 5-3g-i). Brecciation might have facilitated fluid mobility that increased dissolution of ankerite and apatite, which might have resulted in recrystallization and precipitation of fluorapatite and calcite in ferruginous calcio-carbonatite (Fig. 5-3j-k). Ankerite destabilization may indicate why some ferruginous calcio-carbonatites plots in magnesio-carbonatite and calcio-carbonatite fields (Fig. 5-4).

Magnesio-carbonatite seems to have formed from alteration siderite (Fig. 5-3m-n-o). Apatite-rich magnesio-carbonatite siderite/ankerite are replaced by dolomite. The early stage of replacement is marked by zoning (Fig. 5-3m), while the late stage is marked by skeletal texture (Fig. 5-3n). Apatite-poor magnesio-carbonatite seems to have complete dissolution as zoning and skeletal texture are scarce (Fig. 5-3q). Synchysite overprints quartz in association with barite strontianite (Fig. 5-3o-p), suggesting late formation. Furthermore, no brecciation was observed in magnesio-carbonatite, which might indicate that brecciation occurred prior to the emplacement of the magnesio-carbonatite. The proposed timing of brecciation is supported by the observed Y/Ho ratio that ranges from 21 to 35. The above observation suggests the formation of magnesio-carbonatite precedes ferruginous calcio carbonatite.

The observed mineral paragenetic relationship is also similar to observed geochemical composition trends for Fe_2O_3 , Mn, and BaO among the three lithotypes.

The observed trend was evidenced by an increase in contents of Fe_2O_3 (0.6-30.3 wt. %), MnO (0.3-6.0 wt. %), BaO (20151-95412 ppm) from calcio-carbonatite through ferruginous calcio-carbonatite to magnesio-carbonatite due to magmatic differentiation (e.g. Wyllie, 1965). The observed increase in SrO might be influenced by meteoric. This is supported by the wide range of Y/Ho observed in ferruginous calcio-carbonatite and magnesio-carbonatite. The observed correlation between SrO and REE_2O_3 (Fig. 5-7) in ferruginous and magnesio-carbonatite might be due to contamination.

Based on the above observations, the Tundulu carbonatite composition differentiation formed from calcio-carbonatite by fractionating calcite magnetite and apatite, through ferruginous calcio-carbonatite by fractionating ankerite, and fluorapatite to magnesio-carbonatite by fractionating siderite and dolomite. (Figs. 5-1, 5-4).

5.3.3 Implication to REEs mineralization

REEs mineralization in the Tundulu carbonatite is represented by synchysite, apatite, and fluorapatite. REEs mineralization occurs as disseminated form. Based on mineral paragenetic sequence and textural observations, REEs mineralization can be classified into early-magmatic and late-magmatic-hydrothermal stages. The early-magmatic mineralization stage is characterized by synchysite with glomeroporphyritic texture associated with subhedral apatite and magnetite and synchysite inclusion in euhedral calcite (Fig. 5-3a-b-c-e) observed in calcio-carbonatite. The late-magmatic-hydrothermal mineralization is characterized by synchysite forming in hexagonal pseudomorph and consertal to strontianite, barite, quartz (Fig. 5-3f) and synchysite overprinting quartz (Fig. 5-3i-n) and synchysite with fibrous texture overprinting recrystallized calcite, fluorapatite (fig. 5-3j-p). A proposed REE mineralization paragenetic sequence is presented in Fig. 5-10.

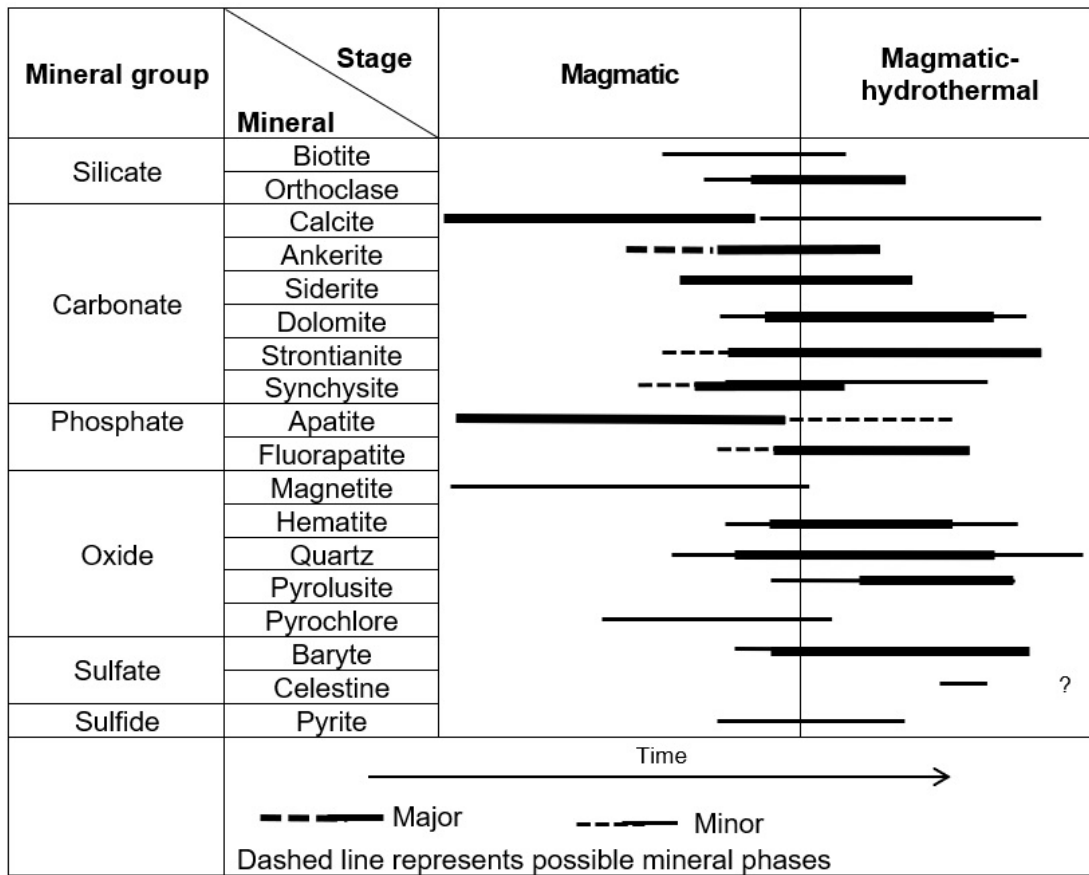


Figure 5-10 Paragenetic sequence for the Tundulu carbonatite

Mineralized hexagonal pseudomorph observed in ankerite of ferruginous calcio-carbonated indicates a mineralization peak and might imply more REE concentration. However, the average ratio of $(La/Yb)_N$ increases from ferruginous calcio-carbonatite (44), calcio-carbonatite (110), and magnesio-carbonatite (1265), indicating that LREEs were more enriched in magnesio-carbonatite. This variation is attributed to magma fractionation and redistribution of the REEs due to hydrothermal processes. The observed elevated concentration of middle rare earth elements (MREEs: Sm-Ho) and heavy rare earth elements (HREEs: Ho-Lu) in ferruginous calcio-carbonatite is due to multiple fluids generation that affected fluorapatite. Multiple fluid generation is evidenced by overgrown and dissolution textures in fluorapatite (Fig. 5-3i). Fluorapatite dissolution and precipitation transporting the LREE out of the original apatite and preferentially re-precipitates some LREEs on its rim and some LREE remains in solution (Broom-Fendley et al. 2016). Synchysite also shows dissolution texture in both ferruginous calcio-carbonatite and magnesio-carbonatite (Fig. 5-3j-p). Experimental studies and natural observation have shown LREE preference for Fe-dolomite carbonatite (Anenburg et al., 2021). The observed higher concentration of LREEs in magnesio-carbonatite and calcio-carbonatite was possibly influenced by hydrothermal processes. While the observed strong correlation of REEs and P_2O_5 in ferruginous calcio-carbonatite is due to fluorapatite abundance (Fig. 5-7a). Similarly, there is a strong correlation between Nb and $TREE_2O_3$ in calcio-carbonatite and ferruginous calcio-carbonatite (Fig. 5-7f). due to the presence of pyrochlore as it has higher unity mineral-melt partition coefficients for the REEs (e.g. Mitchell, 2015; Chakhmouradian et al., 2017b; Walter et al., 2018; Patel et al., 2023) and may significantly affect the REEs budget when crystallized early in carbonatite evolution even when present in accessory amounts (Anenburg et al., 2020; Klemme & Berndt, 2020).

The observed Y/Ho indicates both magmatic and hydrothermal contamination pattern among the lithotypes (Fig. 5-5a). The Y/Ho in calcio-carbonatite (26-33) indicate the less evolved nature compared to ferruginous calcio-carbonatite (24-38) and magnesio-carbonatite (22-35). These observations are comparable to other carbonatites elsewhere (Fig. 5-6, e.g. Zheng et al., 2023). Furthermore, the observed negative Y anomaly (Fig. 5-5a) and O isotope ratio of quartz from magnesio-carbonatite indicates a hydrothermal process (Fig. 5-8).

5.3.4 Implication of tectonic controls on the carbonatite evolution.

The Unango subdomain experienced less deformation and amphibolite metamorphic facies due to compression forces during the closure of Kuunga ocean and as well as W-E and NW-SE compressions of the Pan-African. orogeny. These compression episode results in the doming and directed flow of magma within the initiated conduits (Fullgraf et al., 2022b). This tectonism might have limited magma underplating and REE enrichment from the crustal rock to their deposition location within the Unango subdomain. This suggestion helps to explain the less evolved nature of Tundulu carbonatite and proximal occurrence of syenite. This observation is common in other Carbonatite in the eastern belt including Nkalonje, and Songwe carbonatites. A proposed 2D model of the Tundulu carbonatite highlighting lithology with high REEs concentration is given in figure 5-11.

.

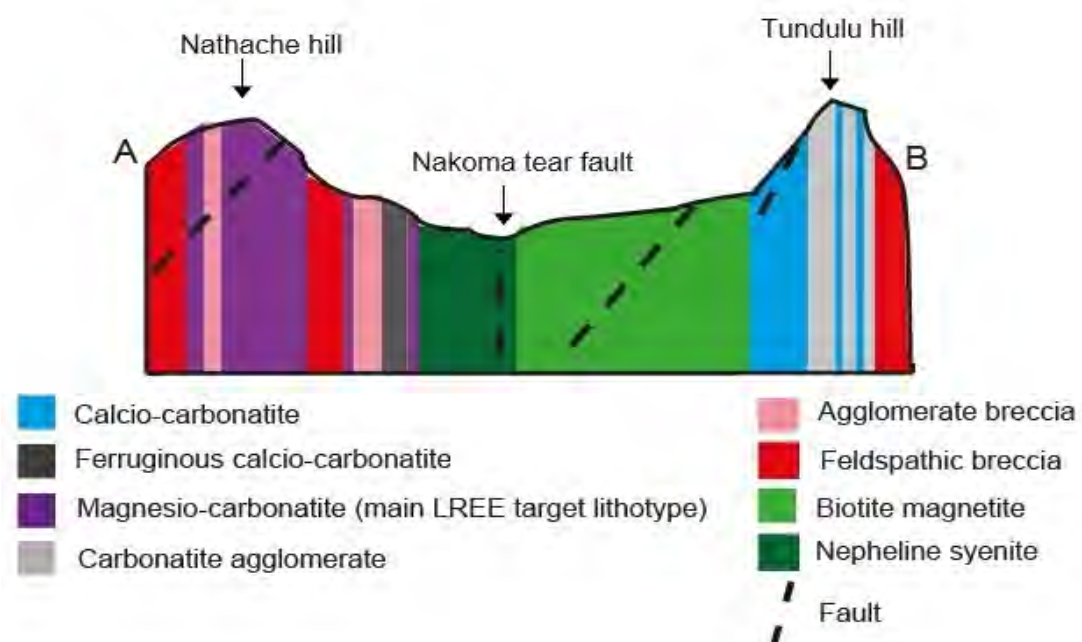


Fig. 5-11 Cross section of Tundulu carbonatite facing NW. Cross section line A-B on Fig. 5-1 highlighting the magnesio-carbonatite. Section inferred from Fig 5-1 and carbonatite emplacement model by Garson 1965.

5.4 Summary

The Tundulu carbonatite was emplaced as a ring structure with three centres and comprised of calcio-carbonatite, magnesio-carbonatite, and ferruginous calcio-carbonatite. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ spans from 3.24 to -3.74 ‰ and +6.39 to 6.39 ‰ and quartz $\delta^{18}\text{O}$ yielded +13.9‰. The observed spatial association of the Tundulu carbonatite and nepheline syenite supported by the depletion Nb (1.3–321.0 ppm) and Zr (5.3–3600 ppm) in carbonatite and enrichment syenites Nb (230.6–524 ppm) and Zr (99.3–4864.7 ppm) sample indicate carbonatite melt to have formed from liquid immiscibility of a mantle derived silicate-carbonate magma. The acidic nature of the syenite suggest immiscibility occurred at shallow depth. Furthermore, the emplacement conduit might have been same for both carbonatite and silicate magma.

The abundance of calcite and apatite suggest the carbonatite magma to evolved from Ca and P-rich to a relatively Ca- P-poor. The Fe_2O_3 and MnO contents increase from calcio-carbonatite (0.6–12.3 wt. % and 0.3–2.2 wt. %), ferruginous calcio-carbonatite (5.2–15.4 wt. % and 0.1–2.3 wt. %) and magnesio-carbonatite (11.2–30.3 wt. % and 2.0–6.0 wt. %) respectively. The Sr and Ba contents increase from calcio-carbonatite (1050–20151 ppm and 58–22290 ppm), ferruginous calcio-carbonatite (1370–30821 ppm and 857–25468 ppm) and magnesio-carbonatite (1898–43507 ppm and 3129–95412 ppm). These trends suggest differentiation of magma. Both petrography and geochemical data suggest a trend from calcio-carbonatite that fractionated calcite and apatite to ferruginous calcio-carbonatite that fractionated ankerite and fluor apatite, and magnesio-carbonatite that fractionated siderite and dolomite.

The main REEs bearing mineral in Tundulu carbonatite is synchysite. Minor REE bearing minerals are apatite and fluorapatite. REE mineralization at the Tundulu carbonatite occurred as disseminated and can be classified into magmatic stage and late-magmatic-hydrothermal stage. The magmatic mineralization stage is characterized by synchysite that occurs as inclusion in calcite and zoned synchysite in calcio-carbonatite. Late-magmatic-hydrothermal stage is characterized by synchysite that overprints quartz, recrystallised calcite and fluorapatite in ferruginous calcio-carbonatite and magnesio-carbonatite. The $(\text{La}/\text{Yb})_{\text{N}}$ in calcio-carbonatite ranges from 33 to 289, ferruginous

calcio-carbonatite from 30 to 56 and magnesio-carbonatite from 122 to 3035. These ranges suggest LREE are more enriched in magnesio-carbonatite. REE enrichment was influenced by magmatic and hydrothermal process.

Reference

- Anenburg, M., Broom-Fendley, S., and Chen, W. (2021). Formation of rare earth deposits in carbonatites. *Elements*, 17(5), pp.327–332.
- Anenburg, M., Burnham, A. D., and Mavrogenes, J. A. (2018). REE redistribution textures in altered fluorapatite: Symplectites, veins, and phosphate-silicate-carbonate assemblages from the Nolans Bore P-REE-Th deposit, Northern Territory, Australia. *The Canadian Mineralogist*, 56, pp.331–354.
- Bau, M. (1996). Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems : evidence from Y/Ho, Zr/Hf , and lanthanide tetrad effect. *Contributions to Mineralogy and Petrology*, 123, pp.323–333.
- Benkó, Z., Molnár, K., Magna, T., Rapprich, V., Palcsu, L., Pour, O., Čejková, B., Futó, I., and Czuppon, G. (2021). Combined petrography, noble gas, stable isotope and fluid inclusion chemistry of carbonatites from Uganda: Implications for the origin of the carbonatite melt in continental rift setting. *Chemical Geology*, 578, pp.1–19.
- Broom-fendley, S. (2016a). Chilwa Alkaline Province field guide : Tundulu. HiTech AlkCarb Workshops in Malawi, 1–22 October, 2016, pp.45–48.
- Broom-Fendley, S., Styles, M. T., Appleton, J. D., Gunn, G., and Wall, F. (2016b). Evidence for dissolution-reprecipitation of apatite and preferential LREE mobility in carbonatite-derived late-stage hydrothermal processes. *American Mineralogist*, 101(3), pp.596–611.
- Cartigny, P., Harris, J. W., Phillips, D., Girard, M., and Javoy, M. (1998). Subduction-related diamonds? - The evidence for a mantle-derived origin from coupled $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ determinations. *Chemical Geology*, 147(1), pp.147–159.
- Chakhmouradian, A. R., Reguir, E. P., Zaitsev, A. N., Couëslan, C., Xu, C., Kynický, J., Mumin, A. H., and Yang, P. (2017). Apatite in carbonatitic rocks: Compositional variation, zoning, element partitioning and petrogenetic significance. *Lithos*, 274–275, pp.188–213.

- Deines, P. (1992). Mantle Carbon: Concentration, mode of occurrence, and isotopic composition. In Schidlowski M. (Ed.), *Early Organic Evolution* Springer. pp.133–146.
- Garson, M. S. (1962). The Tundulu carbonatite ring-complex in Southern Nyasaland. Government Printer, Memoir 2. 235p.
- Gittins, J., and Harmer, R. E. (1997). What is ferrocarbonatite? A revised classification. *Journal of African Earth Sciences*, 25(1), pp.159–168.
- Mines and Mineral Act, (2019).
- Hou, Z., Liu, Y., Tian, S., Yang, Z., and Xie, Y. (2015). Formation of carbonatite-related giant rare-earth-element deposits by the recycling of marine sediments. *Nature*, 5(1), pp.1–10.
- Klemme, S., and Berndt, J. (2020). Trace element partitioning between pyrochlore, microlite, fersmite and silicate melts. *Geochemical Transactions*, 21(1), pp.1–14.
- Kyser, T. K. (1990). Stable isotopes in the continental lithospheric mantle. *Oxford Monographs on Geology and Geophysics*, 16, pp.127–156.
- Le Bas, M. J. (1981). Carbonatite magmas. *Mineralogical Magazine*, 44(6), pp.133–140.
- Lee, W.-J., and Wyllie, P. J. (1998). Petrogenesis of carbonatite magmas from mantle to crust, constrained by the system $\text{CaO}-(\text{MgO} + \text{FeO}^*)-(\text{Na}_2\text{O} + \text{K}_2\text{O})-(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2)-\text{CO}_2$. *Journal of Petrology*, 39(3), pp.495–517.
- Mitchell, R. H. (2015). Primary and secondary niobium mineral deposits associated with carbonatites. *Ore Geology Reviews*, 64, pp.626–641.
- Ngwenya, B. T. (1994). Hydrothermal rare earth mineralisation in carbonatites of the Tundulu complex, Malawi: Processes at the fluid/rock interface. *Geochimica et Cosmochimica Acta*, 58(9), pp.2061–2072.
- Patel, A. K., Upadhyay, D., Mishra, B., and Pruseth, K. L. (2023). Magmatic rare earth element mineralization and secondary fluid-assisted redistribution in the Kamthai carbonatite complex, NW India. *Lithos*, 456(7), pp.107294.
- Prokopyev, I. R., Borisenko, A. S., Borovikov, A. A., and Pavlova, G. G. (2016). Origin of REE-rich ferrocarbonatites in southern Siberia (Russia): Implications based on melt and fluid inclusions. *Mineralogy and Petrology*, 110(6), pp.845–859.
- Ray, J. S., and Ramesh, R. (2006). Stable Carbon and Oxygen Isotopic Compositions of Indian Carbonatites Stable Carbon and Oxygen Isotopic Compositions.

- Interernational Geological Review*, 48, pp.17–45.
- Sartori, G., Galli, A., Weidendorfer, D., and Schmidt, M. W. (2022). A tool to distinguish magmatic from secondarily recrystallized carbonatites—Calcite/apatite rare earth element partitioning. *Geology*, 51(1), pp.54–58.
- Snelling, N. (1965). Age determination of three African carbonatites. *Nature*, 205, pp.491.
- Tappe, S., Romer, R. L., Stracke, A., Steenfelt, A., Smart, K. A., Muehlenbachs, K., and Torsvik, T. H. (2017). Sources and mobility of carbonate melts beneath cratons, with implications for deep carbon cycling, metasomatism and rift initiation. *Earth and Planetary Science Letters*, 466, pp.152–167.
- Veksler, I. V., Dorfman, A. M., Dulski, P., Kamenetsky, V. S., Danyushevsky, L. V., Jeffries, T., and Dingwell, D. B. (2012). Partitioning of elements between silicate melt and immiscible fluoride, chloride, carbonate, phosphate and sulfate melts, with implications to the origin of natrocarbonatite. *Geochimica et Cosmochimica Acta*, 79, pp.20–40.
- Walter, B. F., Parsapoor, A., Braunger, S., Marks, M. A. W. W., Wenzel, T., Martin, M., and Markl, G. (2018). Pyrochlore as a monitor for magmatic and hydrothermal processes in carbonatites from the Kaiserstuhl volcanic complex (SW Germany). *Chemical Geology*, 498(8), pp.1–16.
- Woolley, A. R. (1982). A discussion of carbonatite evolution and nomenclature, and the generation of sodic and potassic fenites. *Mineralogical Magazine*, 46(3), pp.13–17.
- Woolley, A. R., and Kempe, D. R. C. (1989). Carbonatites: Nomenclature, average chemical compositions, and element distribution. In Bell K. (Ed.), *Carbonatite: Genesis and Evolution* 1st ed., UnwinHyman. pp.1–13.
- Xu, C., Kynicky, J., Chakhmouradian, A. R., Campbell, I. H., and Allen, C. M. (2010). Trace-element modeling of the magmatic evolution of rare-earth-rich carbonatite from the Miaoya deposit, Central China. *Lithos*, 118(4), pp.145–155.
- Yaxley, G. M., Anenburg, M., Tappe, S., Decree, S., and Guzmics, T. (2022). Carbonatites: Classification, sources, evolution, and emplacement. *Earth and Planetary Sciences*, 50, pp.261–293.
- Zheng, X., Liu, Y., Smith, M. P., Kynický, J., and Hou, Z. (2023). Carbonatitic magma fractionation and contamination generate rare earth element enrichment and

mineralization in the Maoniuping giant REE Deposit, SW China. *Journal of Petrology*, 64(6), pp.1–36.

Chapter 6 : Petrochemistry of the Nkalonje carbonatite

6.1 Introduction

The Nkalonje carbonatite is located about 11 km SW of Tundulu carbonatite (Fig. 1-1; Garson, 1965). The Nkalonje carbonatite forms a bi-conical hill, Nyama Hill to the east and Nkalonje Hill to the west. The two hills are connected by a saddle. The Nkalonje carbonatite is about 1.5 km long N-S and 1.8 km E-W (Fig. 6-1). Nkalonje carbonatite is one of the least studied in the C.A.P and was not subjected to the same detailed evaluation of its paragenesis and rare earth elements (REEs) mineralization potential. An interest on the Nkalonje carbonatite stemmed mainly from its form of occurrence as a vent. Nkalonje carbonatite represents a third form in which carbonatites occur in the C.A.P. Furthermore, the study builds on the previous mention of REEs occurrence. This study contributed to the magmatic processes, paragenetic sequence, and REEs mineralization.

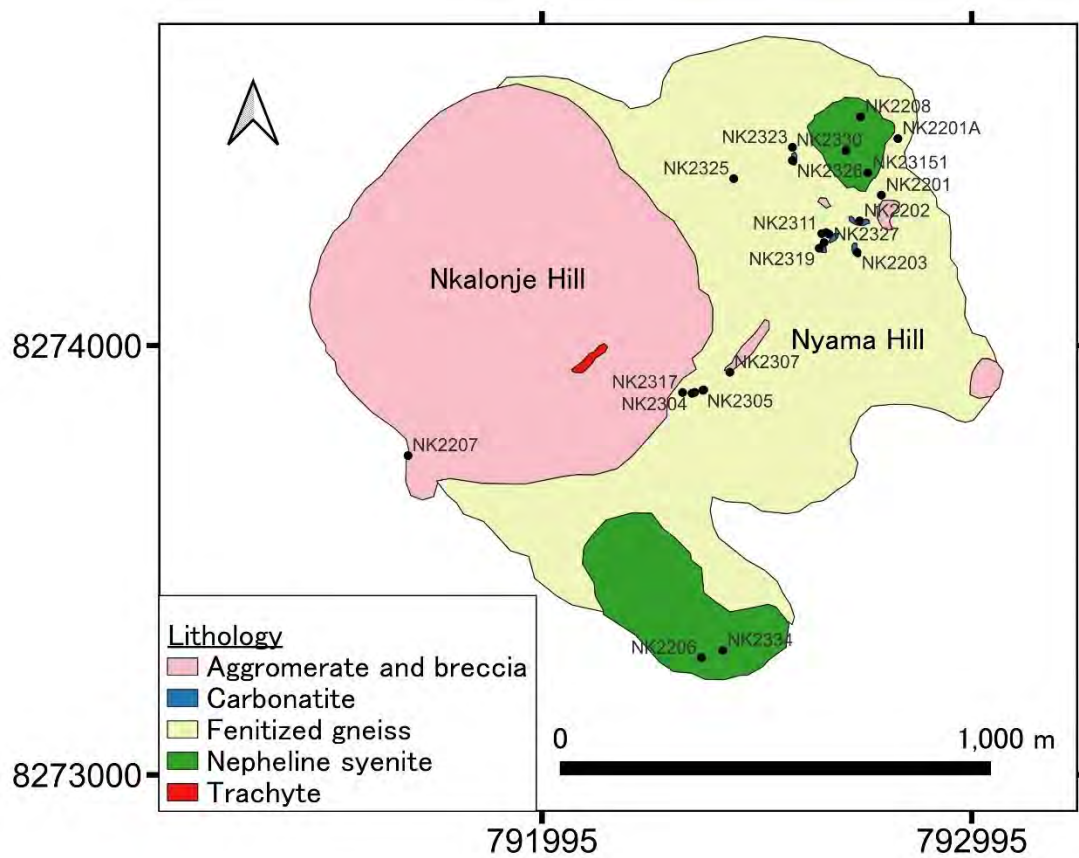


Fig. 6-1 A map of the Nkalonje carbonatite showing the geology of the carbonatites.

The regional basement rocks in the locality comprise Proterozoic gneisses and granulites. The gneisses were formed by regional metamorphism of arkose or feldspathic sandstone within intercalations of more argillaceous sediments (Bloomfield and Garson 1965). The gneisses underwent several stages of intrusion and deformation, including the placement of a much earlier episode of late Precambrian alkaline magmatism (Bloomfield, 1968).

The geology of the Nkalonje carbonatite and associated vents is given by Garson (1965). The lithology of the hill comprises fenitized gneiss that covers most of Nyama Hill, agglomerate and breccia that covers most of Nkalonje Hill and represents the early igneous activity, nepheline syenite, phonolite, trachyte, and carbonatite that intruded part of Nyama Hill and represented the second igneous activity (Garson, 1965). Garson (1965) suggests the emplacement of the Nkalonje carbonatite between 2.4-2.7 km below sea level.

6.2 Results

6.2.1 Field observations

6.2.2.1 Lithological variation

Carbonatite occurs as small discontinuous dykes on the northeastern flanks of Nyama Hill. These dykes rarely exceed 2 m in width (Fig. 6-2a). The most common variety is coarse-grained white calcio-carbonatite (Fig. 6-2b). Dark calcio-carbonatite occurs at one locality above a satellite breccia vent (Fig. 6-2c).

Feldspathic breccia and agglomerate dominate the main vent of the Nkalonje carbonatite, covering an area of about 900m in diameter. Smaller bodies occur on Nyama Hill, with the largest covering an area of approximately 60 m by 80 m in the southeast. The breccia consists of both angular and rounded clasts that have been intensively fenitized. The typical size of the clast ranges (5-20 cm), although others reach 0.5 m in diameter (Fig. 6-2d-e). The clasts at the main vent are held together by Mn-Fe-rich matrix (Fig. 6-2e), whose abundance tends to increase towards the center of the vent. The vent breccia is locally calcareous, evidenced by effervescent upon contact with diluted HCl. Furthermore, on Nyama Hill, the agglomerate also occurred with a

pseudo trachytic matrix (Fig. 6-2f).

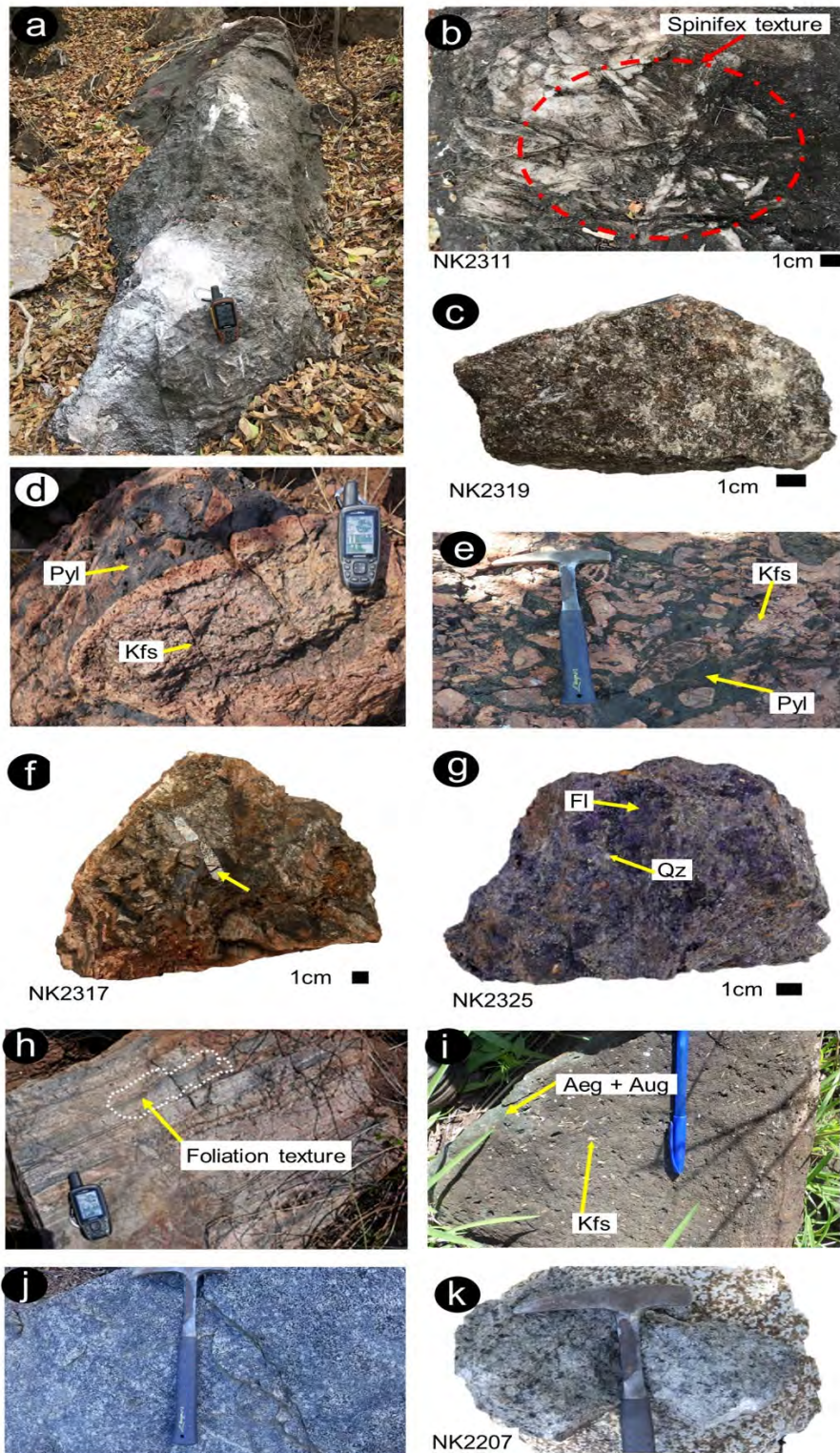


Fig. 6-2 Representative photos of rock chip samples. (a) calcio-carbonatite dyke, (b) whitish calcio-carbonatite with spinifex texture, (c) dark calcio-carbonatite, (d-e) feldspathic breccia with large and small feldspar xenolith cemented by pyroclastic (f) agglomerate with pseudotrachytic matrix, (g) quartz-

flourite, (h) fenitized gneiss with remnant of foliated and magmatic texture, (i) phonolite with sanidine phenocryst, (j-k) nepheline syenite, Abbreviation: Cal— calcite, Kfs —K-feldspar., Fl— Fluorite, Aeg— aegirine, Aug— augite.

Quartz-fluorite dyke with feldspar inclusion occurs north of Nyama Hill with NW-SE strike. The dyke intruded the fenitized gneiss. The quartz-fluorite dyke is highly weathered, forming dark brown and purple colors (Fig. 6-2g).

Fenite is the dominant rock type on Nyama Hill. The rock was originally a gneiss and underwent varying degrees of fenitization. However, the degree of fenitization tends to increase with proximity to the main agglomerate and breccia body and carbonatite dykes. Places where the original gneiss texture is preserved show a migmatitic texture (Fig. 6-1h). The rocks typically dip steeply, with no apparent preferred orientation, probably because of the intrusion.

Two bodies of nepheline syenite occur north and south of Nyama Hill (Figs. 6-1, 6-2j-k). The nepheline syenite body on the south is coarse-grained, contains abundant nepheline, and develops a craggy appearance upon weathering. Nepheline syenite contacts with the surrounding fenitized gneisses are sharp. Phonolite bodies are common throughout the complex but often too small to form mappable units (Fig. 6-2i).

6.2.2 Petrography

6.2.3.1 Calcio-carbonatite

Calcio-carbonatite is composed mainly of calcite, apatite, strontianite, synchysite, and barite. Hematite, celestine, quartz and pyrolusite occur as accessories. Apatite is euhedral to anhedral and is replaced by calcite-2 (Cal-2), which is altered or recrystallized. (Fig. 6-3a). Cal-2 is anhedral and re-crystallized in equilibrium with synchysite, which has a corroded texture (Fig. 6-3b). Strontianite is subhedral to anhedral, and it occurs in association with synchysite, and they both replace apatite (Fig. 6-3c-d). Quartz is scarce and occurs as an infill in Cal-1 (Fig. 6-3e). Celestine is anhedral and replaces synchysite (Fig. 6-3f). Baryte is subhedral, associated with subhedral strontianite overprinting Cal-1 (Fig. 6-3g). Hematite is euhedral to subhedral and replaced magnetite that overprinted Cal-1 (Fig. 6-3h). Pyrolusite is anhedral that replaces celestine and Cal-2 (Fig. 6-3i)

6.2.3.2 Feldspathic agglomerate and breccia

Agglomerate-breccia is composed of orthoclase, fluorite, quartz, and apatite. Orthoclase is dominant turbid, and its margin is filled with Fe and Mn-oxides (Fig. 6-3j). Apatite is subhedral and corroded, rich in REEs, and overprinted with quartz. Quartz occurs euhedral to subhedral and overprinted fluorite. Fluorite is euhedral to subhedral, replacing apatite and quartz. Synchysite also occurred in association with fluorite. (Fig. 6-3k-l) Hematite is placed on the quartz boundary (Fig. 6-3l).

6.2.3.3 Quartz fluorite

Quartz fluorite is composed of quartz fluorite and synchysite. Fluorite occurs subhedral to anhedral and forms a consertal texture with quartz. Quartz is subhedral to anhedral. Synchysite occurred with an idiomorphic texture and overprinted quartz and fluorite (Fig. 6-3m)

6.2.3.4 Fenite

Fenite is composed of quartz, biotite, magnetite, albite, aegirine, and apatite. (Fig. 6-3o-p). Biotite occurred as shreds were replaced by orthoclase. Orthoclase is dominant compared to andesine, and it is turbid and anhedral (Fig. 6-3n). Aegirine is euhedral prismatic and occurs in clusters, replacing anhedral quartz from the rims to the core. Magnetite is euhedral and precipitates on quartz or intestinal to aegirine and quartz (Fig. 6-3o).

6.2.3.5 Syenite

Syenite is composed of orthoclase, nepheline, aegirine, augite, sphene, apatite and biotite. Nepheline is abundant and replaced by augite. Aegirine is replaced by biotite and orthoclase (Fig. 6-3p-q).

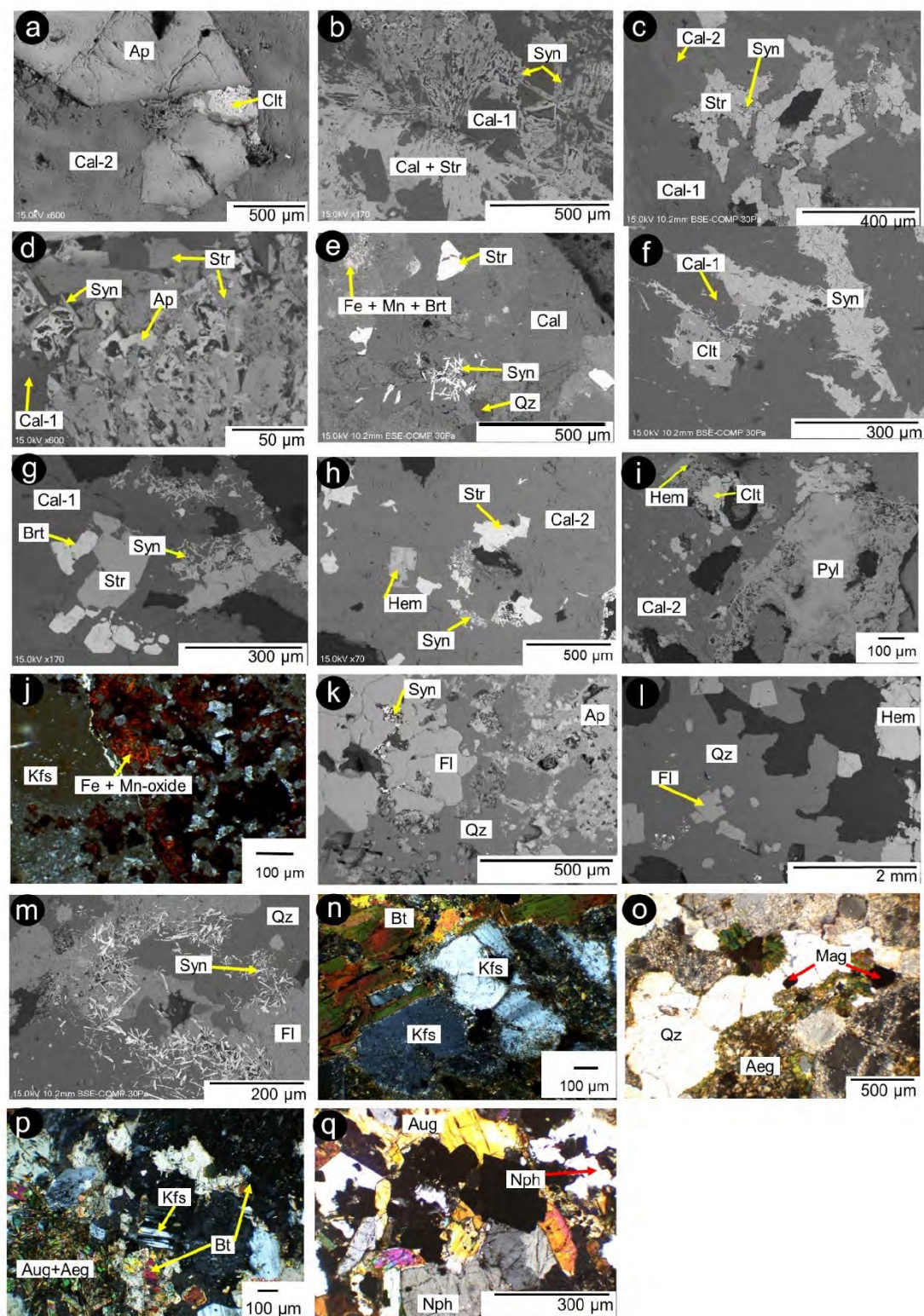


Fig. 6-3 Photo micrographs, Backscatter electron image of samples from Nkallonje carbonatite (a – j) Calcio-carbonatite, (k – n) Feldspathic agglomerate and breccia, (o – p) Fenite, (q-s) Nepheline syenite. Abbreviations: Ap – apatite, Aeg- aegirine, Brt- Barite, Clt- Celestine, Bt – biotite, Kfs – albite, Cal – calcite, Fl- fluorite, Mag – magnetite, Sd – siderite, Hem- hematite, Str – strontianite, Qz – quartz, Px- pyroxene, Nph- nepheline, Aug-Augite, Note: all photomicrographs are cross-polarized light.

6.2.3.6 Mineralization

REEs mineralization in the Nkalonje carbonatite occurred as disseminated. Mineralization occurred in calcio-carbonatite, agglomerate and breccia and quartz fluorite (Fig. 6-3b-m).

6.2.3 Whole-rock geochemistry

6.2.3.1 Major element geochemistry

Major element compositions of carbonatite samples are presented in Appendix A6. Using the classification of Gittins & Harmer (1997), the Nkalonje carbonatite is dominated by calcio-carbonatite (Fig. 6-4). The composition ranges of the calcio-carbonatites samples are 43.6 to 57.5 wt. % CaO, 0.25 to 0.54 wt. % MgO, 1.46 to 5.03 MnO, 2.26 to 9.21 wt. % Fe₂O₃, 0.64 to 5.74 wt. % SiO₂ and 0.04 to 0.90 wt. % P₂O₅. The feldspathic agglomerate and breccia composition ranges are 30.31 to 51.51 wt. % CaO, 0.074 to 0.14wt. %, MgO, 0 to 0.09 MnO, 0.78 to 1.20 wt. % Fe₂O₃, 8.68 to 38.39 wt. % SiO₂ and 0.22 to 4.46 wt. % P₂O₅.

Nepheline-syenite calculated total alkalis (Na₂O+K₂O) ranges from 16.0 to 16.32 wt. % and 0.22 to 1.78 wt. % P₂O₅. The syenite plot in the nepheline-nepheline syenite field defined by Woolley (1987) (Fig. 6-5).

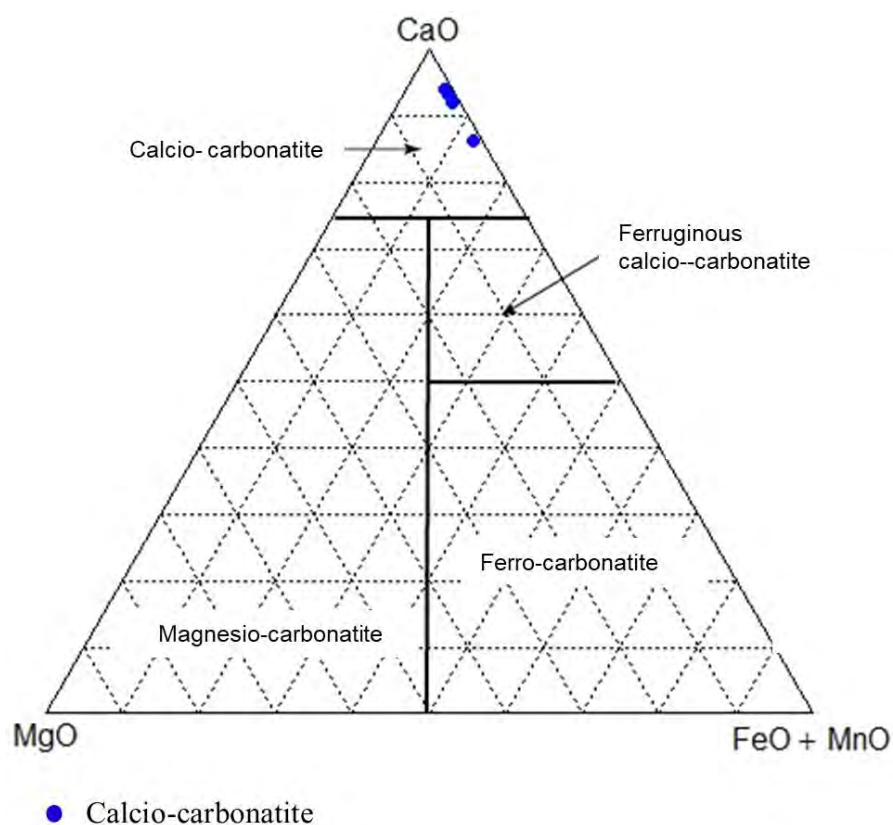


Fig. 6-4 Carbonatite classification using major oxides molar proportion defined by Gittins and Hammer (1997).

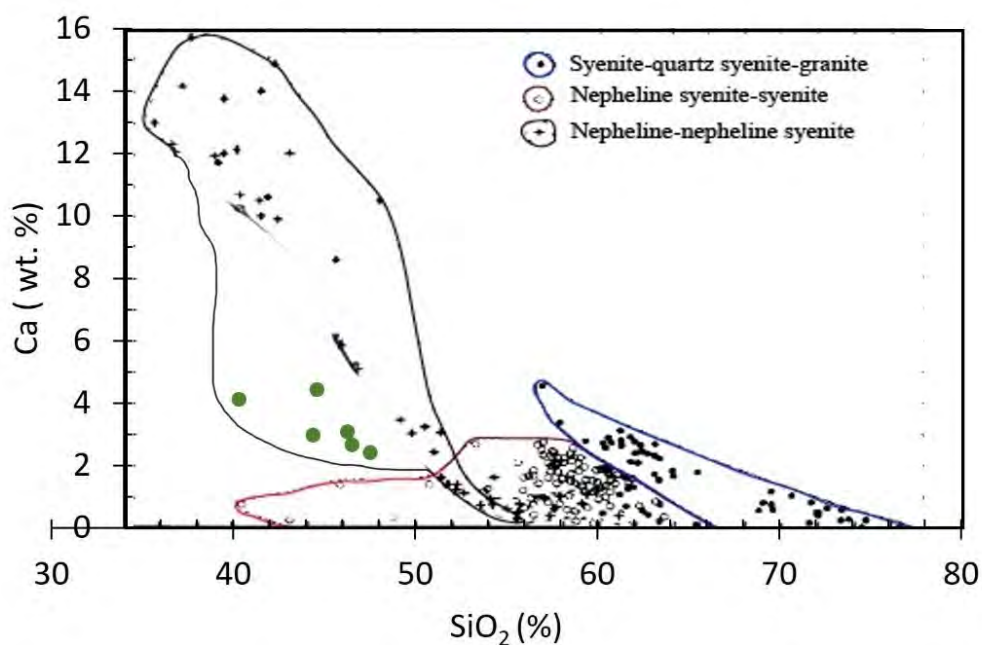


Fig. 6-5 Plot of SiO_2 vs CaO (wt. %) for rocks of the Chilwa Alkaline Province. Most of the data are for the northern part of the province, and a few are for the southern part. The three-magma series of the rock groups was modified after Woolley (1987). The green dot represents this study.

6.2.3.2 Trace-element geochemistry

The trace element compositions of carbonatite samples are presented in Appendix A6. Lithophile (Ta, REEs, Nb, Zr, Hf, Th, U, Ti, Rb) and chalcophile (Pb) elements were used to assess REEs mineralization and magma evolution as these are commonly associated with carbonatite-related REE deposits (e.g. Hou et al., 2015; Jia & Liu, 2020; Slezak & Spandler, 2020; Benkó et al., 2021). The chondrite-normalized ratio of lanthanum and ytterbium ($(La/Yb)_N$) ranges from 22.38 to 709.84 in calcio-carbonatite, 29.6 in quartz-fluorite, 28.57 to 204.27 in feldspathic agglomerate and breccia and 23.04 to 48.81 in Syenite (Fig. 6-6a). Calcio-carbonatite contents of Nb and Zr range from 0.72 to 5.39 ppm and 0.19 to 19.73 ppm, respectively. Agglomerate breccia contents of Nb and Zr range from 0.59 to 19.60 ppm and 46.69 to 58.27 ppm, respectively. Syenite contents of Nb and Zr range from 7.25 to 2015.38 and 396.18 to 4312.39 ppm, respectively.

The primitive-mantle-normalized patterns reveal similarities between the calcio-carbonatite, quartz-fluorite, and feldspathic agglomerate and breccia and a variation with syenite (Fig. 6-6b). The calcio-carbonatite and agglomerate breccia are enriched in Th among high field strength elements (HFSE) and depletion in large-ion lithophile elements (LILE; Rb) and other HFSE such as Zr, Hf, Ti, Ta and Pb, while the, Nb and U contents are variable. The Syenite is enriched in Rb, Th, Ba, Zr, and Nb and depleted in Pb and Ti, while the Nb and Hf content is variable. Quartz-fluorite shows a similar trend to calcio-carbonatite except for a negative anomaly of Sr. The Y/Ho ratio ranges from 23 to 33, 19 to 29, 18 and 17 to 28 in calcio-carbonatite, feldspathic agglomerate, and breccia quartz-fluorite and syenite, respectively (Fig. 6-7).

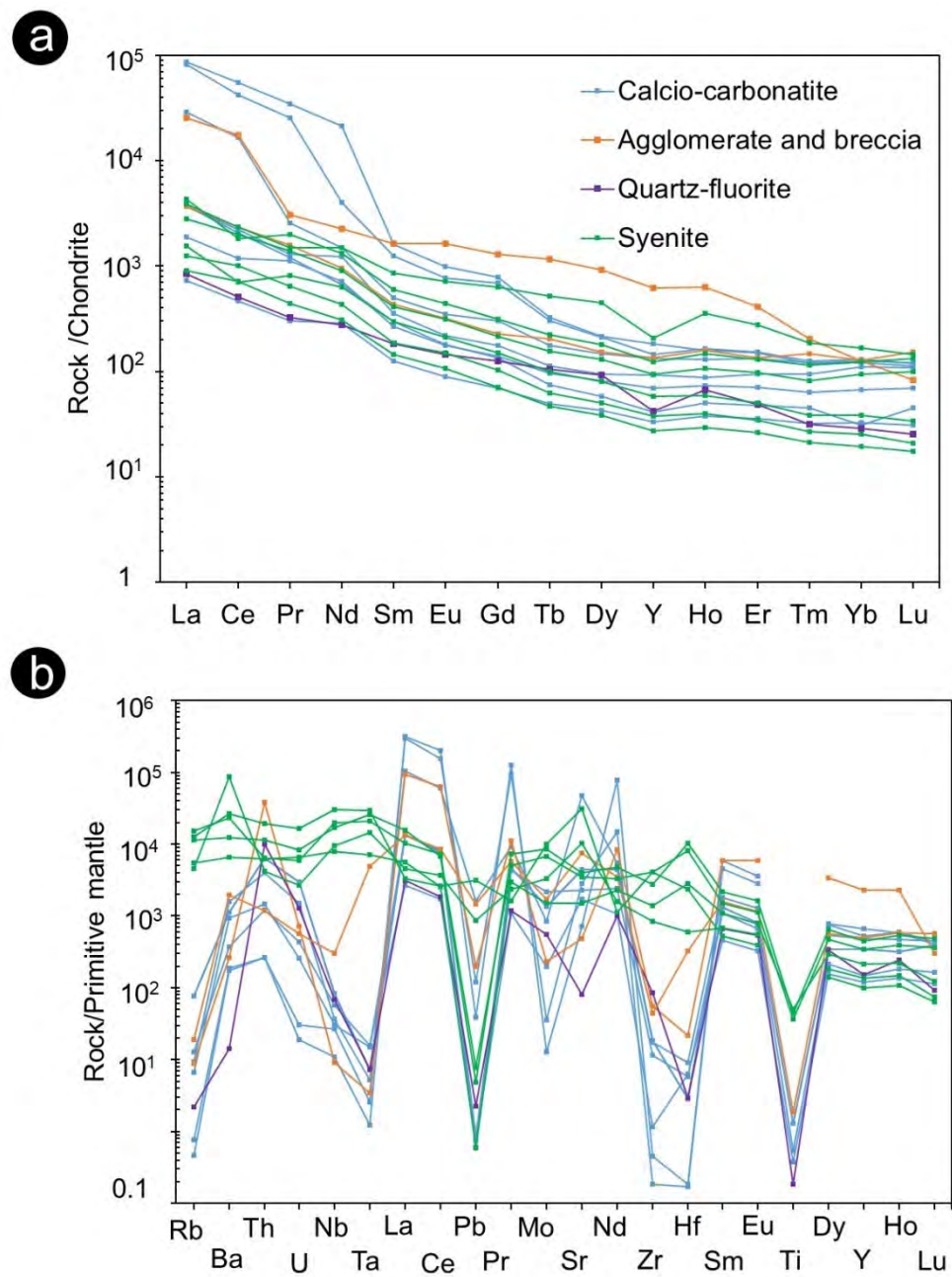


Fig. 6-6 Whole-rock REEs and trace element patterns for calcio-carbonatite, agglomerate, and breccia, and syenite. (a) Chondrite-normalized REE patterns. (b) Primitive mantle normalized LILE and HFSE elements: Chondrite and primitive mantle values from McDonough and Sun (1995).

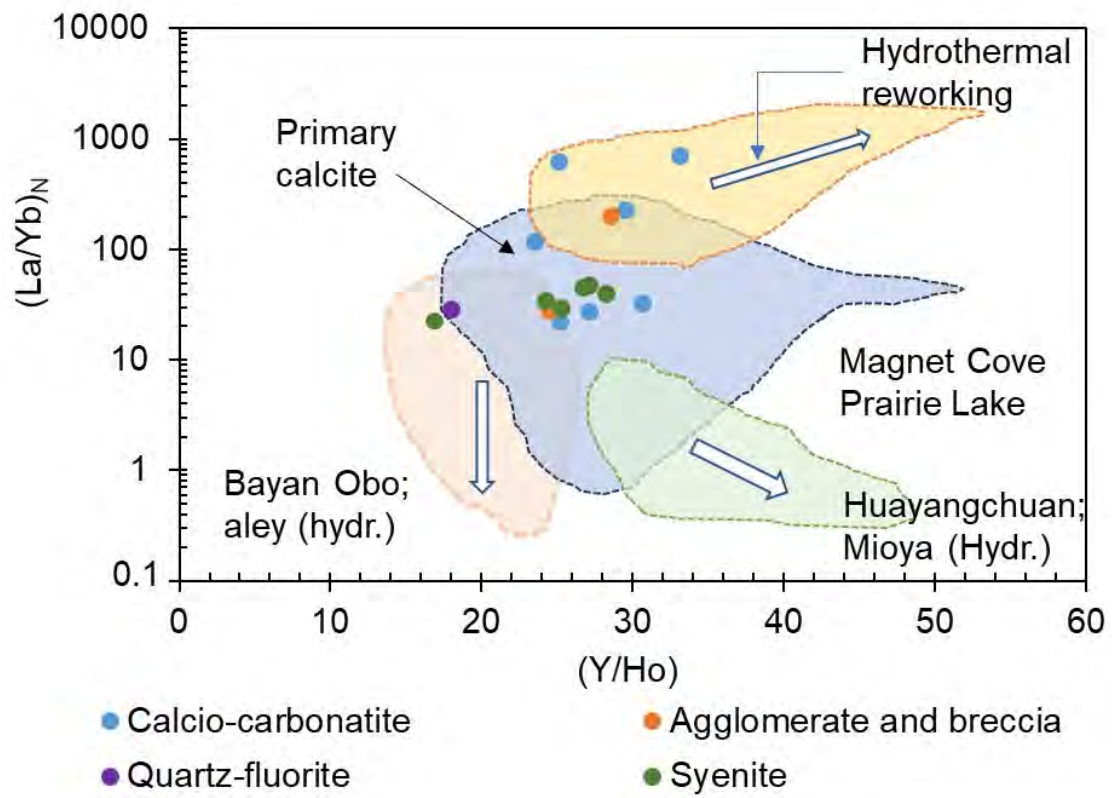


Fig. 6-7 Scatter diagrams of $(La/Sm)_N$ versus Y/Ho . The CHARAC fields and other carbonatites were adapted after Zheng et al. (2023).

6.2.3.3 Correlation between REEs and major and trace elements

The total REEs oxides (TREE_2O_3) and P_2O_3 contents are positively correlated in the agglomerate and breccia, while not correlated in calcio-carbonatite and syenite (Fig. 6-8a). The TREE_2O_3 and SrO contents are strongly positively correlated in the syenite and weakly correlated in the agglomerate and calcio-carbonatite (Fig. 6-8b). The TREE_2O_3 and BaO contents are strongly positively correlated in the agglomerate and breccia and weakly correlated in the calcio-carbonatite and the syenite (Fig. 6-8c). The TREE_2O_3 and (FeO+MnO) contents are strongly correlated in the calcio-carbonatite, agglomerate and breccia and syenite (Fig. 6-8d). The TREE_2O_3 and Nb contents are not correlated in the calcio-carbonatite, agglomerate, and breccia and syenite (Fig. 6-8e).

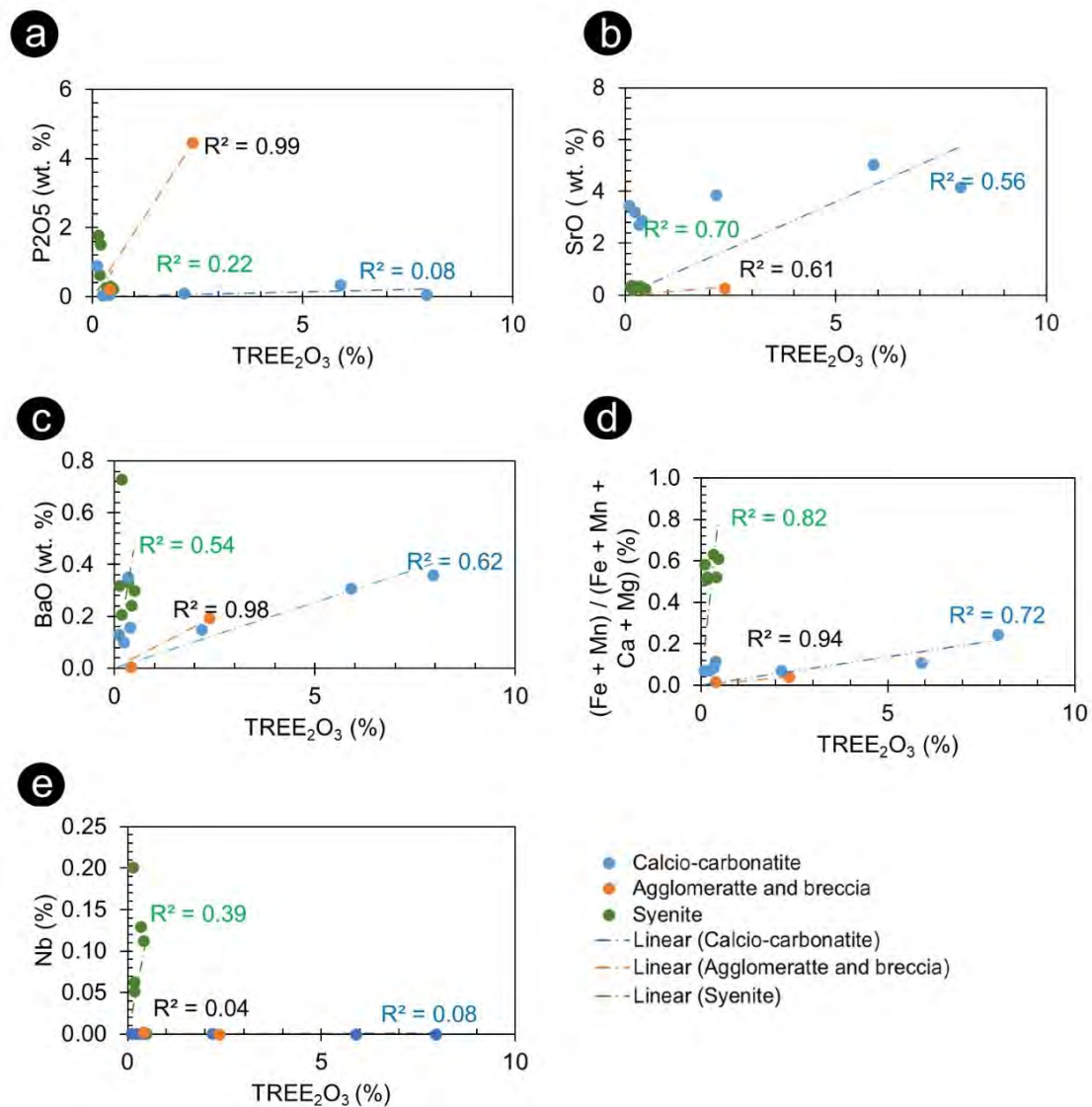


Fig. 6-8 Bivariate plots of major oxides and trace elements against total rare earth elements oxides. (a) P2O3 vs. $TREE_2O_3$, (b) SrO vs. $TREE_2O_3$, (c) Ba vs. $TREE_2O_3$, (d) $(Fe+Mn)/(Fe+Mn+Ca+Mg)$ vs. $TREE_2O_3$, (e) Nb vs. $TREE_2O_3$. R^2 means the linear correlation coefficient.

6.2.3.4 Carbon and Oxygen Isotope

The carbon and oxygen isotopic compositions of the Nkalonje carbonatites are given in Appendix A7. Three samples of calcite from calcio-carbonatite were analyzed. The calcite samples yielded a narrow range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, from -3.67 to -3.11 ‰ and from +1.95 to +8.61 ‰ (Fig. 6-9, Appendix A7).

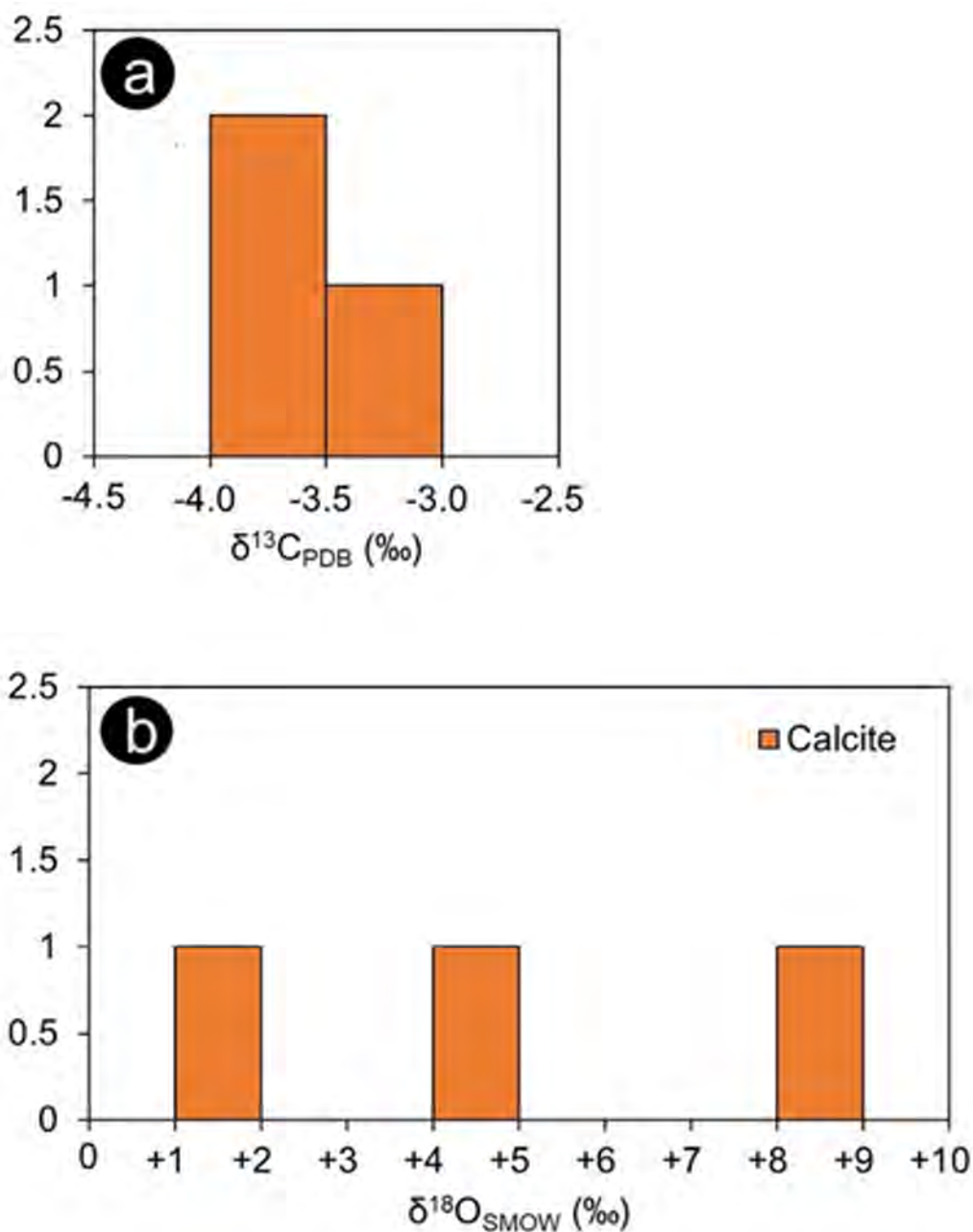


Fig. 6-9 Histogram showing $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope analysis of calcite from calcio-carbonatite.

6.3 Discussion

6.3.1 Origin of carbonatite magma

Based on field observation, the Nkalonje carbonatite occurred with associated alkaline rock (nepheline syenite) (Fig. 6-1). Carbonatite samples studied showed depleted contents of Nb (0.72 to 5.39 ppm), Zr (0.19-19.73 ppm) and while syenite showed enriched content of Nb (0.59-19.60 ppm), Zr (46.69-58.27 ppm) (Fig. 6-6b). The observed enrichment and depletion could be produced by fractionation during liquid immiscibility (e.g. Veksler et al., 1998b, 2012).

A plot of $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ given in Figure 6-10 (Ray & Ramesh, 2006) shows narrow isotopic variation for the Nkalonje carbonatite, with $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ranging from -3.67 to -3.11 ‰ and from +1.95 to +8.61 ‰ respectively. The calcio-carbonatite plot within the primary igneous carbonatite (P.I.C) field as well as high-temperature alteration field (Fig. 5-9). Based on these observations, the Tundulu carbonatite was formed from the liquid immiscibility of a mantle-derived silicate-carbonate magma.

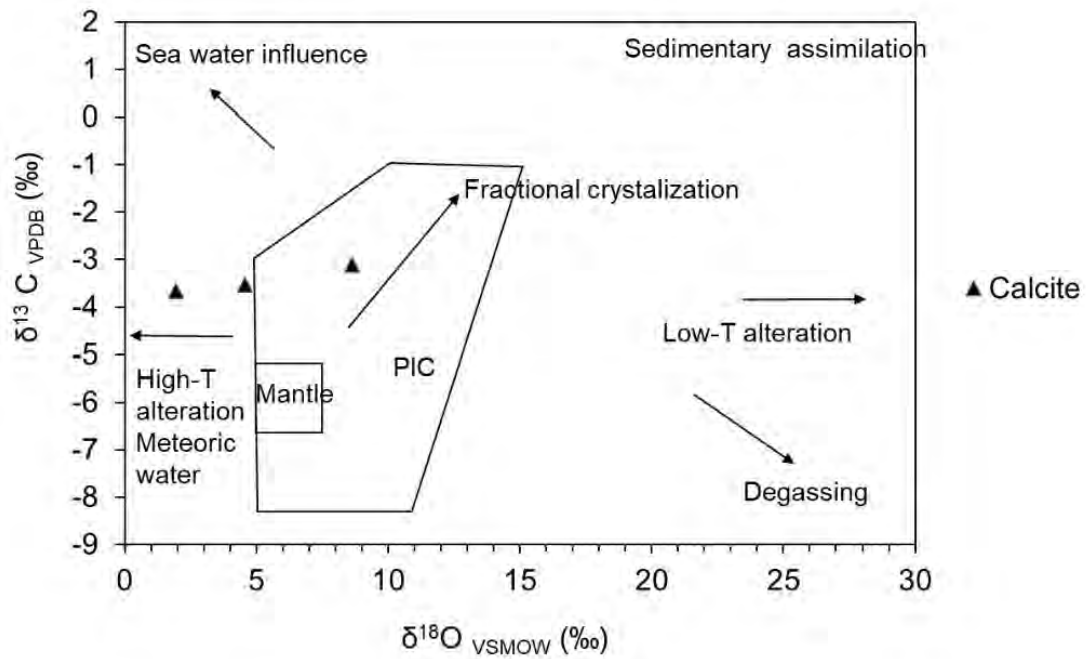


Fig. 6-10. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions of the Nkalonje carbonatites. Arrows indicate possible principal controls on carbonatite O and C isotope ratio after Deines (1989) and Demény et al. (2004). Mantle field is adapted from Kyser (1990), Deines (1992), and Cartigny et al. (1998). Primary igneous carbonatite (PIC) field from Ray & Ramesh (2006).

6.3.2 Evolution of the magma

Although our data was limited, the calcio-carbonatite indicates a minimal isotopic fractionation from parental melt and limited recrystallization (Fig. 6-10; e.g. Moore et al., 2015). Limited fractionation is supported by petrography, which shows primary calcite that is altered hydrothermally while maintaining its main composition. The separation of Ca-rich carbonate melt and silicate melt formed calcio-carbonatite by fractionating calcite (Fig. 6-1). The less evolved nature of the carbonate melt is supported by the observed ratio of Y/Ho in calcio-carbonate (24-33), which is within the Charac range for primary calcite and altered calcite similar to other carbonatites elsewhere (Fig. 6-7; e.g. Zheng et al., 2023). The absence of magnesio-carbonatite and/or ferro-carbonatite indicates a lack of magma differentiation or major alteration (e.g. Wyllie, 1965; Woolley & Kempe, 1989; Lee & Wyllie, 1998; Anenburg et al., 2021).

6.3.3 Order of emplacement between syenite and carbonatite.

The results of the geochemical analysis showed that calcio-carbonatite and syenite formed from the same parental magma. There is no observable structural feature within the complex to indicate a possible conduit of either carbonatite or syenite. Field observation, though circumstantial, favors the utilization of the same conduit because of the spatial proximity and distribution of the lithologies. The calcio-carbonatite, agglomerate and breccia occur between nepheline syenite (Fig. 6-1). The presence of trachyte within the agglomerate breccia (Fig. 6-2) suggests interaction with silicate magma, while the high carbonate content in the breccia (30.31 to 51.51 wt. %) suggests interaction with carbonatite magma. The Nkalonje Hill is an accumulation of agglomerates (Fig. 6-1; Garson, 1965).

6.3.4 Implications to REE mineralization

The mineralization of REEs in the Nkalonje carbonatite is represented by the presence of synchysite in calcio-carbonatite and feldspathic agglomerate and breccia and quartz-fluorite rock. Synchysite occurs in equilibrium with crystallized or altered calcite. Synchysite also replaces apatite and shows a corrosive texture, indicating

magmatic fluids (Fig. 6-3b-c-d) (e.g. Duraiswami & Shaikh, 2014; Chikanda et al., 2019) Synchysite in agglomerate breccia precipitate on fluorite grain boundaries (Fig. 6-3k). Quartz-fluorite shows synchysite overprint quartz and fluorite (Fig. 6-3m). Based on these observations, the mineralization can be classified as magmatic-hydrothermal stage. This is supported by C and O isotope data showing an involvement of the system with hydrothermal fluid at high temperatures (Fig. 6-10) while maintaining minimal isotopic fractionation and limited recrystallization (e.g. Moore et al., 2015). Similar Y/Ho ratio values of feldspathic agglomerate and breccia (18-28) and Quartz fluorite (18) suggest the occurrence of a hydrothermal process. Fluorite is usually available in the carbonate magma from the initial stage but usually concentrates and crystalizes at low temperature together with fluor-carbonates (Anenburg et al., 2021). A proposed mineral paragenetic sequence is shown in Figure 6-11.

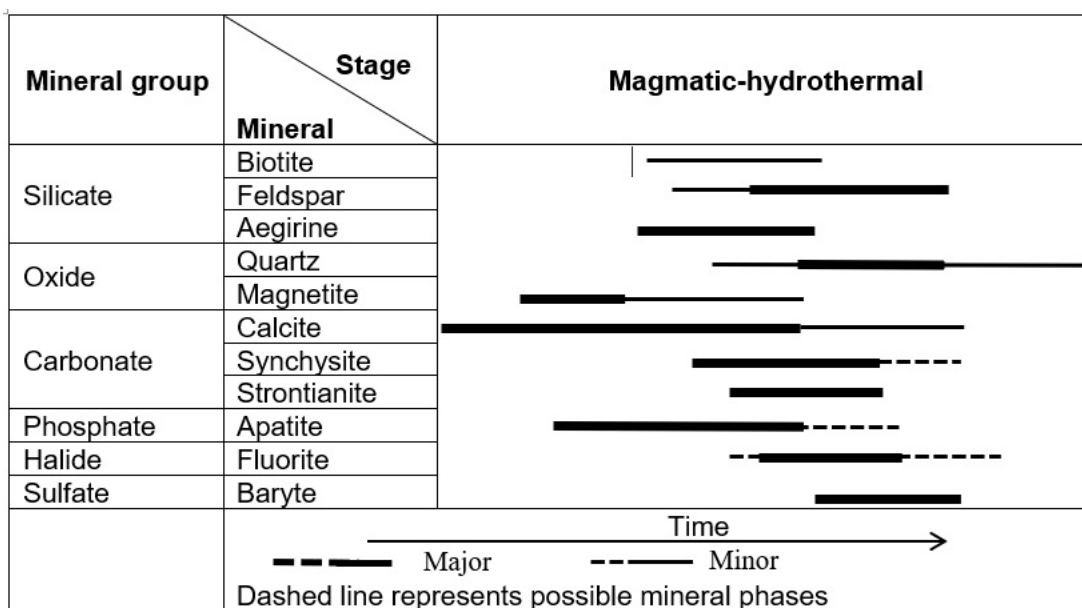


Fig. 6-11 Proposed REEs paragenetic sequence for the Nkalonje carbonatite.

(La/Yb)_N ranges from 22.38 to 709.84 in calcio-carbonatite, 29.6 in quartz-fluorite, 28.57 to 204.27 in feldspathic agglomerate and breccia and 23.04 to 48.81 in Syenite, suggesting that LREEs were more enriched in calcio-carbonatite than other lithotypes probably due to immiscibility and factional crystallization and hydrothermal processes. Although there was no magmatic differentiation to yield other types of carbonatites, the variable concentrations of P₂O₅, SrO, BaO, Fe+Mn, and Nb in the same rock unit, as well as among rock units, has also been interpreted to be a result of element enrichment due to fractional crystallization as well as contamination by hydrothermal processes (Togashi, 1985). In addition, the mineralogy of the rocks could also account for the observed variable element concentration. For example, P₂O₅ and Ba contents of feldspathic breccia are higher than calcio-carbonatites, while Nb is higher in syenite than calcio-carbonatite and feldspathic breccia and agglomerate (Fig. 6-8; Appendix A6).

The association of strontianite, synchysite apatite, and fluorite suggests F, P, and CO₂ as main ligands for REE transportation in the Nkalonje carbonatite (e.g. Samson et al., 1995; Williams-Jones & Palmer, 2002; Strzelecki et al., 2022).

6.4 Summary

The Nkalonje carbonatite was emplaced as a vent made of a conical hill (Nkalonje and Nyama). Nkalonje is mainly composed of agglomerate feldspathic breccia while Nyama is mainly dominated by fenitised gneiss that were intruded by Calcio-carbonatite dykes, nepheline syenite and felspathic agglomerate breccia.

Geochemical analysis of the carbonatite shows depleted contents of Nb, (0.72 to 5.39 ppm), Zr (0.19-19.73 ppm) and while syenite showed enriched content of Nb (0.59-19.60 ppm), Zr (46.69-58.27 ppm) in Nb and Zr contents. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ spanning from -3.67 to -3.11 ‰ and from +1.95 to +8.61 ‰, respectively, show a narrow isotopic variation and plot in the primary igneous carbonate. These factors potentially indicate carbonatite melt to have formed from the liquid immiscibility of mantle-derived silicate-carbonate magma. The observed narrow isotopic variation further suggests minimal fractionation that resulted in the carbonatite maintaining its initial Ca-rich composition. Furthermore, absence of observable conduit and the spatial

association of nepheline syenite and carbonatite suggest use of same conduit by carbonatite and silicate magma.

The main REE mineral at Nkalonje carbonatite is synchysite. Mineralization occurred as disseminated and can be classified as magmatic-hydrothermal stage characterized by synchysite that occurred in equilibrium with recrystallized calcite, replacing apatite and overprint quartz. $(La/Yb)_N$ ranges from 22.38 to 709.84 in calcio-carbonatite. 29.6 in quartz-fluorite, 28.57 to 204.27 in feldspathic agglomerate and breccia and 23.04 to 48.81 in Syenite, suggesting that LREEs were more enriched in calcio-carbonatite than other lithotypes probably due to immiscibility, fractional crystallization and hydrothermal processes.

Reference

- Anenburg, M., Broom-Fendley, S., and Chen, W. (2021). Formation of rare earth deposits in carbonatites. *Elements*, 17(5), pp.327–332
- Bau, M. (1996). Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. *Contributions to Mineralogy and Petrology*, 123, pp.323–333.
- Bloomfield, K. (1968). The Pre-Karoo Geology of Malawi. Government Printer, Memoir 5, 166pp.
- Bloomfield, K., and Garson, M.S. (1965). The Geology of the Kirk Range-Lisungwe valley area. Government Printers, Bulletin 17, 234pp.
- Cartigny, P., Harris, J. W., Phillips, D., Girard, M., and Javoy, M. (1998). Subduction-related diamonds? - The evidence for a mantle-derived origin from coupled $\delta^{13}C$ - $\delta^{15}N$ determinations. *Chemical Geology*, 147(1), pp.147–159.
- Deines, P. (1989). Stable isotope variations in carbonatites.. In Bell K (Ed.). *Carbonatite Genesis and Evolution*. Unwin Hyman, pp.301–359.
- Deines, P. (1992). Mantle Carbon: Concentration, mode of occurrence, and isotopic composition. In M. Schidlowski (Ed.), *Early Organic Evolution* Springer. pp.133–146.
- Demény, A., Sitnikova, M., and Karchevsky, P. I. (2004). Stable C and O isotope compositions of carbonatite complexes of the Kola Alkaline Province: phoscorite-

- carbonatite relationships and source compositions. *Mineralogical Society Series*, pp.407–431.
- Eskola, P. (1939). Die Entstehung der Gesteine. In springer.
- Garson, M. S. (1965). Carbonatites in Southern Malawi. Government Printers, Bulletin 15, 128pp.
- Gittins, J., and Harmer, R. E. (1997). What is ferrocarbonatite? A revised classification. *Journal of African Earth Sciences*, 25(1), pp.159–168.
- Hornig-Kjarsgaard, I. (1998). Rare earth elements in sövitic carbonatites and their mineral phases. *Journal of Petrology*, 39, pp.2105–2121.
- Kyser, T. K. (1990). Stable isotopes in the continental lithospheric mantle. *Oxford Monographs on Geology and Geophysics*, 16, pp.127–156.
- Lee, W.-J., and Wyllie, P. J. (1998). Petrogenesis of carbonatite magmas from mantle to crust, constrained by the system $\text{CaO}-(\text{MgO} + \text{FeO}^*)-(\text{Na}_2\text{O} + \text{K}_2\text{O})-(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2)-\text{CO}_2$. *Journal of Petrology*, 39(3), pp.495–517.
- Martin, L. H. J., Schmidt, M. W., Mattsson, H. B., Ulmer, P., Hametner, K., and Günther, D. (2012). Element partitioning between immiscible carbonatite – kamafugite melts with application to the Italian ultrapotassic Suite. *Chemical Geology*, 320–321, pp.96–112.
- McDonough, W. F., and Sun, S.S. (1995). The composition of the Earth. *Chemical Geology*, 120(5), pp.223–253.
- Ray, J. S., and Ramesh, R. (2006). Stable Carbon and Oxygen Isotopic Compositions of Indian Carbonatites Stable Carbon and Oxygen Isotopic Compositions. *Interernational Geological Review*, 48, pp.17–45.
- Samson, I. M., Liu, W., and Williams-Jones, A. E. (1995). The nature of orthomagmatic hydrothermal fluids in the Oka carbonatite, Quebec, Canada: Evidence from fluid inclusions. *Geochimica et Cosmochimica Acta*, 59(10), pp.1963–1977.
- Strzelecki, A. C., Migdisov, A., Boukhalfa, H., Sauer, K., McIntosh, K. G., Currier, R. P., Williams-Jones, A. E., and Guo, X. (2022). Fluocerite as a precursor to rare earth element fractionation in ore-forming systems. *Nature Geoscience*, 15(4), pp.327–333.
- Togashi, S. (1985). Sr variation by fractional crystallization for volcanic rocks from

- island arcs and continental margins. *Chemical Geology*, 51(1–2), pp.41–53.
- Williams-Jones, A. E., and Palmer, D. A. S. (2002). The evolution of aqueous-carbonic fluids in the Amba Dongar carbonatite, India: Implications for fenitisation. *Chemical Geology*, 185(3–4), pp.283–301.
- Woolley, A. R. (1987). Lithosphere metasomatism and the petrogenesis of the Chilwa Province of alkaline igneous rocks and carbonatites, Malawi. *Journal of African Earth Sciences*, 6(6), pp.891–898.
- Woolley, A. R., and Kempe, D. R. C. (1989). Carbonatites: Nomenclature, average chemical compositions, and element distribution. In Bell K. (Ed.), *Carbonatite: Genesis and Evolution* (1st Ed.,). Unwin Hyman. pp.1–13.
- Wyllie, P. J. (1965). Melting relationships in the system CaO-MgO-CO₂-H₂O, with petrological applications. *Journal of Petrology*, 6(1), pp.101–123.
- Zheng, X., Liu, Y., Smith, M. P., Kynický, J., and Hou, Z. (2023). Carbonatitic magma fractionation and contamination generate rare earth element enrichment and mineralization in the Maoniuping giant REE Deposit, SW China. *Journal of Petrology*, 64(6), pp.1–36.

Chapter 7 Conclusions

8.1. Regional and local Tectonic setting

The Malawi basement complex in the southern region is assigned to the south Irumide domain, which was formed in an island arc setting due to the closure of the Irumide ocean and convergence with the Kalahari craton. The closure resulted in the formation of an island arc setting in western Malawi, where the Unango subdomain overrides the Lilongwe subdomain during the Pan-African orogeny tectonism. The Irumide event amalgamates the pre-Cambrian alkaline magmatic intrusions that are characterized by LREE. The amalgamation of the pre-Cambrian alkaline intrusion with the MBC through the W-E and NE-SW compression facilitated possibly an enriched REE source while the convergence setting created a thick crust along the Lilongwe subdomain.

The Blantyre Suite intrusion created an extension movement that resulted in the rise of a dome-like structure in the Unango domain. The early intrusions are placed along the edge of the Lilongwe and Unango domains. From this observation, probably a thick crust along the Lilongwe subdomain and amalgamation might have created more residence for carbonate magma differentiation and assimilation that help supply REEs budget in the carbonatite within the Lilongwe domain. Later intrusions were emplaced within the Unango domain. This observation suggests late alkaline rock and carbonatites were emplaced in well-defined structure conduit and thin crust. This is evident by the abundance of alkaline rock in the Unango domain and might help to explain the proximity of carbonatites and silicate rocks in the eastern carbonatite belts and the absence of silicate rocks in the western carbonatite belt. Hence, this reduces residence time and possible crustal contamination in the eastern belt. This condition helps to explain why the carbonatites in the east belt are less evolved. Furthermore, the close spatial association of alkaline silicate rock and carbonatite suggest use of same conduits.

8.2. Origin of the carbonatite magma

Carbonatite magma origin remains a debate. The common origin of carbonatite magma conserved includes (1) Direct melting of metasomatized mantle peridotite or 'basaltic' eclogite; (2) Differentiation of a carbonate-bearing alkaline silicate magma produced by

mantle melting;(3) Separation by liquid immiscibility of carbonatite and silicate liquids from a precursor carbonate-bearing alkaline silicate magma such as nepheline or melilite; and (4) Melting of eclogite formed by metamorphism of subducted oceanic or continental crust.

This study identifies liquid immiscibility as the viable origin of carbonatites in the Chilwa Alkaline Province. The observed variation in the final differentiated magma reflects the initial magma. Mg-rich carbonatite on the western belt and Ca-rich carbonatite on the eastern belt probably represent source composition. On the other hand, nepheline magma composition in the C.A.P seems to be the main silicate from which the carbonatite is separated. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of -7.73 to -0.74 ‰ and +4.4 to +26.73 ‰, respectively for Kangankunde carbonatite (western belt) vary much from Tundulu and Nkalonje $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of -3.74 to -2.92 ‰ and +1.92 to 13.9 ‰ respectively eastern belt carbonatite and suggests less evolved magma in the eastern belt.

8.3. Implications of magmatic and hydrothermal processes on REEs mineralization

Magmatic differentiation paths of the western carbonatite (Kangankunde) had two paths, thus beforosite through magnesio-carbonatite to ferro-carbonatite, and beforosite to ferruginous calcio-carbonatite. The eastern belt (Tundulu carbonatite) had one path from calcio-carbonatite through ferruginous calcio-carbonatite to magnesio-carbonatite. Furthermore, no differentiation was observed in Nkalonje carbonatites. Both magmatic and hydrothermal processes were critical for the REE mineralization and enrichment. The main role of magmatic processes was concentration of REEs and primary mineralization. Apparently, dominance of hydrothermal signatures is localized that closely suggest local remobilization of REEs in the Kangankunde, Tundulu, and Nkalonje carbonatites. High enrichment of LREE was observed magnesio-carbonatite and might be best target for detailed exploration The mineralization in Kangankunde and Tundulu carbonatites can be classified into two stages: magmatic, which is characterized by the occurrence of monazite/synchysite interstitials, and grain boundaries of primary carbonate minerals. The magmatic-hydrothermal stages is characterized by the occurrence of monazite/synchysite overprinting primary and

secondary minerals in association with strontianite or barite, dissolution texture of REEs minerals, and apatite. The mineralization in the Nkalonje carbonatite can be classified as magmatic hydrothermal. The main REEs minerals in the Kangankunde carbonatite is monazite, while in Tundulu and Nkalonje carbonatites, is synchysite. The minor REE minerals are synchysite and daqingshanite in Kangankunde carbonatite, while apatite and fluorapatite occur in Kangankunde, Tundulu and Nkalonje carbonatite.

8.4. Proposed genetic model of magma differentiation of the carbonatites.

The model considers the section described above, which includes the tectonic setting, observed mineral assemblages, REEs mineralization, and present physiography of the carbonatites.

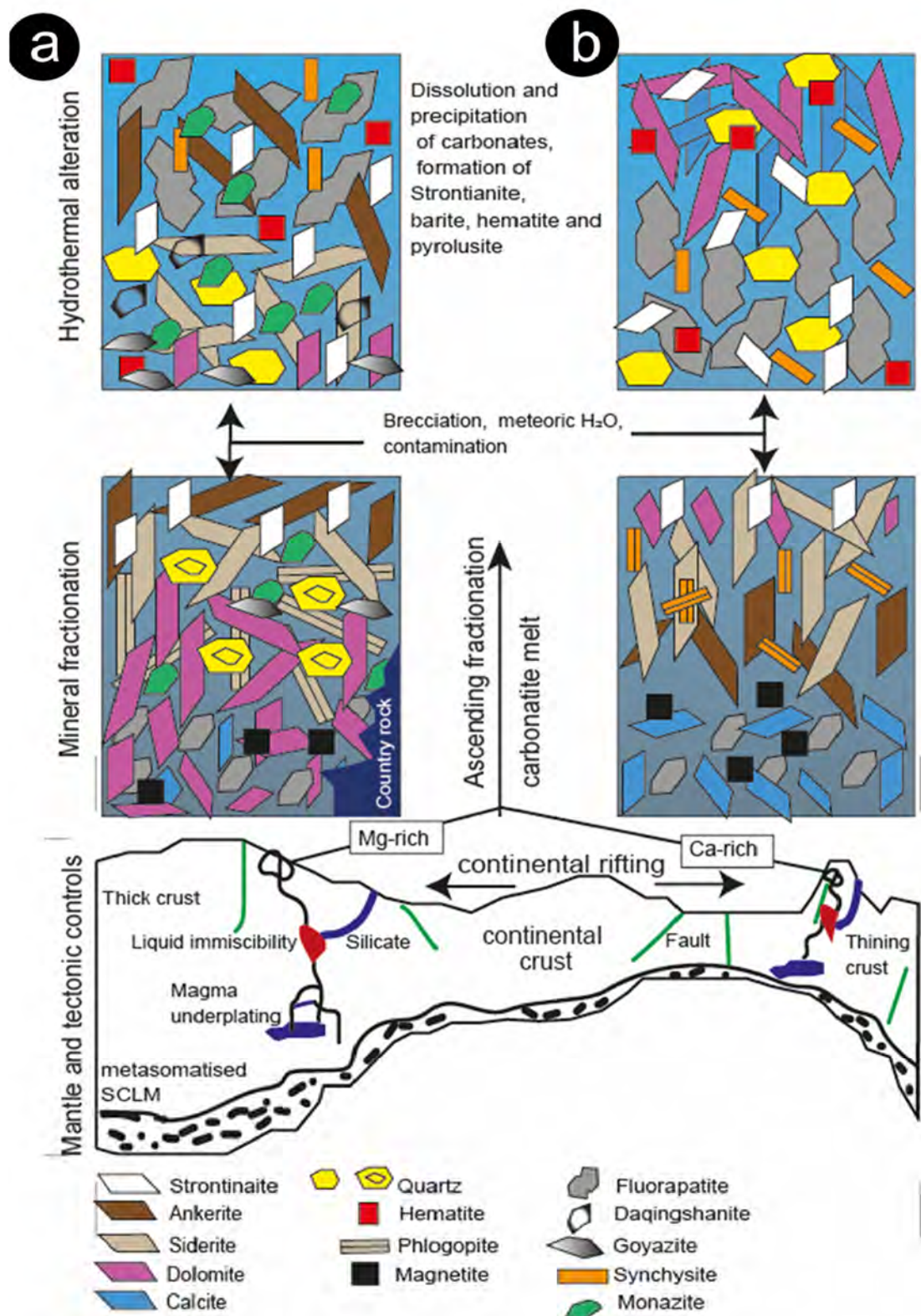
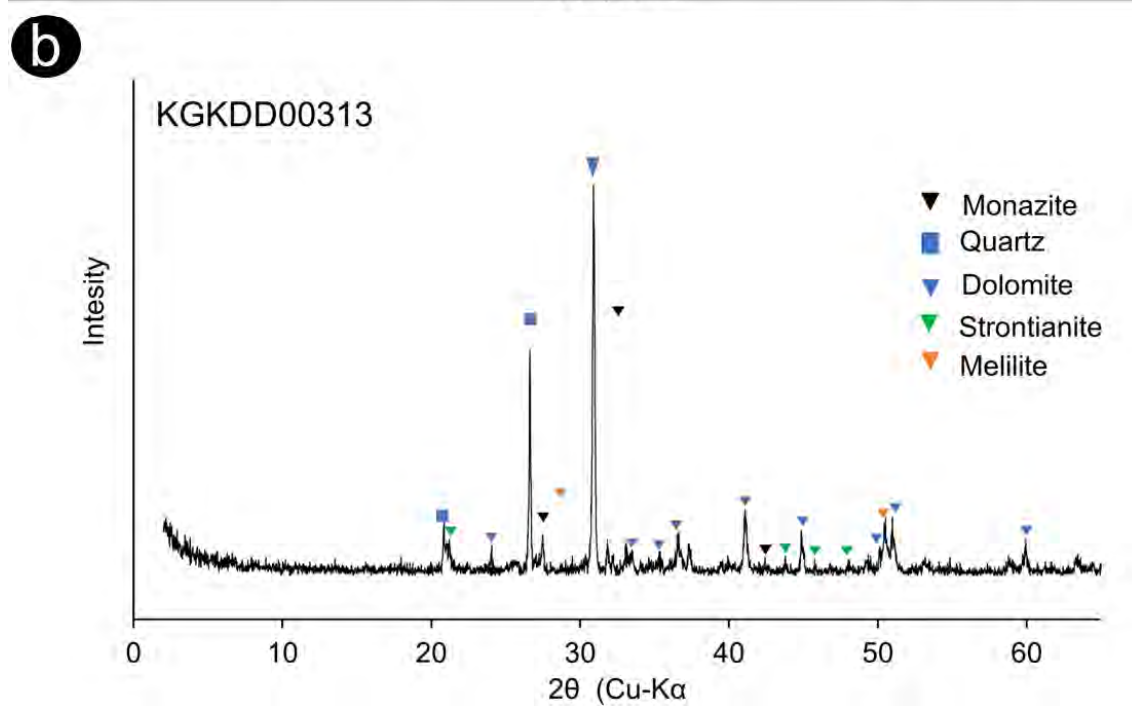
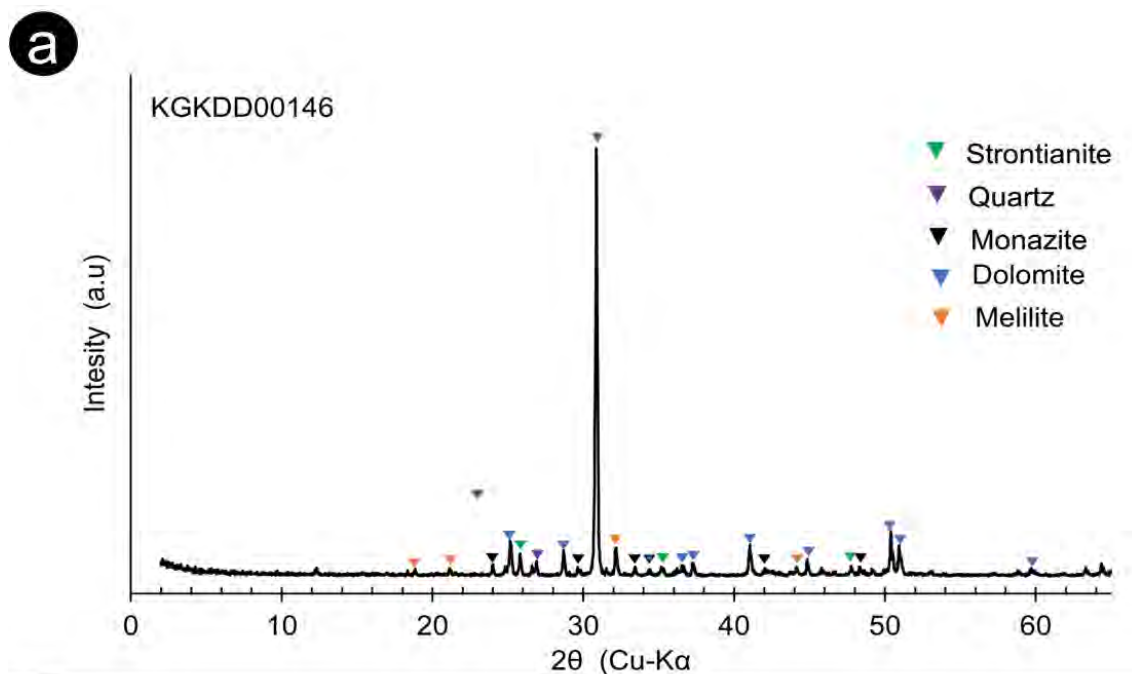
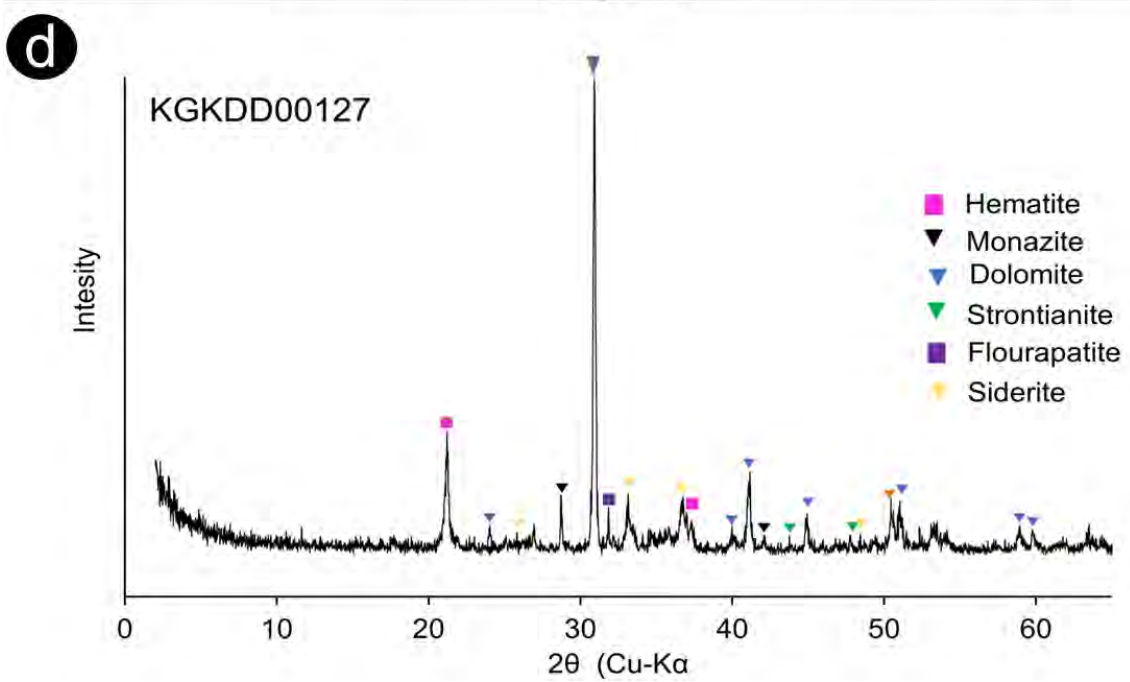
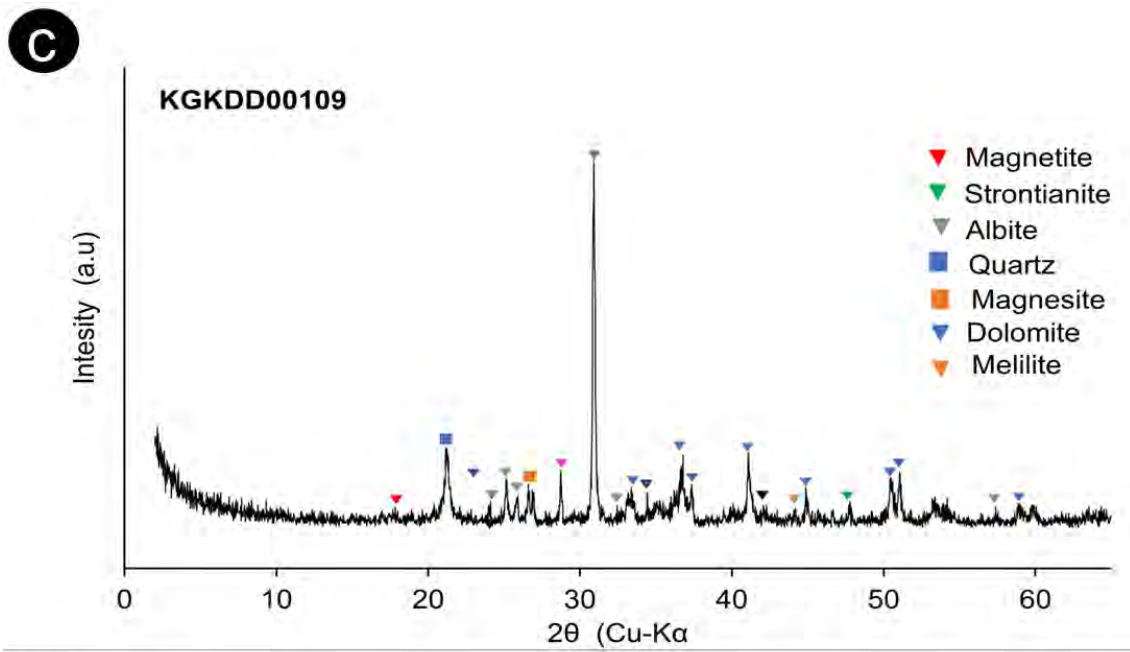
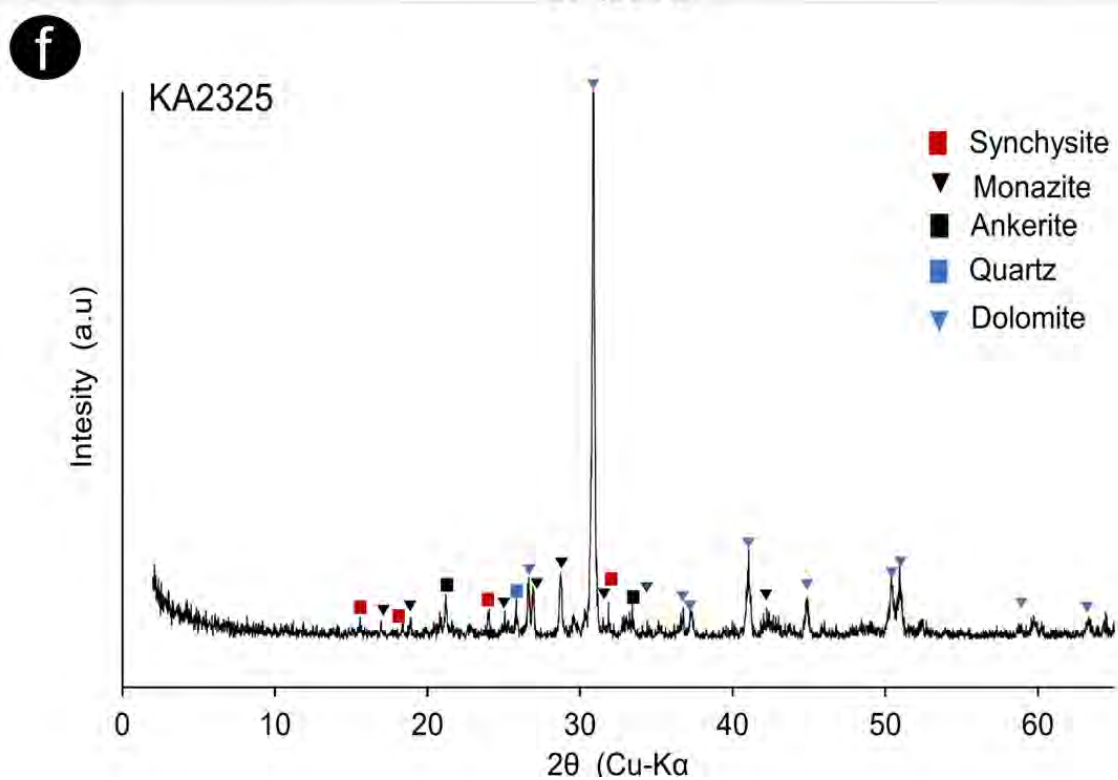
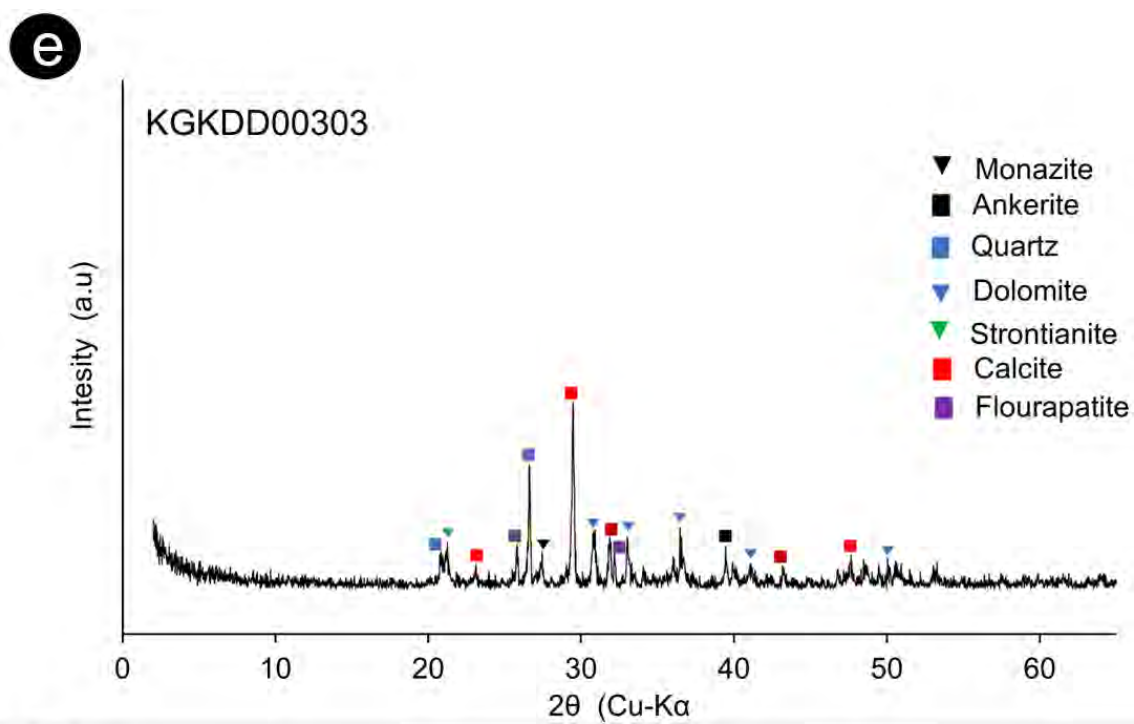


Fig. 7-1 Simplified model for the origin of the carbonatite magma and differentiation paths for the (a) western belt and (b) Eastern belt carbonatite of the Chilwa Alkaline Province, Malawi modified from Anenburg et al. (2021).

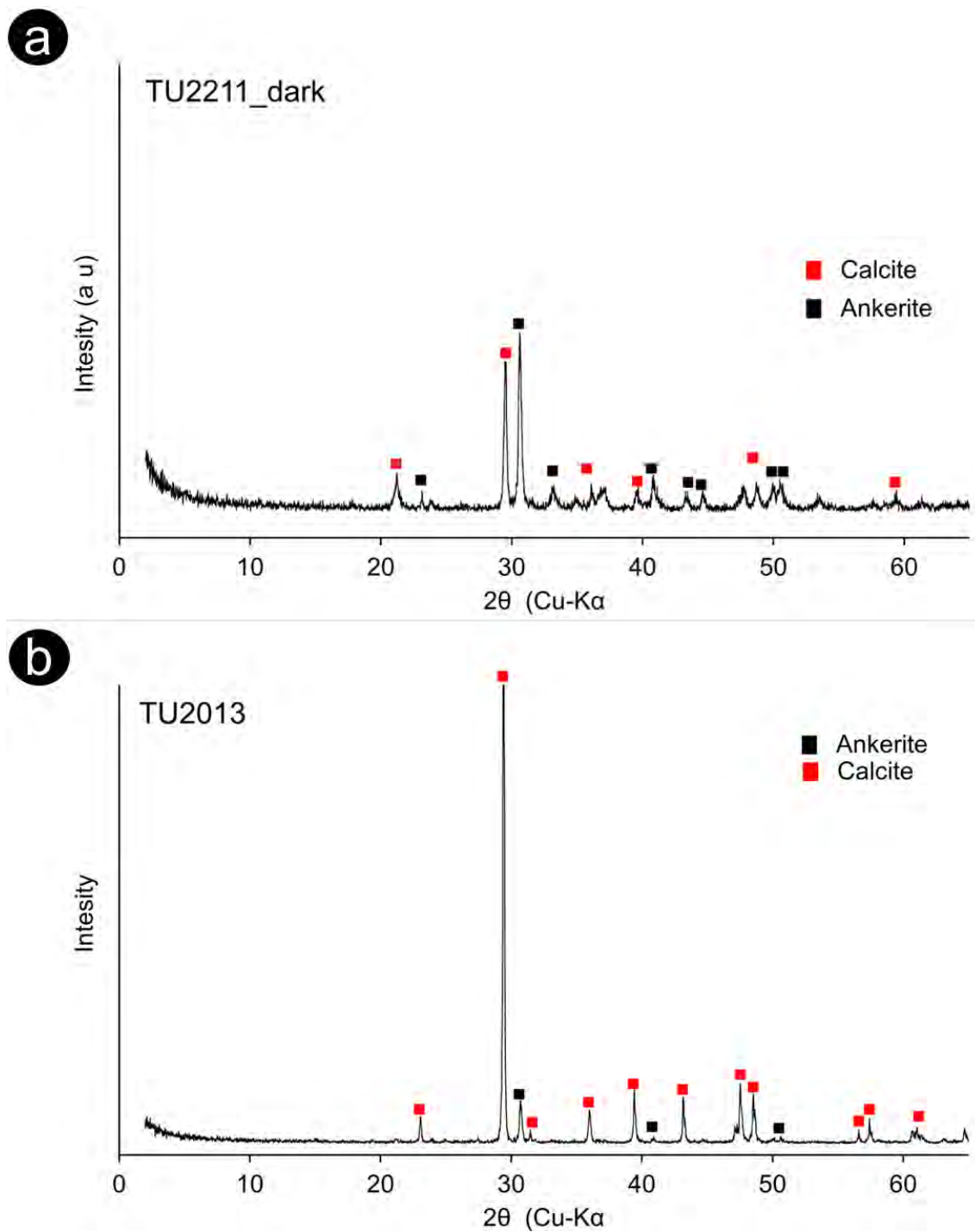
Appendix A1 XRD pattern of representative samples from Kangankunde carbonatite.

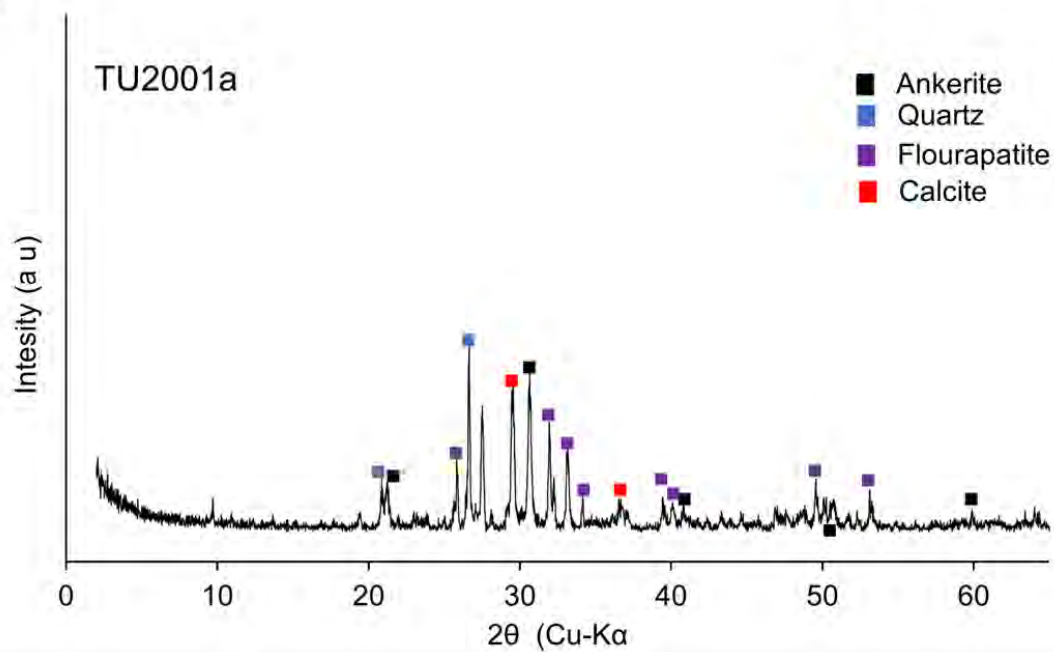
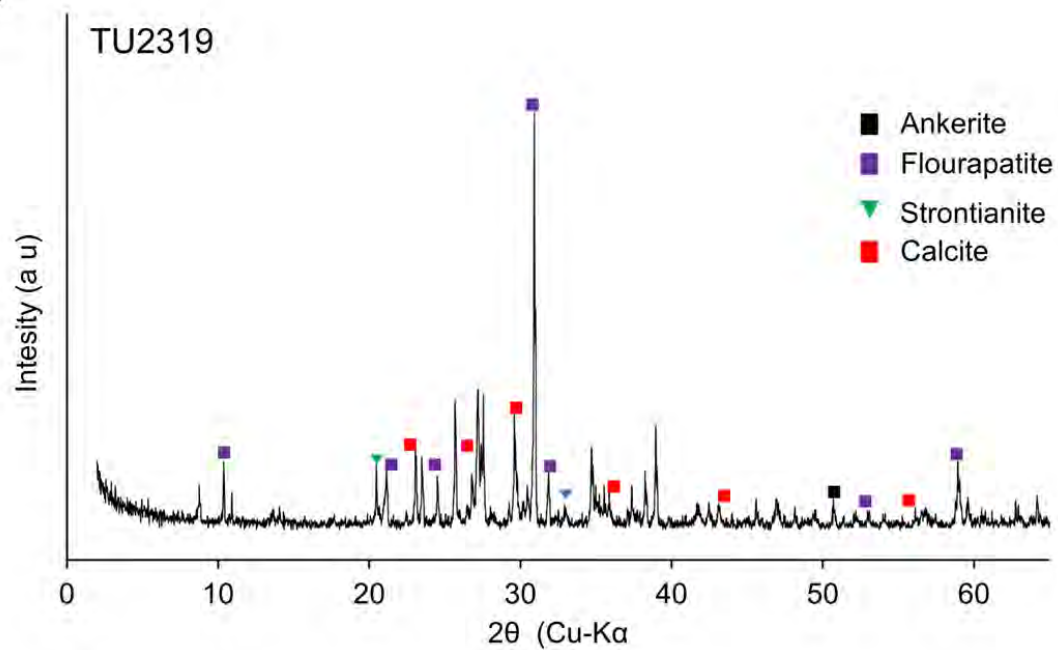


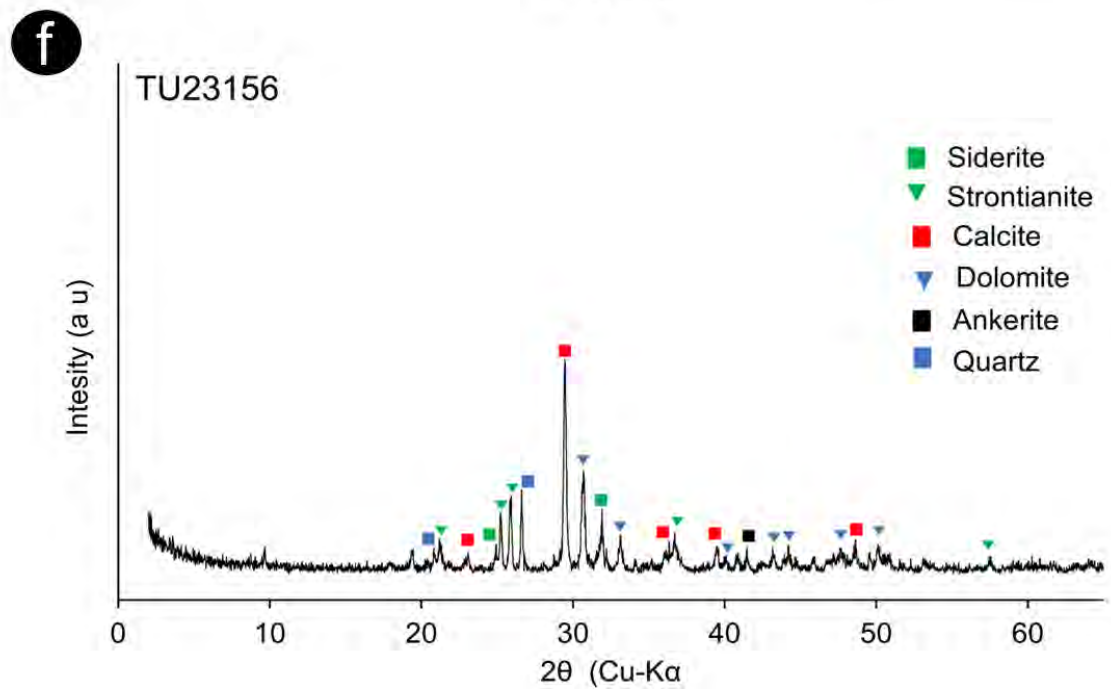
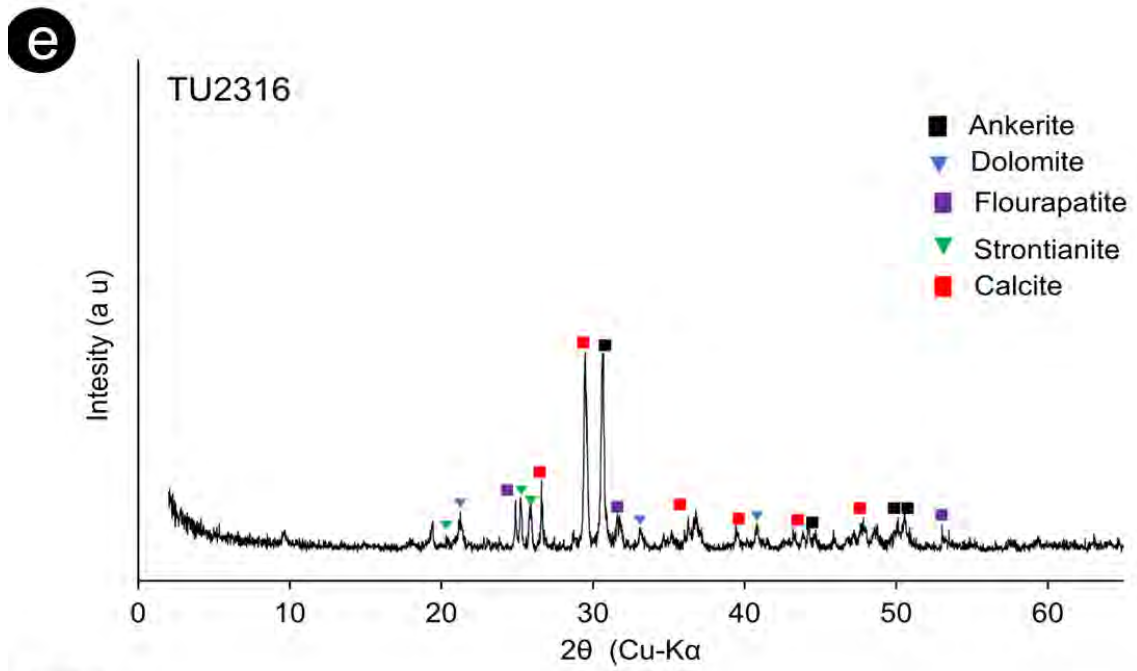




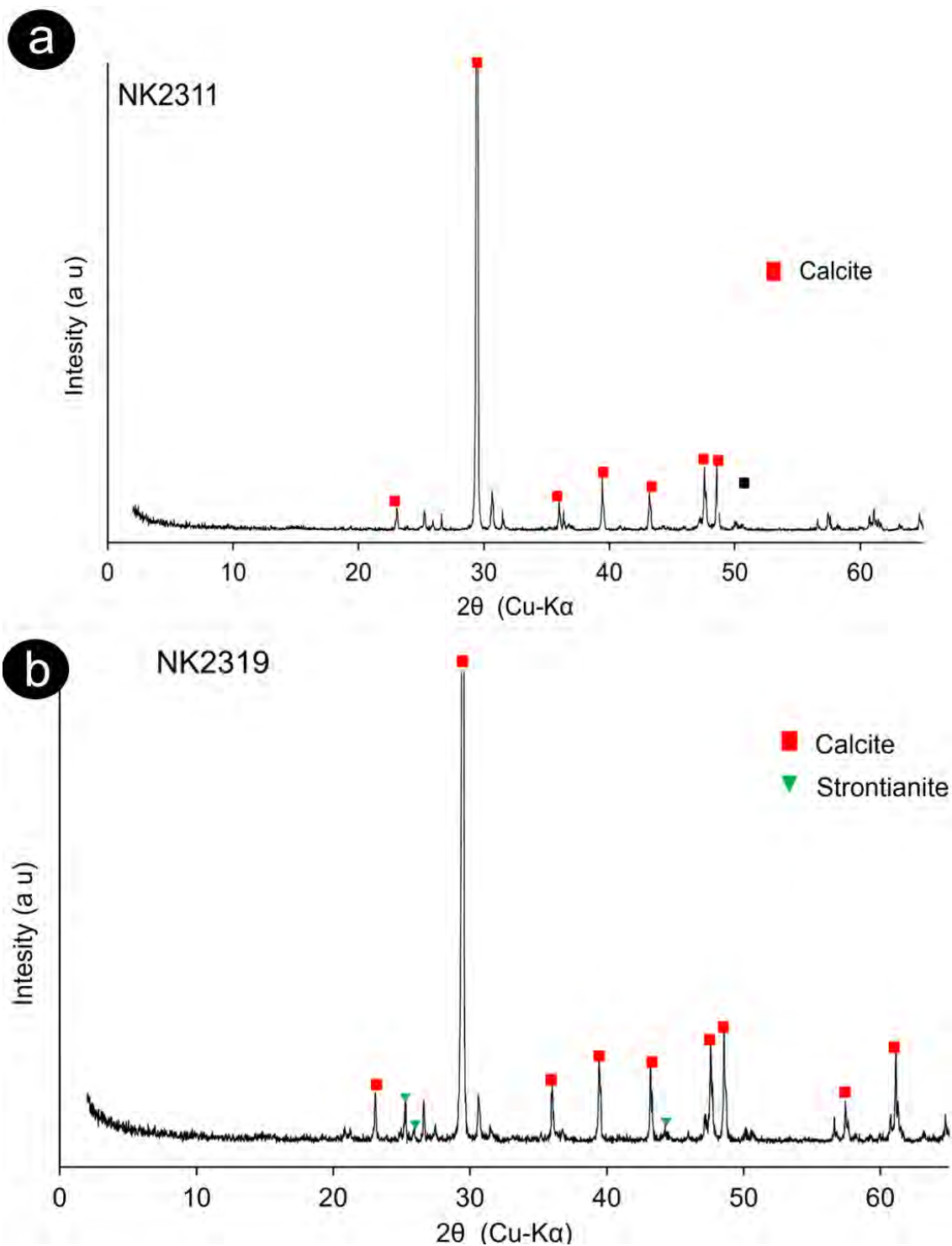
Appendix A2 XRD pattern of representative samples from Tundulu carbonatite.

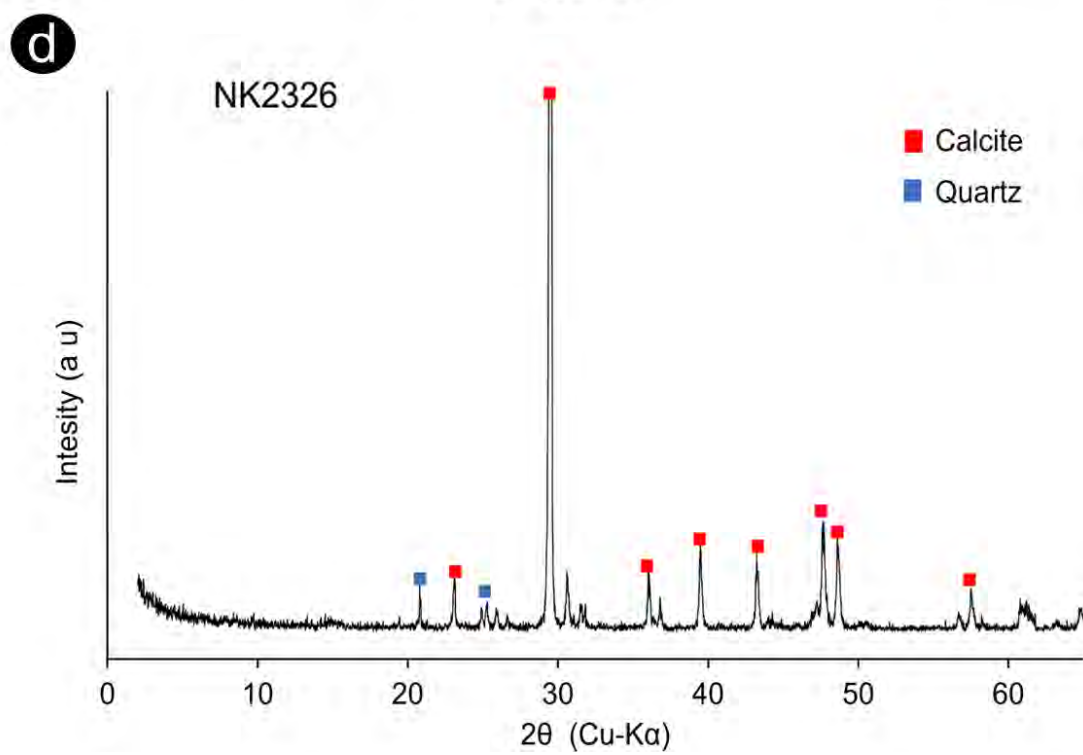
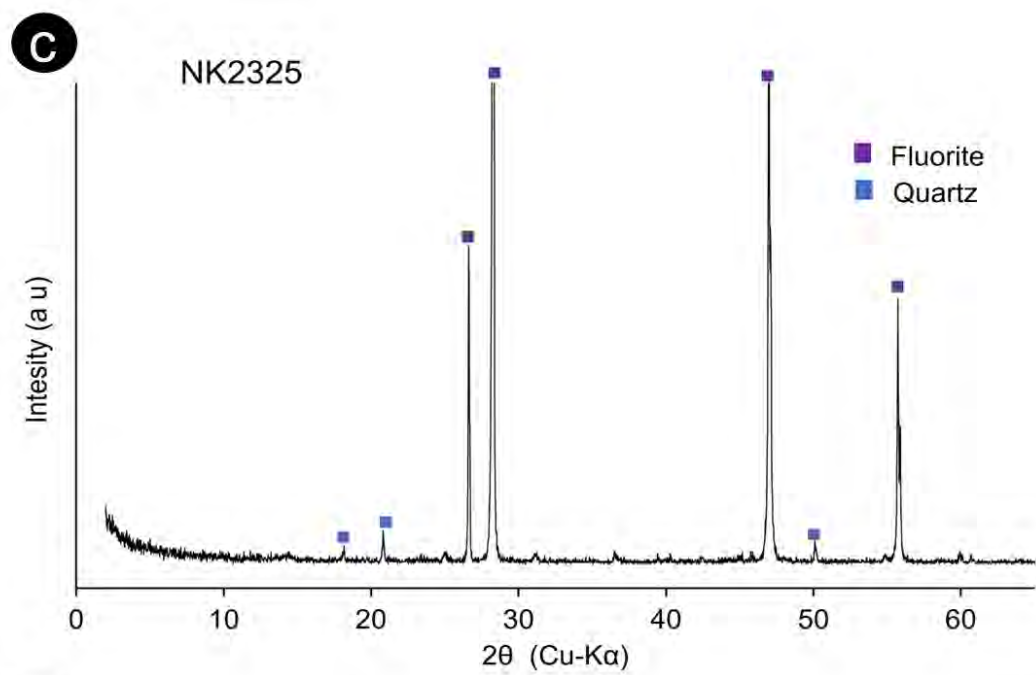


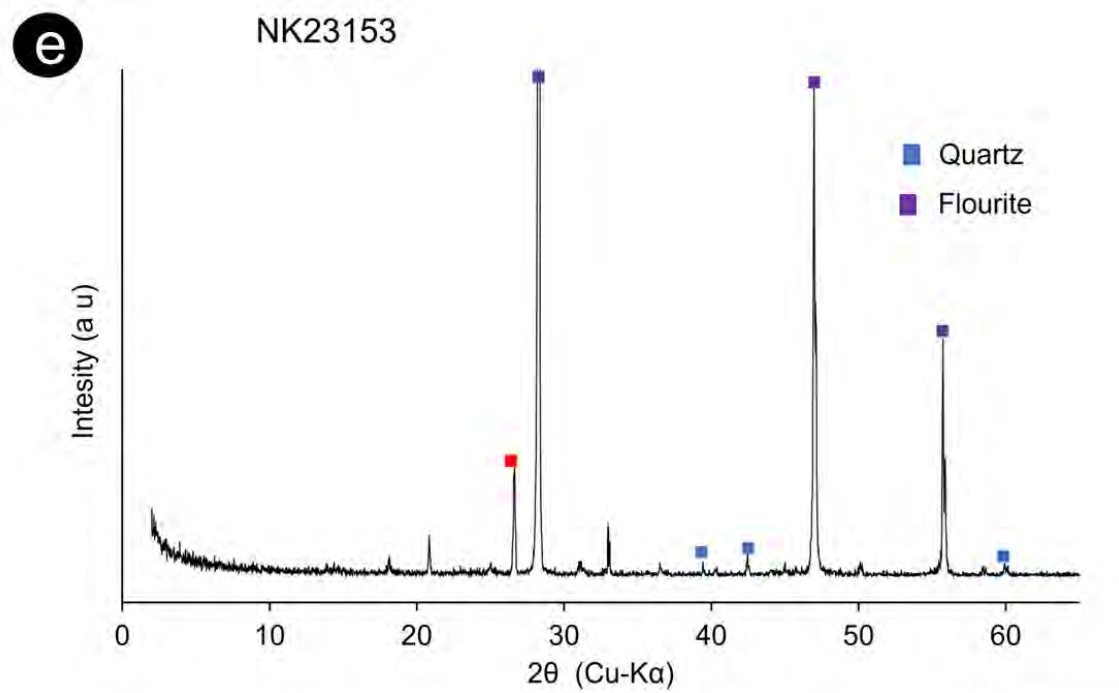
c**d**



Appendix A3 XRD pattern of representative samples from Nkalonje carbonatite.







Appendix A4 Major, minor and trace element compositions of carbonatite rocks in Kangankunde

Rock name	Magnesio-carbonatite					
Sample ID	KGKDD0 0101	KGKDD0 0104	KGKDD0 0105	KGKDD0 0112	KGKDD0 0118	KGKDD0 0120
(wt. %)						
SiO ₂	6.3	1.58	18.86	13.59	19.87	1.33
TiO ₂	0.02	0.01	0.06	0.04	0.16	0.02
Al ₂ O ₃	b.d	b.d	3.69	0.71	6.38	b.d
Fe ₂ O ₃	11.24	8.35	8.52	10.85	12.17	13.77
MnO	3.55	2.93	2.1	3.06	2.67	4.27
MgO	15	16.21	12.66	14.92	13.65	12.49
CaO	25.91	26.86	16.9	20.24	13.9	25.7
Na ₂ O	b.d	b.d	b.d	b.d	b.d	0.03
K ₂ O	b.d	b.d	0.85	0.22	0.78	b.d
P ₂ O ₅	0.59	0.72	1.08	1.27	1.39	6.97
SrO	8.79	5.17	4.17	2.36	1.41	3.37
BaO	0.21	0.59	0.68	0.17	0.33	1.62
LOI	24.77	33.87	28.53	33.3	23.9	26.9
ppm						
La	5502	7317	5695	1092	3313	6902
Ce	8365	10046	9511	1819	6010	12032
Pr	883	1011	941	184	621	1277
Nd	2686	3148	2828	505	1937	4027
Sm	175	225	169	38	138	246
Eu	29	39.41	29	7	25	41
Gd	157	149	117	29	85	144
Tb	5.9	7	5	2	4	8
Dy	11.29	17	12	7	10	22
Y	16.03	32	20	17	21	51

Ho	1	2	1	1	1	2
Er	2.56	4	3	2	3	5
Tm	0.1	0.18	0.12	0.12	0.13	0.34
Yb	0.45	0.78	0.62	1	1	2
Lu	0.04	0.11	0.1	0.08	0.11	0.21
S	164.97	509	975	b.d	605	1670
Sc	3	3	6	7	10	4
Ti	68	70	58	72	108	80
V	29	27	35	34	39	32
Ni	388	283	277	404	495	470
Co	7	1.46	3	4	5	8
Zn	531	348	350	280	526	2359
Ga	111	281	327	102	241	925
Rb	b.d	b.d	6	1	4	b.d
Zr	59	80	240	86	289	130
Nb	534	8	492	944	491	11
Mo	23	11	42	46	39	56
Hf	1	b.d	10	95	60	1
Ta	b.d	b.d	4	35	21	b.d
Pb	b.d	b.d	b.d	b.d	b.d	b.d
Th	57	58	57	38	40	78
U	b.d	1	2	25	17	3
Total	98.35	98.67	100.32	101.32	98.12	99.52
(wt.%)						
(La/Yb)_N	8335	6347	6202	1248	3317	2802
Y/Ho	16.1	19	19	21	20	21
TREE₂O	2	3	2	0.1	1	3

Appendix 4 continue.

Rock name	Magnesio-carbonatite						
Samp le ID	KGKDD 00122	KGKDD 00124	KGKDD 00125	KGKDD 00126	KGKDD 00137	KGKDD 00144	KGKDD 00146
(wt.%)							
SiO₂	4.37	15.88	1.24	14.98	5.02	2.79	4.8
TiO₂	0.01	0.12	0.01	0.2	0.06	0.01	0.01
Al₂O₃	0.28	2.31	b.d	2.73	1.94	0.11	2.27
Fe₂O₃	8.33	13.81	14.18	14.28	11.74	19.87	6.55
MnO	2.89	4.5	5.08	4.27	3.42	6.03	2.55
MgO	14.19	12.79	14.43	15.15	15.83	14.83	13.96
CaO	21.2	18.73	26.63	15.59	22.6	11.24	21.85
Na₂O	b.d	b.d	b.d	b.d	b.d	b.d	b.d
K₂O	b.d	b.d	b.d	b.d	b.d	b.d	b.d
P₂O₅	1.81	1.02	1.68	0.4	1.48	2.87	1.74
SrO	4.87	0.98	1.34	2.07	1.35	4.19	4.3
BaO	1.82	0.7	0.54	0.38	0.11	0.78	1.02
LOI	32.27	27.97	32.67	30.57	33.67	33.5	33.07
ppm							
La	13123	5433	4759	1485	1246	4201	17619
Ce	19283	10795	8830	2774	1999	6526	25102
Pr	1923	1183	1014	245	211	696	2535
Nd	5744	3986	3621	787	584	2207	7437
Sm	309	243	235	44	39	130	405
Eu	42	43	41	7	7	20	64
Gd	182	152	128	21	22	72	219
Tb	7	5	6	1	1	3	8
Dy	14	9	15	2	3	6	17
Y	34	18	39	7	9	11	23
Ho	1	1	2	0.24	0.45	1	2

Er	4	2	3	1	1	2	5
Tm	0.17	0.09	0.24	0.05	0.12	0.08	0.12
Yb	1	0.42	1	0.29	1	0.46	1
Lu	0.14	0.06	0.14	0.05	0.13	0.06	0.07
S	1941	b.d	455	985	2142	1189	1350
Sc	3	5	4	5	4	1	2
Ti	48	108	87	128	83	27	48
V	19	33	28	27	26	9	14
Ni	246	740	700	649	520	569	177
Co	2	10	4	6	9	4	2
Zn	1226	1308	981	347	490	930	293
Ga	817	538	333	226	72	344	547
Rb	b.d	b.d	b.d	b.d	b.d	b.d	b.d
Zr	32	71	44	182	77	99	45
Nb	140	861	27	842	243	543	46
Mo	46	207	61	105	92	11	9
Hf	8	60	b.d	103	14	2	1
Ta	3	24	b.d	41	5	1	b.d
Pb	b.d	b.d	b.d	b.d	b.d	b.d	b.d
Th	75	43	63	24	6	18	56
U	4	18	2	30	3	1	4
Total	96.56	101.40	99.96	101.53	97.99	97.92	97.71
(La/Y b)_N	9412	8815	2887	3443	1209	6162	23063
Y/Ho	24	24	25	30	19	18	15
TRE	5	3	2	1	0.48	2	6
E₂O₃							

Appendix 4 continue.

Rock name	Magnesio-carbonatite					
Sample ID	KGKDD00202	KGKDD00203	KGKDD00207	KGKDD00216	KGKDD00217	KGKDD00218
(wt.%)						
SiO₂	1.73	12.34	1.71	7.01	3.46	7.59
TiO₂	0.02	0.12	0.01	0.01	0.01	0.06
Al₂O₃	0.03	2.99	b.d	b.d	0.06	0.72
Fe₂O₃	14.3	7.16	8.01	4.53	7.15	7.42
MnO	4.6	1.86	2.82	1.47	1.68	1.75
MgO	13.62	18.38	15.63	9.92	12.79	11.91
CaO	25.64	20.48	27.6	14.43	19.81	19.02
Na₂O	0.02	0.02	b.d	b.d	b.d	b.d
K₂O	b.d	1.58	b.d	b.d	b.d	0.16
P₂O₅	5.54	0.76	0.8	2.47	2.32	1.51
SrO	1.71	1.69	1.07	2.27	2.7	2.72
BaO	1.29	0.07	1.19	0.1	1.55	1.06
LOI	28.5	29.5	37.2	22.6	29.2	29.3
ppm						
La	5999	857	14144	10521	6417	7744
Ce	10083	1354	17007	10746	8345	10230
Pr	1044	115	1571	890	940	1135
Nd	3329	352	4646	2345	2908	3396
Sm	200	26	281	108	162	190
Eu	34	5	47	18	26	31
Gd	121	14	156	83	104	112
Tb	7	1	7	3	4	4
Dy	22	3	17	7	7	8
Y	49	9	33	13	15	14
Ho	2.3	0.4	1.8	0.7	0.8	0.8
Er	4.7	1	4.4	1.7	2.8	2.6

Tm	0.3	0.1	0.2	0.1	0.1	0.1
Yb	1.6	0.6	1.1	0.3	0.5	0.4
Lu	0.3	0.1	0.1	0.1	0.1	0.1
S	837	332	1607	14	1344	905
Sc	5	3	7	1	2	2
Ti	76	114	76	14	32	43
V	36	9	38	8	20	26
Ni	564	300	320	54	145	158
Co	7	4	3	b.d	2	2
Zn	2812	157	324	54	797	740
Ga	937	61	823	27	682	443
Rb	b.d	34	b.d	b.d	b.d	1
Zr	136	19	30	15	30	24
Nb	26	2147	240	24	57	94
Mo	52	4	98	5	24	12
Hf	1	26	1	b.d	b.d	1
Ta	b.d	9	b.d	b.d	b.d	b.d
Pb	b.d	b.d	b.d	b.d	b.d	b.d
Th	89	8	56	14	32	34
U	3	3	2	b.d	b.d	b.d
Total	99.66	97.55	100.20	67.30	82.92	85.74
(La/Y	2569	902	8565	21073	8310	14227
b)_N						
Y/Ho	21	20	19	18	19	17
TREE	2	0	4	3	2	3
₂O₃						

Appendix 4 continue.

Rock name	Magnesio-carbonatite					
Sample ID	KGKDD00219	KGKDD00222	KGKDD00301	KGKDD00305	KGKDD00306	KGKDD00307
(wt.%)						
SiO₂	16.2	2.88	9.13	12.22	1.02	13.06
TiO₂	0.24	0.01	0.07	0.26	0.01	0.06
Al₂O₃	0.87	b.d	1.9	3.96	b.d	0.58
Fe₂O₃	7.58	9.31	15.2	13.35	11.45	7.46
MnO	1.76	2.2	2.72	3.69	4.04	2.4
MgO	13.79	16.93	11.43	13.18	17.44	14.59
CaO	18.35	21.93	23.5	23.4	24.57	23.99
Na₂O	b.d	b.d	b.d	b.d	b.d	b.d
K₂O	0.34	b.d	1.12	0.86	b.d	0.43
P₂O₅	1.05	2.85	5.78	1.12	1.85	1
SrO	3.8	1.09	1.53	6.91	0.91	1.69
BaO	0.79	1.5	0.62	1.16	0.85	0.29
LOI	29.5	32.3	26.9	13.7	36.7	33.8
ppm						
La	11156	33706	2720	9521	6554	2937
Ce	12883	42514	5650	13491	11285	5802
Pr	1260	4320	749	1341	1315	707
Nd	3390	12631	2693	3634	4163	2543
Sm	184	751	223	169	229	201
Eu	31	130	41	29	36	39
Gd	116	426	101	103	106	103
Tb	4	20	5	5	5	7
Dy	8	51	14	12	11	19
Y	15	90	30	24	18	40
Ho	0.9	5.1	1.6	1.3	1.1	1.8
Er	2.6	11.1	4	3.1	2.7	3.8

Tm	0.1	0.5	0.3	0.1	0.1	0.3
Yb	0.4	2	1.7	0.8	0.5	1.9
Lu	0.1	0.2	0.2	0.1	0.1	0.2
S	1004	1710	639	776	633	527
Sc	6	8	7	5	6	9
Ti	114	71	109	155	78	100
V	55	48	25	29	44	37
Ni	228	400	645	410	515	333
Co	4	4	9	4	4	3
Zn	220	502	1464	814	986	611
Ga	451	1154	462	625	547	226
Rb	2	b.d	8	4	1	4
Zr	28	113	243	139	31	250
Nb	562	10	322	403	3	204
Mo	28	36	117	13	144	20
Hf	13	19	15	47	b.d	16
Ta	4	7	5	17	b.d	6
Pb	b.d	b.d	9	b.d	b.d	b.d
Th	29	18	40	49	45	123
U	2	4	19	12	3	5
Total	97.45	101.87	101.51	97.00	101.51	100.85
(La/Y	17596	11655	1077	8082	9069	1074
b)_N						
Y/Ho	18	18	18	19	17	21
TREE	3	11	1	3	3	1
₂O₃						

Appendix 4 continue.

Rock name	Magnesio-carbonatite					
Sample ID	KGKDD 00308	KGKDD 00310	KGKDD 00313	KGKDD0 0315	KGKD0 0318	KA2010
(wt. %)						
SiO₂	6.22	2.69	19.61	2.60	2.50	3.11
TiO₂	0.05	0.01	1.19	0.01	0.01	0.01
Al₂O₃	0.80	0.17	2.55	0.14	0.21	0.28
Fe₂O₃	8.41	11.03	14.65	13.45	9.45	11.57
MnO	2.80	3.80	2.91	3.79	2.85	3.19
MgO	15.72	14.44	10.54	13.74	15.87	12.38
CaO	22.74	25.64	18.03	24.64	25.03	22.01
Na₂O	0.07	b.d	b.d	b.d	b.d	0.02
K₂O	0.22	0.13	1.52	0.15	b.d	0.12
P₂O₅	2.06	1.49	3.19	3.57	0.50	3.02
SrO	0.89	3.61	1.21	2.16	5.26	4.26
BaO	2.34	0.65	0.53	0.19	0.40	0.81
LOI	32.20	35.10	24.40	34.10	38.00	32.27
ppm						
La	14428	6948	1669	2154	6048	12672
Ce	25219	11118	3306	3414	7897	18704
Pr	2903	1229	378	349	781	1804
Nd	9332	4041	1282	939	2172	5643
Sm	512	237	91	55	108	439
Eu	82	37	15	9	18	85
Gd	251	118	39	28	63	195
Tb	11	5	2	1	3	15
Dy	23	11	4	4	9	47
Y	33	18	11	11	20	101
Ho	2	1	1	1	1	5
Er	6	3	1	1	2	7

Tm	0.2	0.1	0.1	0.1	0.1	1
Yb	1	1	1	1	1	3
Lu	0.1	0.1	0.01	0.1	0.1	0.4
S	3929	1231	237	4301	2100	b.d
Sc	6	3	8	4	3	10
Ti	101	71	785	72	62	127
V	42	30	53	15	17	61
Ni	381	411	720	556	316	608
Co	10	4	13	13	5	6
Zn	8705	1145	401	2736	1217	2911
Ga	1759	404	378	115	214	102
Rb	2	1	11	1	b.d	2
Zr	105	39	238	61	179	175
Nb	204	121	859	65	103	152
Mo	311	114	246	28	10	40
Hf	5	1	54	1	b.d	3
Ta	2	b.d	19	b.d	b.d	b.d
Pb	b.d	b.d	b.d	b.d	b.d	40
Th	120	42	11	11	18	315
U	8	1	9	1	b.d	3
Total	101.4	101.5	101.4	100	102.2	97.5
(La/Yb)_N	11061	8546	1921	1829	6498	2825
Y/Ho	16	17	22	22	18	22
TREE₂O₃	6	3	1	1	2	5

Appendix 4 continue.

Rock name	Magnesio-carbonatite		Ferruginous calcio-carbonatite			
Sample ID	KA2209	KA2325	KGKDD0 0303	KGKDD0 0320	KA2326	KA2207
(wt. %)						
SiO₂	15.92	4.19	16.43	17.59	6.96	16.5
TiO₂	2.79	0.03	0.43	0.02	0.27	0.45
Al₂O₃	2.23	0.42	3.16	0.92	1.45	4.82
Fe₂O₃	19.98	9.68	16.54	7.85	15.1	15.04
MnO	1.76	2.49	2.4	1.47	2.67	2.18
MgO	14.02	12.76	3.65	0.75	0.94	1.19
CaO	20.9	25.3	27.17	16.16	36.96	31.21
Na₂O	1.54	b.d	b.d	b.d	b.d	b.d
K₂O	0.22	0.04	1.34	b.d	0.86	2.72
P₂O₅	6.68	3.78	6.79	8.63	1.39	1.46
SrO	0.83	0.73	0.94	3.16	0.48	0.52
BaO	0.27	2.77	0.7	2.29	2.16	0.46
LOI	11.7	31	19.2	31.24	29.6	20.35
ppm						
La	1723	23950	2142	8204	211	1260
Ce	3268	30684	3960	10683	334	2452
Pr	368	3331	452	1143	38	261
Nd	1211	10510	1397	3515	115	893
Sm	157	769	140	212	8	93
Eu	37	147	31	36	2	20
Gd	91	415	72	104	4	40
Tb	9	21	6	5	0.1	4
Dy	45	55	22	11	1	24
Y	155	113	57	21	2	109
Ho	7	5.8	2.7	1.1	0.1	4.1
Er	14.7	12.8	5.3	2.7	0.3	9.5

Tm	1.7	0.7	0.5	0.1	0.1	1.2
Yb	9.5	3.5	3.1	0.6	0.2	8.5
Lu	1.3	0.2	0.5	0.1	0.1	1.2
S	b.d	3656	489	922	161	b.d
Sc	28	13	13	2	b.d	20
Ti	9755	90	382	20	18	4093
V	233	55	62	8	5	89
Ni	1636	417	686	99	47	838
Co	42	6	11	1	0	19
Zn	447	391	840	156	7	852
Ga	36	2164	443	659	94	39
Rb	38	1	9	b.d	1	30
Zr	816	58	872	165	1	594
Nb	697	14	795	36	9	1153
Mo	2	22	84	6	1	37
Hf	32	1	171	1	b.d	12
Ta	66	b.d	59	b.d	b.d	19
Pb	15	b.d	b.d	b.d	b.d	5
Th	95	370	81	51	16	34
U	14	10	24	1	1	5
Total	100.9	100.9	100	99.6	98.9	98.1
(La/Yb)_N	123	4634	467	9020	685	101
Y/Ho	22	19	21	19	26	27
TREE₂O₃	1	8	1	3	0	1

Appendix 4 continue.

Rock name	Ferruginous calcio-carbonatite	Ferro-carbonatite				
Sample ID	KA2203b	KGKDD00108	KGKDD00109	KGKDD00127	KGKDD00129	KGKDD00130
(wt.%)						
SiO₂	6.29	2.37	3.35	1.72	2.9	6.51
TiO₂	0.05	b.d	0.01	0.01	b.d	0.04
Al₂O₃	0.26	b.d	b.d	b.d	b.d	1.2
Fe₂O₃	17.39	20.5	32.71	30.43	38.17	24.1
MnO	4.08	5.62	7.61	9.38	10.08	6.84
MgO	5.65	13.91	10.44	10.38	8.97	12.31
CaO	31.92	19.86	13.05	15.46	11.81	17.48
Na₂O	b.d	b.d	b.d	b.d	b.d	b.d
K₂O	0.11	b.d	b.d	b.d	b.d	b.d
P₂O₅	4.31	0.62	0.77	2.92	2.49	1.93
SrO	2.00	4.91	4.15	0.83	0.8	0.86
BaO	0.74	0.88	1.46	0.8	1.23	1.34
LOI	23.04	31.4	25.27	24.6	21.1	25.97
ppm						
La	6312	4515	6061	9883	6569	4423
Ce	11036	6665	9160	15780	12896	8690
Pr	1130	647	943	1726	1575	1049
Nd	3730	2068	2972	5539	5630	3579
Sm	257	128	209	338	392	248
Eu	43	22	35	53	60	40
Gd	82	79	140	191	171	131
Tb	5	3	6	9	7	5
Dy	15	11	13	20	14	11

Y	37	36	26	38	22	20
Ho	1.7	1.4	1.4	2	1.3	1.1
Er	3.2	2.9	3.9	5.4	3.9	3.6
Tm	0.3	0.2	0.1	0.2	0.1	0.1
Yb	2	1	0.7	1	0.8	0.8
Lu	0.3	0.1	0.1	0.2	0.1	0.1
S	b.d	b.d	610	b.d	b.d	45
Sc	21	5	3	3	2	4
Ti	360	48	34	56	38	77
V	38	23	23	16	19	36
Ni	868	708	941	1298	1690	1173
Co	12	4	6	10	11	11
Zn	1006	1414	482	1320	2055	1988
Ga	41	413	596	500	732	817
Rb	2	b.d	b.d	b.d	b.d	b.d
Zr	144	203	25	88	71	167
Nb	121	12	66	14	10	307
Mo	180	249	230	293	777	589
Hf	3	b.d	1	1	1	37
Ta	1	b.d	b.d	b.d	b.d	13
Pb	28	b.d	b.d	b.d	b.d	b.d
Th	45	56	60	82	77	45
U	7	1	1	4	5	9
Total	98.4	101.8	101.1	100.3	100.8	100.9
(La/Yb)_N	2129	2973	6051	6789	5441	3962
Y/Ho	21	26	19	18	17	18
TREE₂	3	2	2	4	3	2
O₃						

Appendix 4 continue.

Rock name	Ferro-carbonatite		Beforsite	Basalt
Sample ID	KGKDD00134	KGKDD00304	KA2303	JB-2
(wt. %)				
SiO₂	1.19	3.89	11.95	54.48
TiO₂	0.01	0.01	0.93	1.14
Al₂O₃	b.d	b.d	2.63	16.46
Fe₂O₃	18.78	25.57	10.69	13.62
MnO	5.01	6.95	0.58	0.22
MgO	13.12	10.61	16.37	3.13
CaO	19.39	19.09	35.3	9.5
Na₂O	b.d	0.02	2.02	2.74
K₂O	b.d	0.03	b.d	0.38
P₂O₅	2.38	4.91	8.72	0.1
SrO	6.92	1.6	0.35	0.02
BaO	0.79	0.86	0.05	0.03
LOI	28.27	24.6	11.8	0.02
ppm				
La	9059	3517	690	2
Ce	14441	6388	1350	6
Pr	1574	803	149	1
Nd	5166	2647	568	6
Sm	318	188	101	2
Eu	47	35	28	1
Gd	159	101	76	3
Tb	6	6	8	1
Dy	13	18	40	4
Y	25	31	58	18
Ho	1.3	1.7	6.4	0.8
Er	4.2	3.1	14.5	2.2

Tm	0.2	0.2	1.6	0.3
Yb	1	0.9	8.8	2.2
Lu	0.2	0.1	0.9	0.4
S	253	1	1517	19
Sc	2	4	8	53
Ti	41	58	125	2341
V	15	26	39	456
Ni	497	1056	836	678
Co	4	13	13	36
Zn	1450	2915	3988	101
Ga	383	517	922	25
Rb	b.d	b.d	1	7
Zr	79	127	142	53
Nb	100	29	87	2
Mo	81	202	13	2
Hf	1	2	1	1
Ta	1	1	b.d	b.d
Pb	b.d	b.d	b.d	5
Th	51	83	71	b.d
U	1	6	4	b.d
Total	99.2	99.9	102.3	102.2
(La/Yb)_N	6109	2802	53	1
Y/Ho	19	18	24	23
TREE₂O₃	4	2	0.4	b.d

Appendix A5 Major, minor and trace element compositions of carbonatite rocks in Tundulu

Rock name	Calcio-carbonatite					
Sample ID	TU2311	TU2317	TU2318	TU2210	TU2012	TU2013
wt. %						
SiO₂	1.36	1.12	1.03	4.48	1.78	0.94
TiO₂	0.03	0.03	0.01	0.16	0.01	0.02
Al₂O₃	b.d	b.d	b.d	0.72	b.d	b.d
Fe₂O₃	1.24	0.57	0.9	12.25	1.97	3.28
MnO.	0.28	0.28	0.35	2.24	0.94	0.85
MgO.	0.16	0.18	0.16	0.63	0.48	1.21
CaO.	52.98	53.93	53.38	42.77	51.51	50.15
Na₂O	b.d	b.d	b.d	b.d	b.d	b.d
K₂O	0.02	b.d	b.d	0.48	b.d	0.09
P₂O₅	1.88	0.46	1.03	1.52	0.58	0.13
SrO	1.49	1.69	1.11	0.4	7.62	2.12
BaO	0.2	0.14	0.15	2.42	1.0	0.47
LOI	37.46	40.86	40.06	29.46	40.1	43.56
ppm						
La	434	391.68	448	2601	458	1023
Ce	721	608.75	682	4594	819	1847
Pr	60	53.22	59	448	73	173
Nd	184	173.99	187	1354	243	600
Sm	27	25	27	120	32	72
Eu	8.8	8	9	24	9	17
Gd	26	23	27	48	21	38
Tb	4	3	4	4	3	4
Dy	24	17	23	15	14	15
Y	125	91	121	77	87	60
Ho	5	3	5	2	3	2
Er	12	8	11	6	7	5
Tm	2	1	2	1	1	1
Yb	9	7	9	6	6	5
Lu	1	1	1	1	1	1
S	547	191	336	b.d	b.d	b.d
Sc	1	1	1	4	2	1
Ti	223	177	168	1348	84	169
V	49	11	12	81	14	16

Ni	117	32	49	640	99	166
Co	15	0.5	0.6	15	1	2
Zn	36	29	29	258	59	72
Ga	156	158	136	132	27	11
Rb	1	b.d	b.d	11	1	2
Zr	47	5	19	18	5	1
Nb	20	5	6	297	8	8
Mo	9	3	5	35	5	8
Hf	9	9	7	b.d	b.d	b.d
Ta	18	17	11	b.d	b.d	b.d
Pb	22	9	29	53	23	25
Th	9	2	6	132	26	9
U	1	1	1	12	2	1
Total	97	99	98	98	100	100
(La/Yb)_N	33	40	34	289	50	150
Y/Ho	26	27	27	32	33	27
TREE₂O	0.2	0.2	0.2	1	0.2	0.5

Appendix 5 continue.

Rock name	Calcio-carbonatite	Magnesio-calcio-carbonatite				
Sample ID	TU2215	TU2303	TU2304	TU2316	TU23152	TU2211
wt. %						
SiO₂	1.74	9.98	0.63	4.06	0.83	2.15
TiO₂	0.34	2.01	0.02	0.06	0.08	0.02
Al₂O₃	0.3	2.52	b.d	b.d	b.d	b.d
Fe₂O₃	2.51	11.16	17.23	13.07	15.58	13.4
MnO.	0.9	2.02	2.75	4.02	3.77	3.62
MgO.	0.16	9.92	9.39	6.73	8.08	10.6
CaO.	51.94	25.26	30.98	30.58	31.92	27.78
Na₂O	b.d	b.d	b.d	b.d	b.d	0.01
K₂O	0.31	1.38	b.d	0.08	b.d	b.d
P₂O₅	0.63	0.27	0.4	1.5	0.03	0.02
SrO	0.14	1.58	2.11	8.47	1.77	3.11
BaO	0.01	1.25	0.5	1.91	2.49	1.11
LOI	39.01	31.5	34.87	31.47	33.47	35.45
ppm						
La	1328	6834	2677	11461	4345	6989
Ce	3046	8187	4425	11144	4598	7408
Pr	47	791	537	877	443	501
Nd	1409	2307	1926	1944	1304	1139
Sm	209	190	201	99	103	74
Eu	52	41	45	21	21	15
Gd	115	117	109	78	65	39
Tb	10	8	7	5	6	2
Dy	35	27	21	21	28	7
Y	159	89	54	84	117	35
Ho	5	4	2	4	5	1
Er	9	9	5	8	11	2
Tm	1	1	0.5	1	1	0.3
Yb	5	4	2	4	5	2
Lu	1	1	0.2	0.4	0.5	0.2
S	b.d	1628	466	3004	1095	b.d
Sc	2	4	5	3	3	6
Ti	2583	1385	97	92	62	355
V	16	108	52	39	31	85
Ni	106	482	691	417	271	845
Co	1	7	4	1	1	5
Zn	107	158	94	450	434	2960

Ga	2	981	248	1003	760	62
Rb	6	16	b.d	1	b.d	b.d
Zr	7	77	3	12	14	3
Nb	77	1650	563	101	67	3600
Mo	11	84	2	22	35	74
Hf	b.d	24	20	25	17	b.d
Ta	1	45	37	49	30	b.d
Pb	15	127	72	49	77	55
Th	44	5	2	4	3	116
U	6	4	5	3	3	6
Total	98	100	99	100	99	98
(La/Yb)_N	175	1157	844	1782	551	3035
Y/Ho	31	24	22	24	24	35
TREE₂O₃	1	2	1	3	1	2

Appendix 5 continue.

Rock name	Magnesio-calcio-carbonatite				Magnesio-calcio-carbonatite	ferruginous calcio-carbonatite
Sample ID	TU2204	TU2310	TU2315	TU2308	TU23156	TU2001a
wt. %						
SiO₂	2.09	4.24	12.6	12.36	5.83	19.
TiO₂	0.01	0.03	1.6	3.24	0.01	0.1
Al₂O₃	b.d	b.d	2.84	3.15	b.d	2.81
Fe₂O₃	12.43	18.74	30.27	13.56	12.12	11.54
MnO.	4.04	5.96	2.94	2.4	3.75	2.09
MgO.	11.56	0.71	4.5	0.6	4.06	4.1
CaO.	27.3	32.64	23.81	31.02	32.76	28.07
Na₂O	0.08	0.01	b.d	b.d	b.d	0.05
K₂O	0.05	b.d	2.05	2.52	b.d	2.1
P₂O₅	0.01	0.18	0.1	0.73	5.65	9.02
SrO	2.76	0.49	0.19	0.31	7.89	0.27
BaO	1.15	11.76	0.96	0.95	1.51	0.09
LOI	36.29	24.58	16.48	27.37	26.23	19.08
ppm						
La	4191	595	2257	10013	7350	1541
Ce	5118	912	2592	12399	8207	2993
Pr	394	80	186	1090	765	322
Nd	1065	232	453	2940	2196	1009
Sm	85	29	31	228	169	164
Eu	18	10	6	57	36	51
Gd	44	38	23	152	104	134
Tb	3	2	1	11	9	20
Dy	11	10	4	37	46	120
Y	49	48	14	108	195	642
Ho	1	2	1	5	8	21
Er	3	4	1	10	19	46
Tm	0.4	1	0.1	1	2	4.7
Yb	2	3	1	4	9	23
Lu	0.3	0.5	0.1	0.3	0.9	2.6
S	b.d	35899	1102	986	2543	b.d
Sc	3	7	3	6	6	6
Ti	621	150	1228	1339	119	1003
V	29	72	870	64	60	129
Ni	556	753	1988	416	479	633
Co	1	13	19	7	3	6

Zn	1223	350	743	351	791	309
Ga	50	10324	693	1015	1141	14
Rb	2	1	101	20	b.d	29
Zr	5	6	27	13	23	142
Nb	336	34	1057	1487	111	360
Mo	198	91	135	274	61	21
Hf	b.d	33	11	43	37	1
Ta	b.d	65	21	74	66	1
Pb	57	36	15	130	251	41
Th	78	3	5	5	9	147
U	2	7	3	6	6	11
Total	99	99	99	99	101	99
(La/Yb)_N	1344	123	1651	1628	539	45
Y/Ho	33	30	25	22	24	31
TREE₂O₃	1	0	1	3	2	1

Appendix 5 continue.

Rock name	ferruginous calcio-carbonatite					Syenite	
Sample ID	TU2001b	TU2319	TU2212	TU2009	TU2214	TU2006	TU2007
wt. %							
SiO₂	12.41	20.68	7.77	16.84	40.91	60.42	43.77
TiO₂	0.01	1.69	0.03	1.78	1.3	0.18	0.62
Al₂O₃	0.16	17.09	0.21	4.64	18.13	14.66	20.81
Fe₂O₃	11.03	5.18	12.32	15.39	5.67	5.44	3.28
MnO.	1.35	0.15	2.32	2.14	0.19	0.2	0.09
MgO.	3.04	1.65	0.61	4.92	1.61	0.74	0.71
CaO.	31.69	3.55	38.0	23.57	6.37	1.36	3.15
Na₂O	0.1	7.43	0.14	0.03	6.95	2.13	8.91
K₂O	0.19	5.17	0.17	3.81	7.83	12.01	7.97
P₂O₅	13.46	1.41	11.03	1.8	0.52	0.47	0.14
SrO	3.86	0.21	0.6	0.26	0.27	0.07	0.07
BaO	0.77	0.29	3.23	1.74	0.36	0.15	0.15
LOI	15.2	34.97	19.71	23.3	8.86	1.5	10.8
ppm							
La	3045	109	2008	505	95	97	39
Ce	5659	192	3437	1204	178	145	64
Pr	611	23	334	144	18	14	6
Nd	2114	85	1174	598	66	49	23
Sm	299	13	205	106	10	7	4
Eu	88	4	65	28	3	2	1
Gd	239	10	187	66	7	5	3
Tb	35	1	30	8	1	1	0.4
Dy	213	6	161	46	5	4	2
Y	1154	27	1036	259	26	53	15
Ho	37	1	27	8	1	1	0
Er	81	3	54	18	2	2	1
Tm	8	b.d	5.3	2	0	0.3	0.1
Yb	38	2	24	11	2	2	1
Lu	4	0.3	2.6	1.4	0.2	0.3	0.1
S	b.d	17	b.d	b.d	b.d	b.d	b.d
Sc	5	2	7	9	2	9	1
Ti	122	1233	304	15647	11799	1601	5781
V	82	44	107	169	149	215	91
Ni	574	278	615	885	419	350	226
Co	9	7	2	9	5	2	3
Zn	573	61	214	534	140	80	60
Ga	40	126	146	14	45	37	62

Rb	3	60	3	58	257	350	207
Zr	168	321	160	245	327	525	231
Nb	833	146	514	714	220	4865	99
Mo	4	3	23	13	5	2	5
Hf	2	4	1	3	6	8	3
Ta	b.d	7	b.d	12	6	1	2
Pb	44	13	17	24	2	7	1
Th	333	5	152	57	4	6	2
U	15	2	6	14	1	1	1
Total	95	100	98	100	101	100	101
(La/Yb)_N	54	33	57	30	36	29	27
Y/Ho	31	24	39	34	29	68	35
TREE₂O₃	2	0	1	0.4	0.0	0.0	0.0

Appendix A6 Major, minor and trace element compositions of carbonatite rocks in Nkalonje

Rock name	Calcio-carbonatite						
Sample I D	NK2202	NK 2203	NK2204	NK2311	NK2319	NK2326	NK2327
wt. %							
SiO ₂	0.95	5.74	0.64	1.37	3.45	1.88	2.65
TiO ₂	0.01	0.18	0.01	0.01	0.05	0.03	0.01
Al ₂ O ₃	b.d	b.d	b.d	b.d	0.26	0.08	0.20
Fe ₂ O ₃	3.51	9.21	2.26	2.50	4.03	2.44	2.37
MnO.	2.78	5.03	2.14	1.46	2.37	2.27	1.74
MgO.	0.54	0.30	0.25	0.48	0.32	0.45	0.39
CaO.	51.50	43.57	57.50	51.64	48.28	49.01	52.44
Na ₂ O	b.d	b.d	b.d	b.d	b.d	b.d	0.03
K ₂ O	0.02	0.10	b.d	b.d	0.28	b.d	0.20
P ₂ O ₅	0.34	0.06	0.10	0.04	0.06	0.06	0.89
SrO	5.04	4.18	3.87	3.22	2.89	2.72	3.46
BaO	0.31	0.36	0.15	0.10	0.16	0.35	0.13
LOI	30.90	26.33	31.81	39.60	37.56	39.40	33.50
ppm							
La	19510	20312	6836	448	872	886	173
Ce	25863	33814	10153	724	1366	1263	285
Pr	2363	3225	238	104	120	111	28
Nd	1840	9643	680	325	559	304	132
Sm	184	239	74	39	53	44	19
Eu	43	56	20	10	12	10	5
Gd	138	155	60	28	35	27	14
Tb	11	12	6	3	4	3	2
Dy	52	53	36	20	23	14	10
Y	226	288	209	108	147	64	52
Ho	9	9	7	4	5	3	2
Er	25	24	21	11	15	8	6
Tm	3	3	3	2	2	1	1
Yb	21	19	20	11	18	5	5
Lu	3	3	3	2	3	1	1
S	589	91	103	2854	253	916	672
Sc	b.d	b.d	1	1	2	b.d	b.d
Ti	b.d	b.d	b.d	103	158	65	45
V	b.d	b.d	11	11	27	3	1

Ni	8	6	87	223	117	100	46
Co	b.d	b.d	b.d	11	5	3	1
Zn	10	28	84	33	52	34	10
Ga	17	5	161	5	8	9	2
Rb	b.d	b.d	1	b.d	5	0	1
Zr	b.d	b.d	18	20	19	12	1
Nb	2	1	2	4	5	2	4
Mo	b.d	b.d	4	25	7	11	1
Hf	b.d	b.d	b.d	b.d	b.d	b.d	b.d
Ta	b.d	b.d	b.d	b.d	b.d	b.d	b.d
Pb	2	0.59	24	b.d	b.d	b.d	b.d
Th	2	2	32	23	51	12	10
U	b.d	b.d	3	5	6	1	1
SUM	101	102	101	101	100	99	98
(La/Yb)_N	634	710	228	28	33	120	22
Y/Ho	25	33	29	27	31	24	25
TREE₂O₃	6	8	2	0.2	0.4	0.3	0.1

Appendix 6 continue.

	Agglomerate breccia				Syenite		
SampleI	Nk220	NK2315	NK232	NK220	NK2327	NK233	NK233
D	7	3	5	6	B	4	0
wt. %							
SiO₂	38.39	8.68	8.88	44.58	44.36	47.51	40.29
TiO₂	0.04	0.02	0.01	2.67	0.98	1.12	2.52
Al₂O₃	1.68	0.04	0.23	19.09	19.53	18.28	17.23
Fe₂O₃	1.20	0.78	0.72	8.73	3.91	4.87	6.73
MnO.	0.09	0.00	0.00	0.25	0.18	0.24	0.18
MgO.	0.14	0.07	0.08	1.93	0.76	0.80	2.22
CaO.	30.31	51.51	43.25	4.44	2.98	2.43	4.13
Na₂O	0.01	b.d	b.d	7.68	10.01	8.70	7.30
K₂O	0.18	b.d	0.02	6.19	6.31	7.30	6.31
P₂O₅	4.46	0.22	0.20	1.78	0.30	0.22	1.51
SrO	0.27	0.30	0.17	0.33	0.25	0.23	0.20
BaO	0.19	b.d	b.d	0.32	0.24	0.30	0.21
LOI	4.41	0.80	6.30	0.42	9.30	7.43	9.73
ppm							
La	6048	873	201	212	1016	914	368
Ce	10644	1437	312	442	1124	1430	431
Pr	286	146	30	41	183	138	75
Nd	1034	439	125	141	601	687	288
Sm	242	64	27	21	88	126	44
Eu	91	18	8	6	25	40	12
Gd	256	46	25	14	63	125	30
Tb	42	7	4	2	8	19	4
Dy	226	38	23	9	44	111	20
Y	982	212	65	43	193	325	91
Ho	34	9	4	2	8	19	3
Er	66	22	8	4	21	44	8
Tm	5	4	1	1	3	5	1
Yb	20	21	5	3	20	27	6
Lu	2	4	1	0.1	3	4	1
S	25	547	31	830	1891	94	1920
Sc	1	1	b.d	31	10	1	7
Ti	b.d	223	22	b.d	5339	153	6125
V	3	49	3	530	322	4	242
Ni	7	117	15	3828	1587	47	1398
Co	b.d	15	1	72	23	4	36
Zn	2	36	4	868	333	15	201

Ga	22	156	b.d	2068	201	1	85
Rb	1	1	b.d	771	693	b.d	325
Zr	58	47	90	4302	2909	396	1454
Nb	1	20	4	2015	1126	7	517
Mo	1	9	3	50	43	6	7
Hf	1	9	b.d	66	289	b.d	80
Ta	b.d	18	b.d	109	96	b.d	27
Pb	3	22	b.d	47	b.d	b.d	b.d
Th	309	9	79	154	90	375	50
U	1	1	3	33	17	8	13
SUM	83	63	60	100	101	100	100
(La/Yb)_N	204	29	30	46	35	23	41
Y/Ho	29	24	18	27	24	17	28
TREE₂O₃	2	0.4	0.1	0.1	0.4	0.5	0.2

Appendix A7 Carbon and Oxygen Isotope composition for Kangankunde, Tundulu and Nkalonje carbonatites.

Study site	Carbonate	$\delta^{13}\text{C}_{\text{VPDB}} \text{‰}$	$\delta^{18}\text{O}_{\text{VSMOW}} \text{‰}$	Comment
Kangankunde	Ankerite	-3.52	14.79	This study
Kangankunde	Ankerite	-0.74	16.21	This study
Kangankunde	Calcite	-4	26.73	This study
Kangankunde	Strontianite	-4.27	12.03	This study
Kangankunde	Dolomite Ap-bearing	-6.02	7.7	Broom-Fendley 2017
Kangankunde	Dolomite Ap-bearing	-3.28	8.66	Broom-Fendley 2017
Kangankunde	Ankerite	-1.96	7.69	Broom-Fendley 2017
Kangankunde	Ankerite	-2.07	8.77	Broom-Fendley 2017
Kangankunde	Ankerite	-0.98	23.43	Broom-Fendley 2017
Kangankunde	Ankerite	-1.16	21.44	Broom-Fendley 2017
Kangankunde	Ankerite	-3.58	11.9	Broom-Fendley 2017
Kangankunde	Ankerite	-0.98	23.67	Broom-Fendley 2017
Kangankunde	Calcite	-2.03	17.97	Broom-Fendley 2017
Kangankunde	Calcite	-1.74	20.65	Broom-Fendley 2017
Kangankunde	Calcite	-7.73	21.39	Broom-Fendley 2017
Kangankunde	Strontianite	-3.45	4.4	Broom-Fendley 2017
Kangankunde	Strontianite	-3.42	4.56	Broom-Fendley 2017
Kangankunde	Quartz		9.7	Broom-Fendley 2017
Kangankunde	Quartz		8.8	Broom-Fendley 2017
Tundulu	Quartz		13.9	This study
Tundulu	Ankerite	-2.92	7.75	This study
Tundulu	Calcite	-3.24	6.15	This study
Tundulu	Calcite	-3.74	6.39	This study
Tundulu	Strontianite	-3.6	3.59	This study
Nkalonje	Calcite	-3.11	8.61	This study
Nkalonje	Calcite	-3.67	1.95	This study
Nkalonje	Calcite	-3.52	4.56	This study