Research Article

Geochemistry of the Neoarchaean Volcanic Rocks of the Kilimafedha Greenstone Belt, Northeastern Tanzania

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The Neoarchaean volcanic rocks of the Kilimafedha greenstone belt consist of three petrological types that are closely associated in space and time: the predominant intermediate volcanic rocks with intermediate calc-alkaline to tholeiitic affinities, the volumetrically minor tholeiitic basalts, and rhyolites. The tholeiitic basalts are characterized by slightly depleted LREE to nearly flat REE patterns with no Eu anomalies but have negative anomalies of Nb. The intermediate volcanic rocks exhibit very coherent, fractionated REE patterns, slightly negative to absent Eu anomalies, depletion in Nb, Ta, and Ti in multielement spidergrams, and enrichment of HFSE relative to MORB. Compared to the other two suites, the rhyolites are characterized by low concentrations of TiO_2 and overall low abundances of total REE, as well as large negative Ti, Sr, and Eu anomalies. The three suites have a ϵNd (2.7 Ga) values in the range of -0.51 to $+5.17$. The geochemical features of the tholeiitic basalts are interpreted in terms of derivation from higher degrees of partial melting of a peridotite mantle wedge that has been variably metasomatized by aqueous fluids derived from dehydration of the subducting slab. The rocks showing intermediate affinities are interpreted to have been formed as differentiates of a primary magma formed later by lower degrees of partial melting of a garnet free mantle wedge that was strongly metasomatized by both fluid and melt derived from the subducting oceanic slab. The rhyolites are best interpreted as having been formed by shallow level fractional crystallization of the intermediate volcanic rocks involving plagioclase and Ti-rich phases like ilmenite and magnetite as well as REE-rich phases like apatite, zircon, monazite, and allanite. The close spatial association of the three petrological types in the Kilimafedha greenstone belt is interpreted as reflecting their formation in an evolving late Archaean island arc.

1. Introduction

The Kilimafedha greenstone belt of northeast Tanzania is one of the six greenstone belts of the Tanzania Craton occurring in the northern part of the country in the area south and east of the Lake Victoria. Other greenstone belts include the Sukumaland, Shinyanga-Malita, Nzega, Musoma-Mara, and Iramba-Sekenke [1, Figure 1]. All of these greenstone belts are prospective for gold mineralization with several large-scale mines now in operation including the Bulyanhulu, Tulawaka, Geita, Buzwagi, North Mara, and Golden Pride (Figure 1). Because of their economic significance, the greenstone belts of the Tanzania Craton have recently been the focus of research on the processes that control gold mineralization (e.g., [2, 3]), lithostratigraphical relationships

(e.g., [4, 5]), geochemistry, and geochronology (e.g., [6–12]). These studies have helped us to better understand, among other things, the timing of and the processes responsible for the formation of the earliest continental crust in Tanzania as well as the ancient tectonic settings in which the greenstone belts formed.

Previous geological work in the Kilimafedha greenstone belt is limited to the geological mapping done by Macfarlane [14] and more recently to geochronological investigation by Wirth et al. [9] who reported zircon Pb-Pb ages from rhyolites and granitic intrusions in the area. In this paper, we present whole-rock major and trace element as well as the Nd-isotopic compositions for the volcanic rocks of the Kilimafedha greenstone belt around the Ikoma area with the aim of unraveling their petrogenesis and tectonic

FIGURE 1: Geological map of the northern part of the Tanzania Craton showing the greenstone belts in the area around Lake Victoria (modified after [13]). The inset frame indicates the area of study in Figure 2.

setting of eruption. The results of this study complement the information available from other greenstone belts of the Tanzania Craton on the processes that led to the growth of the continental crust during the late Archaean.

2. Geological Setting

The Tanzania Craton forms the central nucleus of Tanzania and extends northwards into southwestern Kenya and southeastern Uganda. The Craton is divided into two main lithological units: the Dodoman belt which is comprised of high-grade metamorphic rocks, granite, granitic gneisses, and migmatites of central Tanzania and the low-grade granite-greenstone terrane of northern Tanzania, southwestern Kenya, and southwestern Uganda [15]. The low-grade granite-greenstone terrane comprises mafic to felsic

volcanic rocks and metasedimentary rocks including shales, sandstones, siltstones, chert, and banded iron formation (BIF) which are in turn intruded by granites.

Robust geochronological data shows that the oldest greenstones in the Tanzania Craton are the mafic volcanic rocks of the Rwamagana area in the Sukumaland greenstone belt (Figure 1). These yielded a Sm-Nd isochron age of 2823 ± 44 Ma reported by Manya and Maboko [7]. The youngest volcanism in the greenstone belts of the Tanzania Craton is from the Musoma-Mara greenstone belt reported by Manya et al. [10] as indicated by a zircon U-Pb age of 2667 ± 8 Ma obtained from dacites collected near Tarime (Figure 1). A more thorough review of the geochronology of the greenstones and intruding granites of the Tanzania Craton can be found in Borg and Krogh [6] and Manya et al. [10].

The Kilimafedha greenstone belt forms an asymmetrical horseshoe-shaped exposure of metavolcanic and minor

metasedimentary rocks in the area east and southeast of Lake Victoria (Figure 2). Most of the greenstone exposures including the old Kilimafedha mining district lie within the Serengeti National park. The samples collected for this study, however, were sampled outside the National park boundary in the Ikoma area (Figure 2). According to Macfarlane [14], the greenstone sequences start with a poorly preserved mafic volcanic unit now converted into actinolite and hornblende schist (Figure 3) in the extreme southeastern and northern margins of the belt (within the Serengeti National Park boundary), and the rocks are thus metamorphosed into greenschist facies except for the hornblende schists that are proximal to granitic intrusions. This unit has locally been found to be pillowed suggesting extrusion of the lavas under water.

The mafic volcanic rocks are overlain by a more extensive and better preserved thick sequence of intermediate volcanic rocks with infrequent felsic volcanic rocks patched in the intermediate rocks (Figure 3). This sequence locally contains thin horizons of tuff and metasediments including chert, jaspilite, and quartzite. The felsic volcanic rocks were dated by Wirth et al. [9] who reported $^{207}\text{Pb}/^{206}\text{Pb}$ zircon ages of 2712 ± 5 Ma (MSWD = 0.35) and 2720 ± 5 Ma (MSWD = 1.9).

More fresh exposures of the greenstone sequence occur in the area near Fort Ikoma (Figure 2) close to the northern boundary of the greenstone belt. In this area, the most common rock types include amygdaloidal andesite with streams of vesicles filled up with quartz, epidote, and chlorite (Figure 4). Other less vesicular types have large phenocrysts of albite-oligoclase. Sediments intercalated with metavolcanics are largely metamorphosed ferruginous quartzite, siltstones, mudstones, and felsic tuffs.

The whole sequence has been deformed resulting into the development of a steeply dipping N to NW trending foliation. Folding is indicated by isoclinal contortions in the ferruginous quartzite [14]. Late orogenic granites outcrop along the eastern, northern, and southwestern margins of the greenstone belt. The granite-greenstone contact along the northern margin has been decorated with minor metagabbroic intrusions that have been correlated with the larger Nyamongo gabbros of the Musoma-Mara greenstone belt [16]. Neoproterozoic arenaceous to argillaceous sedimentary rocks of the Ikorongo Group [17] unconformably overlie all the Archaean rocks in the area.

3. Sampling and Analytical Methodology

Samples were obtained from surface outcrops, and sampling was dictated by the degree of accessibility, exposure, and freshness of the outcrops. Fifty volcanic rocks samples were collected in the field and were subsequently prepared for laboratory chemical analyses. All 50 samples were analyzed for major element compositions, but only 18 representative samples from distinguished suites were analyzed for trace element compositions (see Figure 2 for sample locations). For chemical analyses, the samples were pulverized in an agate mill at the Southern and Eastern Africa Mineral Centre (SEAMIC) Laboratories, Dar es Salaam. Samples were

first dried in an oven at 110°C , and 1 g of the powdered sample was mixed with 7 g of lithium metaborate and fused in a furnace at 1000°C for about 10 minutes to make glass beads. The glass beads were analyzed using an SRS 3000 Siemens X-ray Fluorescence Spectrometer at the same laboratories following procedures reported in Messo [18]. Loss on ignition (LOI) was determined by repeatedly heating the samples in a furnace at 1010°C and cooling until constant weight was achieved.

The samples were also analyzed for trace elements at the Activation Laboratories of Ancaster, Ontario, Canada. 0.25 g of each sample was mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The melt was immediately poured into a solution of 5% HNO_3 containing an internal In standard and thoroughly mixed for ~30 minutes to achieve complete dissolution. An aliquot of the sample solution was spiked with internal In and Rh standards to cover the entire mass range and diluted 6000 times prior to introduction into a Perkin Elmer SCIEX ELAN 6000 ICP-MS for trace elements analysis. Precision and accuracy as deduced from replicate analyses of the BIR-1 and W2 standards are 5–10%. The analytical reproducibility deduced from replicate analyses of the samples is better than 8% for most trace elements.

Nine samples were also analysed for Sm-Nd isotopic compositions as well as Sm and Nd concentrations using a Triton-MC Thermal Ionization Mass Spectrometer at the Activation Laboratories of Ontario, Canada. Aliquots of the powdered rock samples were spiked with a ^{149}Sm - ^{146}Nd mixed solution prior to decomposition using a mixture of HF, HNO_3 , and HClO_4 . The REEs were separated using conventional cation-exchange techniques. Sm and Nd were separated by extraction chromatography on HDEHP covered teflon powder. Total blanks are 0.1–0.2 ng for Sm and 0.1–0.5 ng for Nd and are negligible. The accuracy of the Sm and Nd analyses is $\pm 0.5\%$ corresponding to errors in the $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of $\pm 0.5\%$ (2σ). The $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are calculated relative to the value of 0.511860 for the La Jolla standard. During the period of analysis, the weighted average of 10 La Jolla Nd-standard runs yielded 0.511872 ± 15 (2σ) for $^{143}\text{Nd}/^{144}\text{Nd}$, using a $^{146}\text{Nd}/^{144}\text{Nd}$ value of 0.7219 for normalization.

4. Geochemistry

4.1. Alteration and Element Mobility. Alteration of metavolcanic rocks is a common phenomenon, in particular for Archaean greenstones, and is typically characterized by high loss on ignition (LOI) values and increased scatter of major and large ion lithophile elements. In this regard, the volcanic rocks, collected for this study, are variably affected by greenschist metamorphism, so it is expected that major and LILE are also affected by alteration. However, numerous studies have demonstrated that rare earth elements (REEs) and high field strength elements (HFSEs) remain relatively undisturbed at greenschist facies and even higher grades of metamorphism [19, 20]. So in this study major and LILE are used with great care, and emphasis is placed on the REE and HFSE.

FIGURE 2: Geological map of the Kilimafedha greenstone belt showing sample locations (modified after [14]).

4.2. Classification and Petrography. The volcanic rocks of the Kilimafedha greenstone belt represent a mafic, intermediate to felsic compositional continuum as indicated by their wide range of SiO_2 contents (48.48–76.02 wt%). Out of a total of 50 samples that were analyzed for major elements and as shown in Figure 4 and 7 samples are basaltic in

composition ($\text{SiO}_2 = 48.48\text{--}51.57\text{ wt\%}$), 40 samples show intermediate compositions ranging from basaltic andesites to basaltic trachyandesites, which are predominant; andesites to dacites ($\text{SiO}_2 = 52.51\text{--}66.80\text{ wt\%}$); only 3 samples are rhyolites ($\text{SiO}_2 = 75.52\text{--}76.02\text{ wt\%}$, values quoted on water free basis), revealing the sporadic nature of the more felsic

FIGURE 3: Diagrammatic representation of the stratigraphic sequence of Kilimafedha greenstone belt, not to scale (modified after [14]).

(a)

(b)

FIGURE 4: Outcrop photographs showing Ikoma foliated metabasalts with an appearance of a schist (a) and amygdaloidal andesite with vesicles filled in with secondary quartz (b).

rocks. The predominance of the basaltic trachyandesitic rocks and the nature of these rocks are unique to the Kilimafedha greenstone belt (Figure 5).

Using the Winchester and Floyd [22] classification scheme which is suitable for classifying metamorphosed rocks, of the 18 samples that were analyzed for both major and trace elements, four samples plot along the boundary between subalkaline basalt and andesite/basalt, eleven others plot in the fields of andesite/basalt and andesites, and three samples plot as rhyolites (Figure 6). The basalts to andesitic basalts exhibit tholeiitic affinity, the intermediate rocks intermediate geochemical characteristics between tholeiitic and calc-alkaline affinities, whereas the rhyolites are calc-alkaline. Accordingly, the rocks are henceforth subdivided into three suites: the tholeiitic basalts, the intermediate volcanic rocks, and the rhyolites.

The primary petrographic features of the tholeiitic basalts are strongly obliterated by alteration which has resulted in the formation of chlorite, epidote, and hornblende amphibole which appear to form after olivines and pyroxenes. The predominant intermediate rocks are often amygdaloidal, with streams of vesicles filled up with quartz, epidote, and chlorite. Other less vesicular types have large phenocrysts of albite-oligoclase. Most felsic rocks have

fine matrix of quartz and sericitized feldspars with sparse phenocrysts of quartz and altered feldspars. The presence of chlorite and epidote in the Kilimafedha volcanic rocks suggests that these rocks have mainly been metamorphosed into greenschist facies.

4.3. Major and Trace Element Geochemistry

4.3.1. Tholeiitic Basalts. Major and trace element composition of the tholeiitic basalts of the Kilimafedha greenstone belt are presented in Table 1. The rocks have SiO_2 compositions that are in the range of 48.48–51.57 wt%, $\text{TiO}_2 = 0.61$ –1.80 wt%, $\text{Fe}_2\text{O}_3 = 6.32$ –13.92 wt%, $\text{MgO} = 5.56$ –8.49 wt%, and Mg numbers, calculated as $100 \times \text{Mg}^{2+} / (\text{Mg}^{2+} + \text{Fe}_{\text{total}}^{2+})$, range from 47 to 73 (the major elements presented on a water free basis). Cr and Ni contents are 160–240 ppm and 90–190 ppm, respectively. La contents vary considerably (1.7–9.2 ppm), whereas Yb contents range from 1.7 to 3.1 ppm resulting in La/Yb ratios of 1.00–4.00 (Table 1). On major and trace element bivariate plots (Figure 7), Fe_2O_3 , MgO, CaO, and Ni correlate negatively with SiO_2 pointing to fractionation signature or cogenetic relationship. The tholeiitic basalts alone do not show any major trends most

FIGURE 5: TAS classification diagram of Le Maitre et al. [21] for the Kilimafedha volcanic rocks. Also shown in the diagram are fields for volcanic rocks from other greenstone belts of the Tanzania Craton: ISGB: Iramba—Sekenke greenstone belt, SGB: Sukumaland greenstone belt, SMMGB: Southern Musoma—Mara greenstone belt, and NMMGB: Northern Musoma—Mara greenstone belt. Numbers in the diagram indicate fields as follows: 1: basalt, 2: basaltic andesite, 3: andesite, 4: dacite, 5: rhyolite, 6: trachybasalt, 7: basaltic trachyandesite, 8: trachyandesite, and 9: trachydacite.

FIGURE 6: Classification of the Kilimafedha volcanic rocks using the Nb/Y-Zr/Ti diagram of Winchester and Floyd [22]. Symbols are filled triangles: tholeiitic basalts, open squares: intermediate volcanic rocks, and open cycles: rhyolites.

likely due to the small number of samples and their restricted range in SiO_2 content.

The rocks display slightly depleted LREE to nearly flat REE patterns (Figure 8(a)) that are characterized by $\text{La}/\text{Sm}_{\text{CN}}$ and $\text{La}/\text{Yb}_{\text{CN}}$ ratios of 0.8–0.9 and 0.72–1.06, respectively, except for sample MU 69 which is relatively enriched in LREE ($\text{La}/\text{Sm}_{\text{CN}} = 1.7$ and $\text{La}/\text{Yb}_{\text{CN}} = 2.89$) compared to the other three samples (where CN refers to chondrite normalized values). The $\text{La}/\text{Sm}_{\text{CN}}$ and $\text{La}/\text{Yb}_{\text{CN}}$ values of the three samples (MU 69 excluded) are slightly higher than those of NMORB

($\text{La}/\text{Sm}_{\text{CN}} = 0.6$, $\text{La}/\text{Yb}_{\text{CN}} = 0.59$; [23]) indicating relative enrichment of the LREE in the Kilimafedha tholeiites. The samples do not show any Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.90$ – 1.10). The samples were also plotted on primitive mantle spidergrams (Figure 9(a)), where they display enrichment in Rb, Ba, Th, K, and Pb relative to the more compatible elements with flatter multielement patterns characterized by negative Nb anomalies ($\text{Nb}/\text{La}_{\text{pm}} = 0.42$ – 0.64) and minor negative Ti anomalies (where pm refers to primitive mantle normalized values).

TABLE 1: Major (wt%) and trace (ppm) element composition for the Kilimafedha greenstone belt volcanic rocks.

	Tholeiitic basalts										Transitional intermediate volcanic rocks																	
	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU
	14	15	19	20	43	47.8	48.2	49.2	109	12	13	21	27	33	35	36	37	38	39	49	54	57	60	64	65	66	68	
SiO ₂	50.3	47.4	50.4	50.3	47.8	48.2	49.2	49.2	109	12	13	21	27	33	35	36	37	38	39	49	54	57	60	64	65	66	68	62.4
TiO ₂	1.36	0.92	0.60	0.66	1.73	1.75	0.62	0.62	1.53	55.2	52.9	52.8	65.3	60.6	53.7	55.1	54.3	54.1	53.5	53.7	53.5	54.1	54.9	56.0	54.9	55.3	62.4	0.84
Al ₂ O ₃	14.7	16.0	14.4	13.5	14.6	14.1	17.3	13.1	15.1	15.1	15.0	15.5	15.5	16.5	14.0	13.4	14.1	14.3	14.9	14.2	13.7	13.2	13.5	14.7	14.3	13.6	14.2	14.2
Fe ₂ O ₃	12.3	12.4	11.9	12.9	13.3	13.5	6.2	9.3	10.8	11.2	10.8	11.2	4.2	6.7	11.3	12.0	11.2	11.9	12.1	12.1	11.8	11.3	11.7	9.1	10.8	12.0	6.6	6.6
MnO	0.27	0.17	0.17	0.18	0.19	0.18	0.08	0.08	0.25	0.24	0.16	0.06	0.06	0.10	0.11	0.14	0.11	0.14	0.14	0.15	0.12	0.12	0.12	0.19	0.13	0.13	0.09	0.09
MgO	5.45	8.09	7.53	7.32	6.62	6.62	8.30	8.30	6.00	4.66	5.58	2.68	3.57	3.57	3.42	3.71	3.43	3.46	3.62	3.85	4.24	3.53	3.77	5.27	3.80	3.50	2.60	2.60
CaO	10.9	10.9	10.7	10.7	10.3	10.5	12.3	12.3	7.54	10.94	8.54	3.65	2.73	9.62	9.62	6.25	9.49	6.41	5.30	5.69	8.30	6.40	6.94	6.28	7.16	7.43	4.53	4.53
Na ₂ O	2.29	1.84	1.92	1.79	1.96	1.91	2.99	2.99	5.14	2.49	1.74	4.91	6.15	3.12	3.12	4.96	2.70	4.02	5.00	5.34	2.67	4.69	3.10	3.85	3.01	3.94	4.20	4.20
K ₂ O	0.52	0.17	0.15	0.11	0.03	0.10	0.81	0.81	0.79	0.27	1.45	0.83	0.31	1.44	1.44	1.09	1.43	1.88	1.77	1.34	2.09	1.44	2.75	0.37	2.20	0.73	1.50	1.50
P ₂ O ₅	0.04	0.01	0.01	0.01	0.19	0.09	0.01	0.01	0.07	0.06	0.01	0.06	0.08	0.08	0.12	0.12	0.12	0.15	0.15	0.13	0.12	0.13	0.03	0.01	0.11	0.13	0.16	0.16
LOI	1.46	2.14	2.17	2.45	3.19	2.55	2.15	2.15	0.92	1.03	2.29	2.19	2.53	2.53	1.39	1.34	1.72	1.81	1.83	1.75	1.97	3.30	1.66	2.93	2.00	1.69	2.80	2.80
Total	99.5	100	99.9	100	99.9	99.8	99.9	99.9	99.9	99.9	99.9	99.6	100	100	99.7	99.6	99.9	99.7	99.9	99.6	99.8	99.5	99.8	99.7	99.6	99.8	100	100
Mg [#]	46.8	56.5	55.6	52.8	49.6	49.7	72.7	72.7	56.1	46.1	49.8	56.0	51.2	37.4	37.4	38.0	37.7	36.5	37.3	38.7	41.5	38.2	39.1	53.3	41.0	36.7	43.9	43.9

TABLE 1: Continued.

	Tholeiitic basalts										Transitional intermediate volcanic rocks																	
	MU 14	MU 204	MU 27	MU 15	MU 19	MU 66	MU 20	MU 43	MU 69	MU 109	MU 12	MU 13	MU 21	MU 27	MU 33	MU 35	MU 36	MU 37	MU 38	MU 39	MU 49	MU 54	MU 57	MU 60	MU 64	MU 65	MU 66	MU 68
Ba		204	27	3.00	1.70				140					1230			418				329		97	763				755
Rb		26	9	5	5			5						16			35				40		2	97				18
Sr		147	106	101				214						428			236				239		293	320				423
Ni		100	190	90				120						30			80				90		60	90				30
Cr		160	200	240				170						30			40				70		40	90				20
V		342	228	232				249						76			171				154		162	153				108
Th		0.5	0.3	0.2				1						3.9			8				8.7		7	8.9				5.8
Pb		5	5	5				5						7			5				9		42	6				10
U		0.2	0.1	0.1				0.4						1.3			2.1				2.9		1.9	2.5				1.4
Nb		3	2	1				4						4			8				8		7	8				7
Ta		0.3	0.2	0.1				0.3						0.4			0.6				0.8		0.6	0.7				0.5
Zr		80	53	31				88						126			163				177		147	184				176
Hf		2.2	1.4	1				2.4						3.2			4.3				4.9		3.9	4.7				4.6
Y		29	20	16				23						15			23				24		21	24				24
La		4.60	3.00	1.70				9.20						22.1			26.2				28.1		23.8	28.2				33.7
Ce		12.4	8.2	4.6				21.6						42.2			53.5				60		49.4	59.9				69.3
Pr		1.96	1.27	0.75				3.05						4.99			6.46				7.74		6.21	7.49				9
Nd		6.58	6.70	4.10				17.82						17.9			24.4				28.1		22.9	28.5				31.6
Sm		1.63	2.1	1.3				6.1						3.5			5.7				6.4		5.4	6.2				6.5
Eu		1.11	0.84	0.57				1.36						1.06			1.37				1.66		1.68	1.65				1.62
Gd		4.3	3.0	2.0				4.1						3.3			5.7				5.8		4.8	6.1				5.3
Tb		0.8	0.5	0.4				0.7						0.5			0.8				0.9		0.8	0.9				0.8
Dy		5.0	3.4	2.5				4.0						2.6			4.7				4.7		4.0	4.8				4.2
Ho		1.1	0.7	0.6				0.8						0.5			0.9				0.9		0.8	0.9				0.8
Er		3.3	2.1	1.7				2.4						1.5			2.4				2.5		2.1	2.5				2.5
Tm		0.48	0.32	0.26				0.36						0.22			0.34				0.35		0.29	0.34				0.37
Yb		3.10	2.10	1.70				2.30						1.40			2.10				2.20		1.80	2.10				2.30
Lu		0.46	0.31	0.26				0.35						0.22			0.31				0.31		0.26	0.3				0.34

TABLE 1: Continued.

	Tholeiitic basalts										Transitional intermediate volcanic rocks																		
	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	
La/Yb	1.5	1.4	1.0								15.8										12.8								
La/Nb	1.53	1.5	1.7								5.53										3.51								
Eu/Eu*	0.90	1.02	1.08								0.95										0.83								
La/Sm _{CN}	0.90	0.92	0.84								4.08										2.83								
La/Yb _{CN}	1.06	1.02	0.72								11.3										9.16								
Nb/La _{pm}	0.63	0.64	0.57								0.17										0.27								
Transitional intermediate volcanic rocks																													
	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	
SiO ₂	76	77	78	79	80	81	82	83	84	85	86	87	89	90	91	92	93	94	95	96	97	99	100	16	17	18			
TiO ₂	51.9	51.9	53.2	52.4	53.1	53.3	54.3	53.5	52.2	54.3	55.1	54.3	55.6	55.8	52.8	51.3	52.6	54.9	54.2	53.7	55.4	52.3	74.9	75.5	75.3				
Al ₂ O ₃	14.2	1.38	1.34	1.37	1.49	1.49	0.70	1.51	1.62	1.25	1.35	1.41	1.41	1.43	1.52	0.84	1.20	1.37	1.41	1.09	1.07	1.42	0.03	0.03	0.03				
Fe ₂ O ₃	14.7	14.2	14.1	14.4	14.2	13.9	15.1	14.0	14.7	13.5	14.4	13.8	13.6	13.4	14.4	14.1	14.2	14.6	14.2	15.1	14.2	15.6	14.28	14.38	14.46				
MnO	12.4	12.6	12.2	12.4	12.5	12.6	8.2	12.4	13.0	11.3	11.3	12.2	11.8	11.4	13.5	11.6	12.5	11.4	11.6	12.5	11.3	12.9	0.34	0.28	0.34				
MgO	0.14	0.14	0.14	0.14	0.14	0.14	0.13	0.14	0.14	0.13	0.14	0.13	0.13	0.12	0.16	0.15	0.19	0.13	0.14	0.15	0.17	0.15	0.02	0.01	0.01				
CaO	4.40	4.20	4.04	4.10	3.88	3.92	6.47	3.86	3.89	4.44	3.60	3.68	3.72	3.55	3.82	7.08	4.89	3.66	4.10	4.56	4.26	3.64	0.23	0.22	0.25				
Na ₂ O	7.36	7.97	8.36	8.38	6.74	7.00	8.87	6.82	6.01	7.40	6.36	7.03	6.39	7.13	6.32	9.37	5.66	5.84	5.56	5.28	5.40	5.97	0.26	0.10	0.15				
K ₂ O	3.66	2.83	2.88	2.87	4.32	3.92	3.14	4.20	4.63	2.91	5.57	3.79	3.73	3.62	4.63	2.41	4.53	4.55	4.00	4.91	5.04	4.75	5.14	5.17	5.32				
P ₂ O ₅	1.25	1.91	1.48	1.67	1.60	1.52	0.57	1.57	1.79	2.89	1.27	1.47	1.91	0.15	0.95	0.88	2.06	1.66	2.57	1.77	1.62	1.16	3.98	3.61	3.41				
LOI	0.11	0.02	0.11	0.11	0.12	0.13	0.11	0.13	0.14	0.11	0.12	0.13	0.14	0.13	0.13	0.03	0.09	0.10	0.13	0.10	0.09	0.12	0.01	0.01	0.01				
Total	2.48	2.35	1.78	1.79	1.59	1.57	2.46	1.52	1.49	1.70	1.40	1.97	1.65	2.94	1.70	2.27	1.87	1.40	1.63	0.94	1.50	1.99	0.75	0.69	0.69				
Mg [#]	99.8	99.5	99.6	99.7	99.7	99.6	100	99.6	99.6	99.9	101	99.9	100	99.6	100	100	99.8	99.6	99.5	100	100	100	100	100	100	100			
	41.3	39.7	39.6	39.5	38.1	38.1	60.9	38.2	37.2	43.9	38.8	37.4	38.4	38.3	35.9	54.8	43.6	38.9	41.2	42.0	42.8	35.8	57.3	60.9	59.3				

TABLE 1: Continued.

	Transitional intermediate volcanic rocks														Rhyolites											
	MU 76	MU 77	MU 78	MU 79	MU 80	MU 81	MU 82	MU 83	MU 84	MU 85	MU 86	MU 87	MU 88	MU 89	MU 90	MU 91	MU 92	MU 93	MU 94	MU 95	MU 96	MU 97	MU 100	MU 16	MU 17	MU 18
Ba				504								415	643						626				485	301	220	217
Rb				56								48	61						54				40	91	83	77
Sr				349								398	395						296				312	37	32	31
Ni				160								90	80						80				43	20	20	20
Cr				40								70	70						30				40	20	20	20
V				180								155	149						163				175	5	5	5
Th				7.8								8.9	8.8						7.2				7.5	3.1	2.9	2.7
Pb				5								14	18						5				5	9	5	5
U				2.2								2.5	3.1						2				2.2	2.5	2.1	2
Nb				7								9	8						6				7	5	5	4
Ta				0.6								0.7	0.8						0.6				0.6	0.6	0.6	0.6
Zr				158								179	173						137				155	34	36	33
Hf				4.3								4.6	4.9						3.7				4.1	1.9	2	1.9
Y				25								24	24						23				25	12	9	10
La				23.6								27.4	28.0						22.8				20.1	6.60	3.90	3.70
Ce				50.7								58.3	59.5						47.4				46.6	13.2	9.3	12.3
Pr				6.35								7.2	7.68						5.82				6.24	1.90	1.31	1.12
Nd				24.4								27.3	27.9						22.7				23.6	7.80	5.40	4.60
Sm				5.8								6.2	6.6						5.2				5.7	2.1	1.4	1.4
Eu				1.78								1.6	1.81						1.63				1.62	0.12	0.09	0.1
Gd				6.0								6.2	5.7						5.3				5.5	2.1	1.4	1.5
Tb				0.9								0.9	0.9						0.8				0.9	0.4	0.3	0.3
Dy				4.9								4.7	4.7						4.4				4.7	2.0	1.5	1.5
Ho				0.9								0.9	0.9						0.8				0.9	0.4	0.3	0.3
Er				2.6								2.4	2.5						2.3				2.6	1	0.8	0.9
Tm				0.36								0.34	0.36						0.32				0.36	0.15	0.13	0.14
Yb				2.20								2.00	2.20						2.00				2.20	0.90	0.80	0.90
Lu				0.32								0.3	0.31						0.3				0.33	0.13	0.12	0.12

Transitional intermediate volcanic rocks																Rhyolites									
MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU	MU						
76	77	78	79	80	81	82	83	84	85	86	87	89	90	91	92	93	94	95	96	97	100	16	17	18	
La/Yb			10.7							13.7	12.7				11.4							9.1	7.3	4.9	4.1
La/Nb			3.37							3.04	3.50				3.80							2.87	1.32	0.78	0.925
Eu/Eu*			0.92							0.79	0.90				0.95							0.89	0.17	0.20	0.21
La/Sm _{CN}			2.63							2.85	2.74				2.83							2.28	2.03	1.80	1.71
La/Yb _{CN}			7.69							9.83	9.13				8.18							6.55	5.26	3.50	2.95
Nb/La _{ppm}			0.29							0.32	0.28				0.25							0.34	0.73	1.24	1.04

FIGURE 7: Major and trace elements variation diagram for the Kilimafedha volcanic rocks. Symbols as in Figure 6.

4.3.2. Intermediate Volcanic Rocks. The intermediate volcanic rocks have a wide range of SiO_2 contents (52.51–66.80 wt%) spanning from basaltic andesites through basaltic trachyandesites and andesites to dacites. The compositions, however, are skewed to the basaltic andesitic compositions as indicated by the averages ($\text{SiO}_2 = 52.51\text{--}66.80$ wt%, average = 55.67 wt%, $n = 40$, Table 1, Figures 5 and 6), and only 5 samples have $\text{SiO}_2 > 57$ wt%. TiO_2 contents are 0.59–1.65 wt%, $\text{Fe}_2\text{O}_3 = 4.26\text{--}13.78$ wt%, $\text{MgO} = 2.68\text{--}7.25$ wt%, and Mg numbers range from 36 to 61. Cr and Ni contents are 20–90 ppm and 30–160 ppm, respectively. La varies from 20.1–33.7 ppm and Yb from 1.4–2.3 ppm which results in La/Yb ratios of 9.14–15.8.

The intermediate volcanic rocks display fractionated REE patterns (Figure 8(b)) and in comparison with the tholeiitic basalts are characterized by an enrichment of the LREE relative to the MREE and HREE ($\text{La}/\text{Sm}_{\text{CN}} = 2.3\text{--}4.1$, $\text{La}/\text{Yb}_{\text{CN}} = 6.5\text{--}11.3$). The degree of REE fractionation,

however, is less than that of adakites which have $\text{La}/\text{Sm}_{\text{CN}} = 5.8$, $\text{La}/\text{Yb}_{\text{CN}} = 43.5$ [25, Figure 8(b)]. The rocks show slightly negative to nonexistent Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.74\text{--}1.01$). On the primitive mantle-normalized diagram (Figure 9(b)), the samples display fractionated patterns with enrichment of the incompatible elements (Rb, Ba, Th, K, and Pb) relative to the compatibles ones and are associated with negative anomalies of Nb, Ta, and Ti relative to adjacent elements ($\text{Nb}/\text{La}_{\text{pm}} = 0.17\text{--}0.34$).

4.3.3. Rhyolites. The rhyolite samples have a restricted range in SiO_2 contents (75.52–76.02 wt%, $n = 3$). TiO_2 contents are 0.03 wt% for all the 3 samples, whereas Fe_2O_3 and MgO vary from 0.28 to 0.34 wt% and from 0.22 to 0.25 wt%, respectively. The samples are depleted in Cr and Ni (≤ 20 ppm) as well as in Zr (33–36 ppm). Compared with the tholeiitic basalts and the intermediate volcanic rocks, the rhyolites have lower total REE contents. La varies from 3.7 to

FIGURE 8: Chondrite normalized REE diagrams for the Kilimafedha volcanic rocks normalizing values from Sun and McDonough [23]. (a) Tholeiitic basalts superimposed with NMORB, (b) intermediate volcanic rocks superimposed with adakites, and (c) rhyolites.

6.6 ppm, whereas Yb is restricted in the range of 0.8–0.9 ppm resulting into La/Yb ratios of 4.11–7.13.

The rhyolites are characterized by slight enrichment of the LREE relative to MREE and HREE ($\text{La}/\text{Sm}_{\text{CN}} = 1.7\text{--}2.0$, $\text{La}/\text{Yb}_{\text{CN}} = 2.95\text{--}5.26$) with characteristic strong negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.17\text{--}0.21$, Figure 8(c)). On primitive mantle-normalized plots (Figure 9(c)), the samples show enrichment in incompatible elements (Rb, Ba, Th, K, and Pb), negative anomalies of Nb, Ta, Eu, Sr, and Ti anomalies relative to adjacent elements.

4.4. Sm-Nd Isotopic Composition. Sm-Nd isotopic compositions for the Kilimafedha greenstone belt rhyolites are reported in Table 2. Also shown in the Table are the ϵ_{Nd} values calculated assuming a crystallization age of 2712 ± 5 Ma reported by Wirth et al. [9]. The ϵ_{Nd} (2.7 Ga) values range from +1.87 to +2.18 for the tholeiitic basalts, +1.57 to +2.46 for the intermediate volcanic rocks, and −0.51 to +5.16 for the rhyolites (Figure 10), and these values are comparable with those from the volcanic rocks from the northern Musoma-Mara greenstone belt reported by Many et al. [11, 12], some few hundreds of km north of

the Kilimafedha greenstone belt. Their respective depleted mantle (T_{DM}) ages are 2980–3763 Ma, 2846–2970 Ma, and 2557–3914 Ma (Table 2).

5. Discussion

5.1. Petrogenesis

5.1.1. Tholeiitic Basalts. The slight depletion in LREE to nearly flat REE patterns shown by the tholeiitic basalts coupled with their close compositional similarity to N-MORB suggests that these rocks were generated in a source similar to that generating modern N-MORB. Unlike NMORB, however, these patterns display negative anomalies in Nb and Ti, features which together with tectonic setting discrimination diagrams (see next section) are suggestive of derivation in a subduction setting. The nature of the mantle source rocks can further be constrained by the trace element ratios Nb/Yb, Zr/Yb, and Th/Yb [26]. When plotted on the Nb/Yb versus Zr/Yb diagram (Figure 11), the tholeiitic basalts plot around NMORB with a general trend towards increasing mantle enrichment to E-MORB within the MORB

FIGURE 9: Primitive mantle normalized diagrams for the Kilimafedha volcanic, normalizing values from Sun and McDonough [23]. (a) Tholeiitic basalts, (b) intermediate volcanic rocks, and (c) rhyolites.

TABLE 2: Sm-Nd isotopic data for the Kilimafedha greenstone belt volcanic rocks.

Sample	Rock suite	Sm (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	ϵNd (at 2.7 Ga)	T_{DM} (Ma)
MU 14	Tholeiite basalts	1.68	6.57	0.1545	0.511995	2.18	2980
MU 69		6.12	18.82	0.1965	0.512731	1.87	3763
MU 49	Transitional intermediate volcanic rocks	6.09	29.4	0.1252	0.511451	1.82	2923
MU 57		5.06	24.2	0.1263	0.511481	1.99	2910
MU 68		6.08	33.3	0.1103	0.511218	2.46	2846
MU 89		6.02	28.7	0.1267	0.51148	1.83	2926
MU 100		5.45	24.6	0.1339	0.511594	1.57	2970
MU 16	Rhyolites	1.94	6.81	0.1721	0.512459	5.10	2557
MU 17		1.37	4.51	0.1835	0.512378	-0.51	3914

Calculations are based on a decay constant of 6.54×10^{-12} per year for ^{147}Sm and DM values for Nd are $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{today}} = 0.51316$, $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{today}} = 0.2137$.

FIGURE 10: Plot of ϵ_{Nd} versus t (Ma) for the Kilimafedha greenstone belt volcanic rocks. The depleted mantle model is from DePaolo [24] and the northern Musoma-Mara greenstone belt high-Mg andesites and dacites data is from Many et al. [11].

array. This suggests that the enrichment observed in the Kilimafedha tholeiites can be explained by their derivation from an initially homogeneous MORB-like source that was differentially metasomatized by an aqueous fluid derived from the subducting slab [26]. Fluxing of the source by the metasomatizing fluid most likely enhanced melting of the mantle wedge at a relatively low pressure. Melting of the mantle wedge which was not affected significantly by the metasomatism yielded the La-depleted basalts, whereas the La-enriched basalts were produced by melting of a mantle wedge that has been slightly metasomatized. The compositional similarity to NMORB is also reflected in similar ϵ_{Nd} (2.7 Ga) of the samples (+2.18 for sample MU 14) to the depleted mantle value of 2.2 [24] at the same time. The slightly lower ϵ_{Nd} (2.7 Ga) values of 1.87 for sample MU 69 would indicate minimal contamination of the magmas by older continental crust.

5.1.2. Intermediate Volcanic Rocks. Unlike the flat REE patterns that characterize the tholeiitic basalts, the intermediate rocks show fractionated patterns characterized by La/Yb ratios of 9.14–15.8. These ratios are, however, lower than those reported in adakites (La/Yb = 40; [23]). In adakites, such high ratios are indicative of the presence of garnet $\pm$ amphibole in the source during partial melting. Thus, the lower La/Yb ratios of the rocks preclude the involvement of garnet $\pm$ amphibole in their magma genesis. In Figure 11, the intermediate volcanic rocks cluster just above E-MORB out of the MORB array towards increasing Zr content, which according to Pearce and Peate [26] signifies the involvement of both slab melt and hydrous fluid in metasomatism of the source rocks. The metasomatism resulted in the enrichment of the source mantle wedge in the HFSE that has been scavenged from the subducting oceanic slab thereby explaining the observed enrichment in the HFSE relative to MORB (Figure 11). The involvement of slab partial melts in the petrogenesis of the intermediate volcanic rocks suggests

that temperatures in the subduction zone were sufficiently high to initiate partial melting of the slab. According to Pearce and Peate [26], the onset of melting of the subducting slab in the Phanerozoic occurs at relatively greater depth (>100 km) beneath the subduction zone. This suggests that, unlike the tholeiitic basalts that were formed at relatively shallow depths, the primary magmas for the intermediate volcanic rocks originated at greater depth, but outside the garnet stability field. The intermediate volcanic rocks have ϵ_{Nd} (2.7 Ga) values of +1.57 to +2.46 similar to those of the tholeiitic basalts and are indicative of the juvenile nature of the magmas accompanied by minimal crustal contamination. Such a conclusion was also reached for the northern MMGB high-Mg andesites and dacites [11] which share similar ϵ_{Nd} values with the Kilimafedha greenstone belt volcanic rocks.

5.1.3. Rhyolites. Rhyolites differ from the other two suites in having lower contents of TiO_2 , P_2O_5 , Zr, and overall lower abundances of the REE (Table 1). In chondrite normalized REE diagrams (Figure 8) and extended trace element diagram (Figure 9), the rhyolites are characterized by large negative Eu ($\text{Eu}/\text{Eu}^* = 0.17\text{--}0.21$, Table 1) accompanied by negative Sr anomalies as well as Nb and Ti anomalies. The close spatial association of the rhyolites and other suites of the Kilimafedha greenstone belt coupled with their trends towards lower Fe_2O_3 , MgO, CaO, TiO_2 , Cr, and Ni with increasing SiO_2 (Figure 7) may suggest that the rhyolites may be products of extensive fractional crystallization of the same magmas that generated the more basic members. Such a model is also supported by experimental studies which showed that low-pressure fractional crystallization of olivine, pyroxene, plagioclase, and Fe-Ti oxides can produce rhyolites [27] with relatively flat HREE patterns. Thus, the generally lower REE abundances, TiO_2 , P_2O_5 , and Zr contents can be explained by shallow level fractionation of Ti-rich phases (e.g., titanomagnetite) and REE-rich phases such as apatite,

FIGURE 11: Nb/Yb-Zr/Yb diagram (after Pearce and Peate, [26]) for the Kilimafedha tholeiitic basalts (filled triangles) and intermediate volcanic rocks (open squares). The tholeiitic basalt samples plot around the NMORB field tending towards the mantle enrichment direction within the MORB array suggestive of metasomatism by aqueous fluid. The intermediate rocks plot just above the EMORB tending to higher Zr values illustrating input of the HFSE from the subducted slab. NMORB, EMORB, and OIB data are from Sun and McDonough [23].

monazite, zircon, and allanites, whereas the large negative Eu and Sr anomalies could be due to plagioclase fractionation. Compared to the other two suites, the rhyolites show variable ϵ_{Nd} (2.7 Ga) values of -0.51 to $+5.17$ and suggest that older crustal involvement in the genesis of the rhyolites either by partial melting of older crust or contamination of evolving magmatic liquid cannot be ruled out as an important process in the genesis of these rocks. The wide variation in ϵ_{Nd} towards more depleted signatures demands reexamination of the rocks.

5.2. Tectonic Setting. Trace element discrimination diagrams developed for Phanerozoic rocks have been used together with their ratios to infer the tectonic setting for Archaean rocks (e.g., [19]). Using this approach, the Kilimafedha tholeiitic basalts and basaltic andesites were plotted on the Th-Hf-Nb triangular diagram of Wood [28] which is suitable for mafic as well as intermediate volcanic rocks. On this diagram, three of the four tholeiitic basalt samples plot along the boundary between the N-MORB and E-MORB fields, while the other samples together with all intermediate volcanic samples plot in the field of volcanic arc basalts (Figure 12). The similarity of the three tholeiitic basalt samples with N-MORB on the Th-Hf-Nb diagram is also reflected in Figure 8(a). The La/Nb ratio of basaltic samples is particularly important in discriminating basalts that erupted in ocean ridges and ocean plateaus from those that erupted in arcs [29, 30]. According to Rudnick [29] and Condie [30], ocean ridge and ocean plateau basalts have $\text{La/Nb} < 1.4$, whereas arc basalts have $\text{La/Nb} > 1.4$. Both the tholeiitic basalts and intermediate rocks of the Kilimafedha greenstone belt show $\text{La/Nb} > 1.4$ (1.5–2.30 and 2.87–5.53, resp.) suggestive of arc affinities. Thus, the results obtained from the discrimination diagrams combined with trace element ratios data are suggestive of an arc tectonic setting for the Kilimafedha greenstone belts rocks.

This conclusion is supported by the fact that the rocks exhibit negative anomalies of Nb, Ti, and/or Ta anomalies in extended trace element spidergrams (Figure 9), features attributed to magmas generated at subduction zones [26].

6. Comparison with Other Greenstone Belts of the Tanzania Craton

A closer review of geochemistry and geochronology by Many et al. [10] and Many and Maboko [8] showed that the individual greenstone belts of the Tanzania Craton exhibit different formation ages, and their formation occurred in different tectonic settings. This suggestion is also evident in different volcanic rock packages found in these belts. Kilimafedha greenstone belt (KGB) differs from the Sukumaland (SGB) to the west and Iramba-Sekenke (ISGB) to the far south in having predominantly intermediate volcanic rocks with tholeiitic to calc-alkaline intermediate affinities, rare mafic, and felsic volcanic package, which are in contrast to the later that are dominated by tholeiitic basalts and rare intermediate volcanic rocks. The volcanic package in KGB also differs from those of the southern Musoma-Mara greenstone belt (MMGB) to the near north as the later is comprised of bimodal volcanic assemblage [31]. Although the northern part of the MMGB is predominantly comprised of intermediate rocks similar to KGB, the former lacks mafic members.

The foregoing discussion corroborates the findings by Many et al. [10] that the individual greenstone belts evolved as separate entities at different time intervals having different volcanic rocks assemblages. Although volcanism in greenstone belts of the Tanzania Craton seems to have erupted at different time intervals (2823–2780 Ma for SGB, 2755–2712 Ma for MMGB, ISGB, and KGB, 2676–2667 Ma for northern MMGB, [8] and references therein); one thing is common to all of them: they formed exclusively

FIGURE 12: Ta-Hf-Th tectonic setting discrimination diagram [28] for the tholeiitic basalts (filled triangles) and intermediate volcanic rocks (open squares) for the Kilimafedha greenstone belts.

at convergent margins. This signifies the importance of formation and growth of late Archaean continental crust at convergent margins.

7. Conclusion

The Neoarchaean Kilimafedha greenstone belt of north-eastern Tanzania consists of three closely associated suites of volcanic rocks: the predominant intermediate basaltic andesite and dacites, and the volumetrically minor tholeiitic basalts and rhyolites. The tholeiitic basalts have nearly flat REE patterns and show close compositional similarity to NMORB. Trace element systematics of the tholeiites suggest that they were formed by shallow partial melting of a mantle wedge that has been variably metasomatized by an aqueous fluid in a convergent tectonic setting. The intermediate rocks are characterized by fractionated REE patterns, enrichment of the HFSE relative to NMORB, and negative anomalies of Nb and Ta. Such geochemical features are consistent with derivation of these rocks by partial melting of a mantle wedge that has been metasomatized by both fluid and slab melt at a greater depth than the tholeiitic basalts source but outside the garnet stability field. The geochemical features defining the Kilimafedha greenstone belt rhyolites include low TiO_2 , P_2O_5 , Zr, and overall lower abundance of total REE compared with the other two suites and large negative Eu, Sr, and Ti anomalies in extended trace element spidergrams. These features can be explained by shallow level fractional crystallization of the parent magma of the intermediate volcanic rocks involving plagioclase, Ti-rich phases like ilmenite and magnetite as well as REE-rich phases like apatite, zircon, monazite, and allanite. The close spatial association of the three petrological types in the Kilimafedha greenstone belt is interpreted as reflecting their formation in an evolving late Achaean island arc.

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