

RESEARCH ARTICLE

Geochemistry of Volcanic Rocks in Ponelo Island, North Gorontalo, Indonesia

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Received: Apr 14, 2024; Accepted: Aug 19, 2024.
DOI: 10.25299/jgeet.2024.9.3.16832

Abstract

Ponelo Island is located in the northern part of Sulawesi, which is still an enigma regarding the genesis of the volcanic rocks found on this island. Therefore, the objective of this study is to understand the petrogenesis and tectonic implication of these volcanic rocks. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to obtain trace and rare earth elements is the method of this study. The volcanic rocks found on Ponelo Island consist of basalt and basaltic andesite rocks with a calc-alkaline affinity. The transition data suggested a highly fractionated cause of low transition element (Ni=17-38 ppm; Cr=13-47) compared to primary magma concentration, anomalies negative of Ba, Sr, and Ti of spider diagrams, and negative anomaly of Eu (Eu/Eu*=0.88-0.99). Relationship between low concentration between Ce/Y (0.74-0.76) and La/Yb vs Sm/Yb ratio indicated ~5% spinel-lherzolite mantle source partial melting. On the other hand, incompatible element ratios, such as Ba/Nb (39.03-45.28), Ba/Th (75.52-82.67), Rb/Nb (3.93-6.22), K/Nb (1772.22-2703.45), Ba/La=13.67-14.57, Th/La (0.17-0.18), La/Nb (2.91-3.16), depleted Nb/U (6-6.74), and also lack of xenolith or enclaves indicate cryptic crustal contamination. The slab-derived fluid indicated by ratios of Rb/Y (0.019-0.05), Nb/Y (0.10-0.11), Th/Yb (0.52-0.61), and Ba/La ratio (13.29-14.57). Ponelo volcanic rocks shows typical calc-alkaline island arc tectonic setting particularly with enrichment in ion lithophile element (LILE) and light rare earth elements (LREE) along with depletion in high field strength elements (HFSE) and heavy rare earth elements (HREE), as shown by spider diagrams.

Keywords: Geochemistry, Subduction, Island Arc Volcanics, North Sulawesi Arc

1. Introduction

The convergence zone of Eurasia, Indian-Australian, and Pacific plates is where Sulawesi island is located (Hall, 2012; White et al., 2014; Maulana et al., 2016). It has complicated geological conditions and the K-shape of this island has been subject of geological interest for many years. Sulawesi may be categorized into several tectonic units, including the North-West Sulawesi Volcanic-Plutonic Arc, the Central Sulawesi metamorphic belt, the Eastern Sulawesi Ophiolite, and the two microcontinents of Banggai-Sula and Tukang Besi-Buton (Hall and Wilson, 2000). This island has been thought to be a part of at least three subduction episodes since the late Mesozoic, as shown by the existence of the Early Cretaceous Bantimala Mélange in West Sulawesi, Late Eocene ophiolites and metamorphic sole rocks in Central and East Sulawesi, and also magmatic rocks with calc-alkaline affinity in North Sulawesi Arc (Maulana et al., 2016; Böhnke et al., 2019; Hasria et al., 2020, 2023; Gan et al., 2022; Zhang et al., 2022; Advokaat & van Hinsbergen, 2024). According to Zhang et al., (2020), the North Arc Sulawesi is separate from the West Sulawesi tectonic unit because it show different geochemical signatures.

North Sulawesi Arc is an intra-oceanic island arc covered by Cenozoic volcanic-sedimentary rock and presently experiencing the subduction of Celebes Sea plate, which is dipping toward the south (Bachri, 2006; Hall, 2019,

2012; Kavalieris et al., 1992; Li et al., 2023). The magmatic rocks of this region contain the following: mafic-felsic volcanic and intrusive rock with calc-alkaline, back-arc basin basalt, island arc tholeiitic, potassic calc-alkaline, and shoshonite affinity associated to multiple plate subduction events, such as the Celebes Sea plate subduction, the Molucca Sea plate subduction, and the Indian oceanic subduction with mafic basement (Elburg & Foden, 1998; Elburg et al., 2003; Polvé et al., 1997; Rangin et al., 1997; Maulana et al., 2016; Gan et al., 2022; Sendjaja et al., 2020; Zhang et al., 2020, 2022). Ponelo is a small island located north of the North Sulawesi Arc. Based on the Geological Map of the Tilamuta Sheet (Bachri et al., 2011) the island exhibits only of Pliocene-Pleistocene sedimentary rocks (TQsl). However, in the field survey by researchers, volcanic rocks were found on this island. The genesis of volcanic rocks in Ponelo Island are seriously questioned by the paucity of knowledge available regarding these magmatic rocks. Therefore, the geochemistry of these volcanic rocks will provide previously unknown information on the magmatism episode on Ponelo Island and its consequences for the tectonic setting in North Sulawesi Arc.

2. Geological Background

The West Sulawesi and North Sulawesi Arc are separate tectonic units due to North Sulawesi Arc absence of continental basement and post-collision ultra-potassic

magmatism during Miocene (Elburg and Foden, 1998; Maulana et al., 2016; Zhang et al., 2020) (Fig 1a). The North Sulawesi Arc is typically conceived as an intra-oceanic arc that is constructed on an Eocene oceanic crust (Elburg et al., 2003; Bachri, 2006) without any old basements that have been discovered yet (Hanyu et al., 2012).

The North Sulawesi Arc's tectonic setting has been revealed by magmatism activity that has taken place since Eocene. Numerous significant subduction events resulted in North Sulawesi Arc, including Indian oceanic subduction underneath mafic basement, Molucca Sea plate subduction, and Celebes Sea plate subduction (Hanyu et al., 2012; Hall, 2019; Sendjaja et al., 2020; Gan et al., 2022; Song et al., 2022; Zhang et al., 2022). A number of rock series may be distinguished within the North Sulawesi Arc's magmatism:

the Older Series, which includes 50-30 Ma back-arc basin (BAB) affinity magma and 30-16 Ma tholeiitic-calc alkaline affinity magma; and *the Younger Series* which includes calc-alkaline (CA), potassic calc-alkaline (CAK), and shoshonitic (SH) series that intruded through the older series (Bellon & Rangin, 1991; Elburg & Foden, 1998; Cottam et al., 2011; Polvé et al., 1997; Rangin et al., 1997; Sendjaja et al., 2020; Gan et al., 2022; Zhang et al., 2022). Since the early Eocene, North Sulawesi Arc has been rotating clockwise in the Miocene and located north of equator since early Eocene (Hall, 2012; Sasajima et al., 1980; Surmont et al., 1994). It is suggested that magmatism occurrences recorded in these rocks since the Eocene are the product of an ongoing magmatism process rather than rocks that have been migrated in from somewhere else (autochthon).

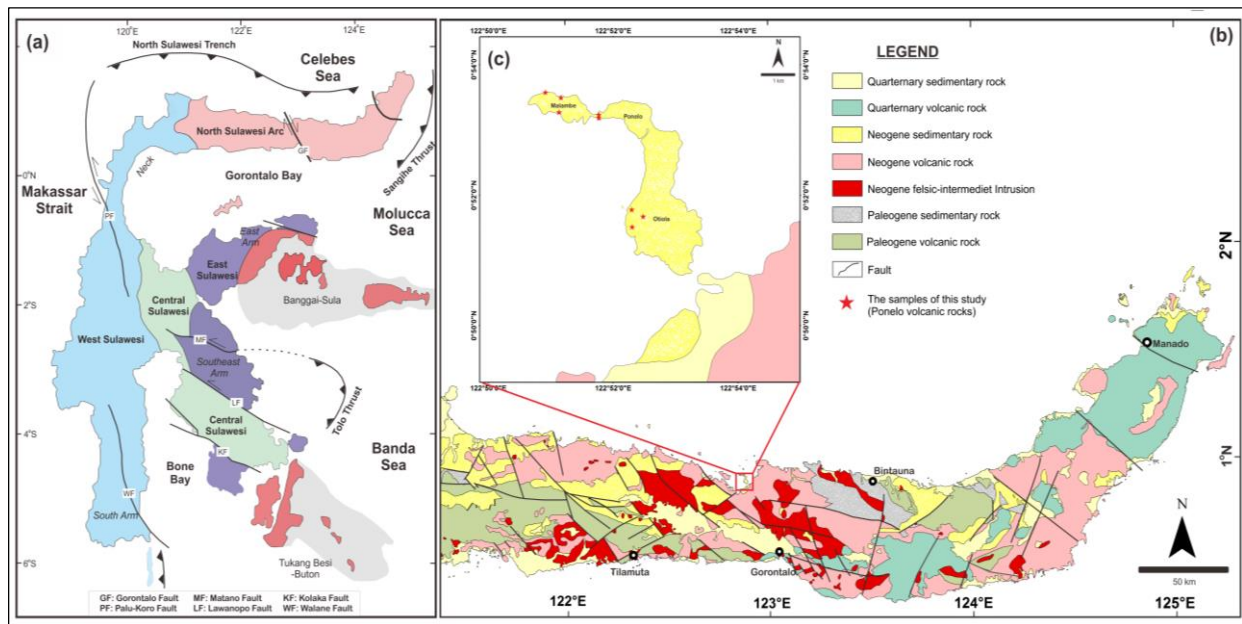


Fig 1. (a) Sulawesi tectonic provinces (modified after Zhang et al., 2020). (b) Geological Map of North Sulawesi Arc (modified after Apandi and Bachri, 1997; Effendi and Bawono, 1997; Bachri et al., 2011) (c) Ponele island map and sampling points.

The following will provide an explanation of the detail tectonic model evolution of North Sulawesi Arc formation.

- a) Early Eocene – late Eocene: the initial stage of the North Sulawesi Arc's formation is the development of mafic basement, which is referred to back arc basin (BAB) types. This process is presumably associated with the back-arc spreading of the Celebes Sea during Eocene (Polvé et al., 1997; Rangin et al., 1997; Zhang et al., 2022). Magmatism was absent in the North Sulawesi Arc region during this period. BAB-type rocks are found in Tinombo Formation in the form of basaltic flow and gabbro-granodiorite intrusions (Bachri et al., 2011; Polvé et al., 1997; Rangin et al., 1997). Seafloor magnetic anomalies suggest that spreading was occurring at this period time in basins of Celebes Sea, presumably as a result of the Indian Ocean Plate's rollback subduction in the northward direction (Nichols and Hall, 1999).
- b) Late Eocene – mid Miocene: Indian oceanic plate northward subduction underneath BAB-type mafic basement in late Eocene-mid Miocene (Zhang et al., 2022). The whole region is covered with mafic-felsic arc magmatism, with two main rock types: calc-alkaline with basaltic dike, andesite, rhyolite, granite and granodiorite intrusions; and island arc tholeiitic with basaltic flow, basaltic dike, and gabbro (Polvé et

- al., 1997; Rangin et al., 1997; Gan et al., 2022; Zhang et al., 2022). The collision of Tukang Besi-Buton microcontinents in mid Miocene (~15 Ma) led the cessation of subduction of the Indian Ocean Plate and magmatism throughout the North Sulawesi Arc (Hall, 2012; Hall and Spakman, 2015; Zhang et al., 2022; Advokaat and van Hinsbergen, 2024).
- c) Mid Miocene – recent: Located on the northeastern margin of North Sulawesi Arc, the Sangihe Arc formed, presumably as a result of the Molucca Sea plate subduction northwestward (Hall, 2012; Hanyu et al., 2012; Advokaat and van Hinsbergen, 2024). This subduction represents post-collisional magmatism and is linked to north-dipping subduction, which is getting younger as it moves eastward (Polvé et al., 1997). This magmatism rocks evidenced by ~14-11 Ma andesites (Zhang et al., 2022) and active volcano in the margin northeast of the North Sulawesi Arc. In addition, there is subduction at North Sulawesi trench. This subduction is caused by south-dipping Celebes Sea plate subducted the North Sulawesi Arc around ~5 Ma until now (Hall, 2019; Dong et al., 2022, 2024; Song et al., 2022; Advokaat and van Hinsbergen, 2024). Celebes Sea is a type of young subduction slab without

producing arc magmatism (Hall, 2019; Dong et al., 2024).

Located in northern part of North Sulawesi Arc, Ponelo Island is entirely composed of the Lokodidi Formation, which was formed in the Pliocene to early Pleistocene (Bachri et al., 2011; Advokaat et al., 2017) (Fig 1c). This formation is part of Celebes Molasse as which unconformably covers the pre-Neogene rocks (Nugraha et al., 2022). The sedimentary rocks in Ponelo Island consist of interbedded sandstone and poorly consolidated polymictic conglomerate (Akase and Supriadi, 2022). Akase and Supriadi (2022) also reported volcanic rocks on Ponelo Island among sedimentary rocks, which will be the subject of this study.

3. Method

The research area is located in Ponelo Island, Ponelo archipelago subdistrict, North Gorontalo. This island has an area of 7.89 km² with coordinates 0°51'35.340" N and 122°46'46.920" E. Outcrops of Ponelo Basalt exposed in three distinct areas: Malambe (north), Ponelo (center) and Otiola (south) (Fig 1c). Ponelo volcanic rocks contain the characteristics of a massive dark gray with porphyritic texture. There are sheeting joints and fractures that develop intensively in some outcrops (Fig 2). Microscopically, the volcanic rocks have porphyritic texture with phenocrysts of plagioclase (andesine-labradorite), clinopyroxene, and opaque minerals. The phenocrysts are embedded in groundmass of pyroxene and plagioclase microlites and also glass. Based on petrographic analysis, type of Ponelo volcanic rocks are basaltic andesite.



Fig 2. The outcrops of Ponelo volcanic rocks with (a) fractures and (b) sheeting joints. The volcanic rocks has porphyritic textures with plagioclase, clinopyroxene, and opaque phenocrysts.

Eight samples were collected based on the representative of the three distinct areas of Ponelo Island. Rock samples were analyzed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to obtain trace and rare earth elements with ppm (*part per million*) measurement units. This geochemical research aims to establish the magma sources and tectonic settings of Ponelo volcanic rocks through analysis of trace and rare earth elements. This geochemical analysis was conducted at PT Intertek Indonesia Laboratory, Jakarta.

4. Result

Trace element and rare earth element data are presented in Table 1. Trace elements are subdivided into two elements which are incompatible elements (which consistently favors melts over coexisting mineral crystals) and compatible elements (prefer to combine in one or more crystallized minerals relative to the melt) (Gill, 2010). Incompatible elements, which favor melts, provide the most useful fingerprints for origin magma. Incompatible elements are typically classified into two categories: *large ion lithophile elements* (LILE) and *high field-strength elements* (HFSE). The LILE contents: Sr, K, Rb, Ba, Cs, and Th in Ponelo volcanic rock samples are 242-262 ppm, 6060-8020 ppm, 12.2-34.7 ppm, 121-163 ppm, 0.2-1.3 ppm, and 1.5-2.01 ppm. The HFSE contents: Ta, Nb, P, Zr, Hf, Sm, Ti, Y, Yb, and Cr in Ponelo volcanic rocks are 0.17-0.23 ppm, 2.9-3.6 ppm, 940-1150 ppm, 88.2-121 ppm, 2.4-3.2 ppm, 3.8-4.7 ppm, 5760-6850 ppm, 26.1-34.2 ppm, 2.9-3.7 ppm, and 13-47 ppm. Three categories of rare earth elements are distinguished: *light rare earth elements* (LREE), *middle rare earth element* (MREE) and *heavy rare earth elements* (HREE) (Rollinson, 2014). The LREE contents: La, Ce, Pr, and Nd, in Ponelo Basalt samples are 8.8-11.4 ppm, 19.8-26.2 ppm, 2.84-3.66 ppm, and 13.1-17.6 ppm. The MREE contents: Sm, Eu, Gd, Tb, Dy, and Ho are 3.8-4.7 ppm, 1.2-1.5 ppm, 4.2-5.3 ppm, 0.69-0.93 ppm, 4.7-6.2 ppm, and 1-1.2 ppm. The HREE contents: Er, Tm, Yb, and Lu are 2.9-3.7 ppm, 0.4-0.5 ppm, 2.8-3.7 ppm, and 0.43-0.53 ppm. It is believed that during low-temperature alteration, rare earth elements, incompatible trace elements, some transitional metals such as Ni, Co, and Cr are essentially immobile. In contrast, during processes of alteration, LILE, including Rb, Ba, K, Sr, and many significant elements, are frequently mobilized.

4.1 Trace element geochemistry

Compared to the primitive mantle composition (Cr > 800 ppm; Ni > 400 ppm), the transitional trace elements (Cr = 13-47 ppm; Ni = 17-38 ppm;) shown depletion (Frey and Prinz, 1978). Trace elements analysis of Ponelo volcanic rocks using primitive mantle normalized spider diagram compared to N-MORB, E-MORB, OIB, and calc-alkaline basalt-andesite types in North Sulawesi Arc (CA NSA basalt-andesite) (Sun and McDonough, 1989; Polvé et al., 1997; Rangin et al., 1997) (Fig. 4). The Ponelo volcanic rocks show a linear graph on the trace element analysis spider diagram indicating the sample is homogeneous/comagmatic. Based on primitive mantle normalized pattern, the samples exhibit typical enriched LILEs (except Ba) and depleted HFSEs characteristics similar to the CA NSA basalt-andesite type, however there are several notable distinctions between these two types. LILEs (Rb, Ba, Th, K, Sr) from CA NSA basalt-andesite types are more enriched, whereas certain HFSE (P, Ti, Y) depleted compared to the samples. The LILEs and HFSEs are generally depleted compared to OIB and more enriched compared to N-MORB and E-MORB.

Diagram discrimination of Nb/Y-Zr/Ti (Pearce, 1996) to identify the classification of rock and diagram discrimination of Ta/Yb-Th/Yb (Pearce, 2008) to magma affinity of volcanic rock in study area. As shown in Fig. 3, the Ponelo volcanic rocks are classified as basalt to basaltic andesite (Fig. 3a) with calc-alkaline magma affinity (Fig. 3b).

Table 1. Trace and rare earth elements of Ponelo volcanic rocks

Sampel	PN005	PN002	PN007	PN008	PN011	PN012	PN022	PN023
Rock type	Basalt	Basaltic Andesite						
Trace Elements, ppm								
Cr	44	30	26	37	13	32	47	15
Co	35	35	35	31	31	34	33	31
Cs	0.2	0.3	0.3	0.2	0.3	0.5	1.3	1.1
Ni	38	37	35	20	17	33	17	17
Sr	246	256	251	253	242	257	262	249
K	7840	6060	6750	6940	8020	6440	6380	6890
Rb	21.7	12.2	22.5	21.7	25	22.5	34.7	31.3
Ba	124	121	123	135	145	122	163	153
Th	1.5	1.58	1.6	1.76	1.92	1.58	2.01	1.98
Ta	0.17	0.18	0.17	0.2	0.21	0.17	0.23	0.22
Nb	2.9	3.1	3.1	3.1	3.6	3	3.6	3.5
P	1000	1020	940	1020	1150	950	1150	1180
Zr	88.2	88.9	92.5	98.6	116	95.4	121	118
Hf	2.4	2.6	2.5	2.5	3	2.5	3.2	3
Ti	6440	6480	5760	6190	6760	5880	6850	7140
Y	26.1	27.8	27.4	28.3	32.5	26.3	34.2	32.3
Yb	2.9	3	2.9	2.9	3.5	2.8	3.7	3.5
Rare Earth Elements, ppm								
La	8.8	9.1	9	9.6	10.5	8.8	11.4	10.5
Ce	19.8	20.6	20.5	21.3	24	19.9	26.2	24.1
Pr	2.84	2.95	2.97	2.96	3.44	2.82	3.66	3.48
Nd	14.1	13.7	14.3	13.9	17	13.1	17.6	16.7
Sm	3.8	4	3.8	3.9	4.5	3.9	4.7	4.4
Eu	1.2	1.3	1.3	1.3	1.4	1.2	1.5	1.4
Gd	4.4	4.6	4.2	4.6	5.2	4.5	5.3	5.1
Tb	0.69	0.76	0.75	0.72	0.9	0.73	0.93	0.88
Dy	4.7	5.1	4.8	5.1	5.6	4.8	6.2	5.7
Ho	1	1	1	1	1.1	1	1.2	1.1
Er	2.8	3.1	3	3	3.6	2.9	3.7	3.5
Tm	0.4	0.4	0.4	0.4	0.5	0.4	0.5	0.5
Yb	2.9	3	2.9	2.9	3.5	2.8	3.7	3.5
Lu	0.43	0.44	0.43	0.45	0.52	0.43	0.53	0.51

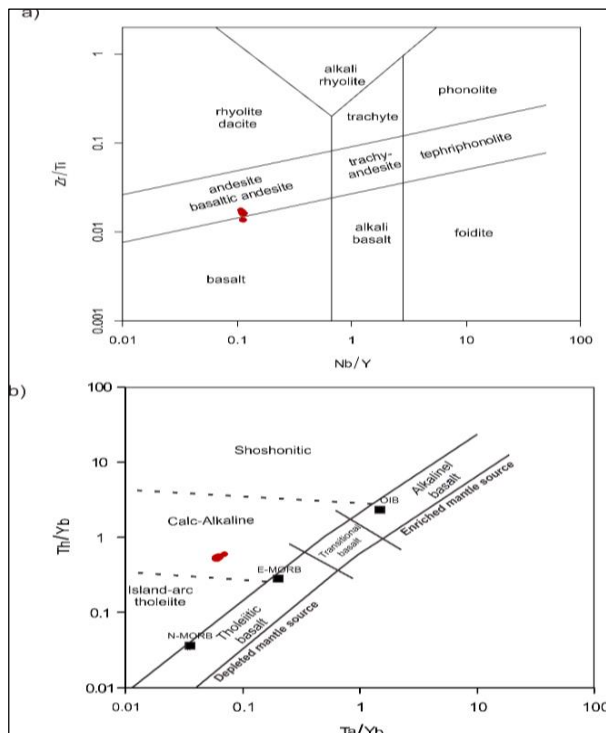


Fig 3. (a) Nb/Y-Zr/Ti discrimination diagram for rock classification (Pearce, 1996) classified volcanic rocks at stury area as basalt-basaltic andesite and (b) Ta/Yb-Th/Yb diagram (Pearce, 2008) shows the volcanic rocks have calc-alkaline affinity.

4.2 Rare earth element geochemistry

Analysis of rare earth elements of Ponelo volcanic rocks using chondrite-normalized spider diagrams (Nakamura, 1974) (Fig 6). The chondrite-normalized pattern shows the samples' LREEs are moderate enriched than MREEs and HREEs. It also reveals that the OIB and CA NSA have enriched LREEs and depleted HREEs whereas N-MORB and E-MORB have depleted LREE contents in comparison to the samples.

Table 2. Trace and rare earth elements of Ponelo Basalt

Sampel	(La/Yb) _N	(La/Sm) _N	(Gd/Yb) _N	(Sm/Lu) _N	Eu/Eu*	Ce/Ce*
PN002	2.18	1.47	1.27	1.51	0.93	0.95
PN005	2.18	1.49	1.25	1.47	0.89	0.93
PN007	2.23	1.53	1.19	1.47	0.99	0.94
PN008	2.37	1.59	1.31	1.44	0.93	0.94
PN011	2.15	1.51	1.22	1.44	0.88	0.94
PN012	2.25	1.46	1.32	1.51	0.87	0.95
PN022	2.21	1.56	1.18	1.47	0.92	0.96
PN023	2.15	1.54	1.20	1.43	0.9	0.95
Average	2.21	1.52	1.25	1.47	0.92	0.95

N : Chondrite-normalized using Sun and McDonough (1986) chondrite value standardization

The samples also have some rare earth element ratios with chondrite-normalized in table 2. The total concentration of rare earth elements in Ponelo Basalt ranges from 67.86 - 87.12 ppm. The concentration of $\Sigma\text{LREE} > \Sigma\text{MREE} > \Sigma\text{HREE}$. LREE is enriched over MREE in the rare earth elements pattern [(La/Sm)_N = 1.46-1.59] and HREE [(La/Yb)_N = 2.15-2.37], and also enrichment of MREE/HREE fractionation [(Sm/Lu)_N = 1.43-1.51; (Gd/Yb)_N = 1.18-1.32]. These results show similarities with the spider diagram.

The equation $Eu/Eu^* = E_{UN}/(Sm_N \times Gd_N)^{1/2}$ is used to calculate the anomaly Eu (Eu/Eu^*) (Taylor and McLennan, 1985). The Ponelo volcanic rocks have negative Eu anomaly ($Eu/Eu^* = 0.88-0.99$) which is shown in spider diagram (Fig 5). In addition to Eu anomalies, Ce anomaly shown in spider diagram (Fig 6). Ce anomaly (Ce/Ce^*) calculation using the equation $Ce/Ce^* = 3Ce_N/(2La_N + Nd_N)$ (Elderfield and Greaves, 1982) shows negative Ce anomaly approaching 1 ($Ce/Ce^* = 0.93-0.95$).

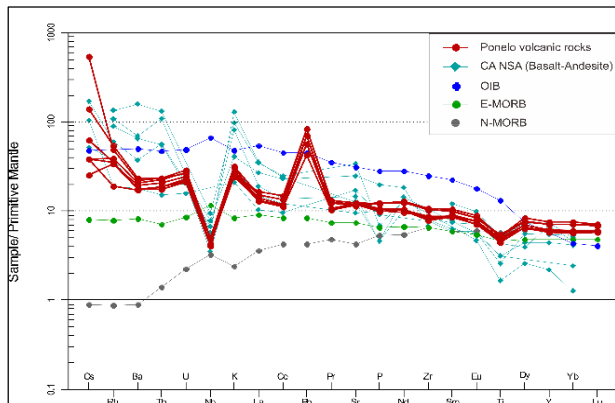


Fig 4. Spider diagrams of trace elements primitive mantle (Sun and McDonough, 1989). CA NSA: Calc-Alkaline North Sulawesi Arc.

5. Discussion

5.1 Origin and formation of Ponelo volcanic rocks: magma source and petrogenesis

Ponelo volcanic rocks have very low transition trace element concentrations compared to primary magma concentrations (with Cr > 1000; Ni > 400-500 ppm) in equilibrium with a typical upper mantle mineral assemblage

(Frey and Prinz, 1978; Ayalew et al., 2016), suggest the samples have highly fractionated. The concentration of Ni (> 250 ppm) and Cr decreases significantly in basalt due to olivine, clinopyroxene, and Cr-spinel crystallization (Perfit et al., 1980). The samples also has a low content of these elements due to crystallization of clinopyroxene as seen in the petrographic observation.

The anomalies negative of Ba, Sr and Ti may be attributed to the process of feldspar (Ba and Sr depletion) and Fe-Ti oxides (Ti depletion) fractionation. The samples also have negative Eu anomaly ($Eu/Eu^* = 0.88-0.99$) which is shown in spider diagram (Fig 5), implying plagioclase fractional crystal or equilibrium with plagioclase-bearing mantle source (Wilson, 2007). Eu is usually associated with Sr in igneous rock process, which also shows depletion, indicated by plagioclase fractionation during magmatic differentiation.

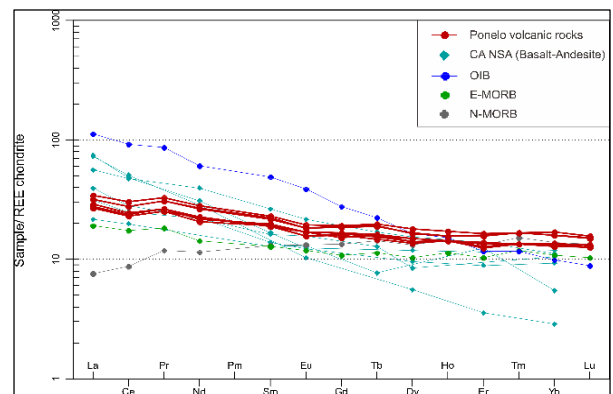


Fig 5. Chondrite-normalized spider diagrams of rare earth elements (Nakamura, 1974). CA NSA: Calc-Alkaline North Sulawesi Arc

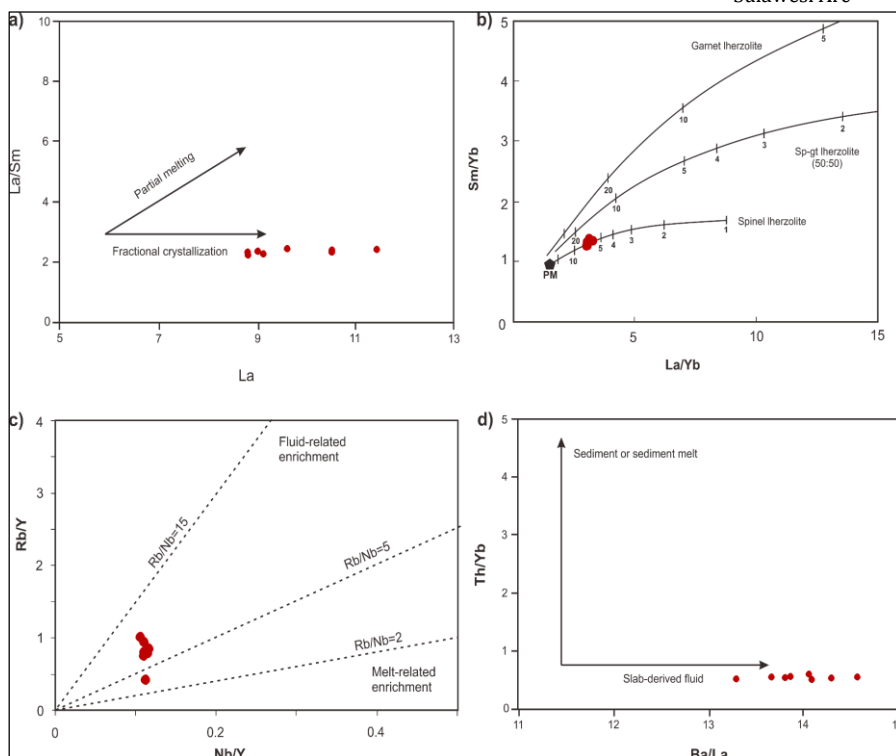


Fig 6. Tectonic settings discriminant diagrams for Ponelo Basalts. (a) La-La/Sm diagram (Allègre and Minister, 1978) to distinguish between fractional crystallization or partial melting in Ponelo volcanic rocks genesis. (b) La/Yb-Sm/Yb diagram to identify mantle source (Zhao dan Zhou, 2009) (c) Nb/Y-Rb/Y diagram (Zhao dan Zhou, 2007) shows the samples fluid-related enrichment dominant than melt-related enrichment, and (d) Ba/La-Th/Yb diagram suggest slab-derived fluid in the samples.

The majority of magmatic rocks have undergone varying degrees of fractional crystallization (FC) and partial melting (PM). La/Sm ratio (2,26-2,46) vs La (8,8-11,4) discriminant diagram (Allegre and Minster, 1978) shows that fractional crystallization plays a dominant role instead of partial melting in the genesis of Ponelo Basalts (Fig 6a). Partial melting 'fingerprints' are recorded in samples even though fractional crystallization dominated the genesis process. According to Mckenzie and Bickle (1988), the Ponelo Basalts comparatively low Ce/Y composition (0.74-0.76) raises the possibility that they were formed within a spinel-garnet stability environment. The discriminant diagram of La/Yb vs Sm/Yb ratio (Zhao and Zhou, 2009) (Fig 6b) shows Ponelo Basalts plot in spinel melting curves with primitive mantle starting composition, with approximately ~5% partial melting of spinel lherzolites mantle source. Eu negative anomaly of Ponelo Basalt also suggests an absence of garnet in mantle source (Rollinson, 2014).

In addition to slab melts, the subducted sediments or fluids, from the subducting slab are frequently added to the overlying mantle wedge during subduction LILE/LREE, and HFSE/LREE and other trace elements ratio are effective to know potential crustal material contamination in magma. The value of crustal material are Ba/Nb= 54, Ba/Th= 124, Rb/Nb= 4.7, K/Nb= 1341, Ba/La= 25, Th/La= 0.204, La/Nb= 2.2 and values of mantle-derived oceanic basalt are Ba/Nb= 4.3-17.8, Ba/Th= 39-204, Rb/Nb= 0.30-1.41, K/Nb= 66-432, Ba/La= 4-16.6, Th/La= 0.089-0.183, La/Nb= 0.64-1.19 (Weaver, 1991). These ratios suggest that Ponelo volcanic rocks were contaminated by crustal material even though there are variations of the ratio value (Ba/Nb= 39.03-45.28, Ba/Th= 75.52-82.67, Rb/Nb= 3.93-6.22, K/Nb= 1772.22-2703.45, Ba/La= 13.67-14.57, Th/La= 0.17-0.18, La/Nb= 2.91-3.16). The Nb/U ratio of primitive mantle has 30, while the typical value for continental crust and island arc rocks is 10 (Hofmann, 1997). Therefore, Ponelo volcanic rocks has been depleted of Nb/U (6-6.74) implying additional amounts or recycled sediment to the source mantle.

Depletion of HFSEs and enrichment of LILEs and LREEs are primarily attributed to additional slab-dehydrated fluid in the mantle due to contamination from the upper crust (Pearce, 1982; Plank and Langmuir, 1998; Wilson, 2007; Rollinson, 2014). The fluid-related enrichment in Ponelo Basalt magmatism is shown in the Rb/Y ratio (0.019-0.025) vs Nb/Y ratio (0.10-0.11) diagram (Zhao and Zhou, 2007) (Fig. 6c). The negative Ce anomalies value (Ce/Ce* = 0.93-0.95) suggests the presence of fluids produced by the subducted slab's pelagic sediments' dehydration (Gill, 2012). Fig. 6d shows Th/Yb ratio (0.52-0.61) vs Ba/La ratio (13.29-14.57) (Woodhead et al., 2001) involvement of slab-derived aqueous fluids dominates rather than subducted sediment-derived melts.

We assume, the petrogenesis of Ponelo Basalts involved fluids, crustal contamination, and some melts of lherzolite mantle. Though the theory of crustal contamination doesn't appear to fit with the lack of xenoliths and enclaves as occurred in the formation of granites and diorite enclaves as interaction between crust and mantle during the early Miocene in North Sulawesi Arc (Gan et al., 2022), the "cryptic crustal contamination" proposed by Chen et al. (2013) is speculation for this phenomenon.

5.2 Tectonic Settings of Ponelo volcanic rocks.

The Ti/Y-Zr/Y diagram (Pearce and Gale, 1977) (Pearce and Gale, 1997) are also used (Fig. 7a) to distinguish between basalts formed at the plate boundary and formed within-plate, which are the samples plot in plate boundary. The Th/Yb-Ta/Yb and Zr-Ti plot diagrams (Pearce, 1982), and Th/Yb-Nb/Yb plot diagram (Pearce, 2008) show more specifically that Ponelo volcanic rocks is part of an *island arc/oceanic arc* with calc-alkaline affinity, where this findings are consistent with island arc basalt (subduction products) pattern which has enriched LILEs, Pb, LREE and depletes HFSEs and HREE (Zheng et al., 2020). The samples exhibit low Nb/La ratios (0.31-0.34) and low Nb concentrations (2.9-3.6 ppm) indicated island arc basalts (Xia and Li, 2019). Some LILEs enrichments are assumed to have been created by the inclusion of these elements at the subducted plate source and the presence of negative Nb anomalies may be attributed to the preservation of this element in the residual phase when fractionation (Pearce, 1982; Wilson, 2007). The Th/La ratio of Ponelo volcanic rocks (0.17-0.18) also shows typical island arc lava which is higher than N-MORB (<0.1) and lower than marine sediment (>0.2) (Plank, 2005). The Hf/3-Th-Ta tectonomagmatic ternary diagram (Wood, 1980) show the Ponelo volcanic rocks is the typical of calc-alkaline diagram.

Tectonics models that potentially explain the origin of the Ponelo volcanics rocks in North Sulawesi Arc, such as: (1) northward subduction of Indian Ocean plate from the late Eocene to mid Miocene (Nichols and Hall, 1999; Zhang et al., 2022; Advokaat and van Hinsbergen, 2024) (2) southward subduction of Celebes Sea began ~5Ma and continues now (Hall, 2012; Dong et al., 2022; Song et al., 2022; Advokaat and van Hinsbergen, 2024). It is important to understand that the Celebes Sea is immature subduction slab without arc magma, where the slab 's depth along North Sulawesi Arc is a mere 60-80 km. This subduction lacks a volcanic arc due to circumstances, including the low-angle dip and the shallow slab dehydration depth (around 60-80 km) causes small amount of water entering the heated core of the mantle wedge, and the young subducted plate (Hall, 2019; Dong et al., 2024). The following implies that the Ponelo volcanic rocks are not associated with the southward subduction of Celebes Sea, instead represent the Indian ocean subduction.

The Ponelo volcanic rocks with calc-alkaline affinity exhibit a trend that is similar to the North Sulawesi Arc calc-alkaline (CA NSA) basalt-andesite type, particularly with enrichment in LILE and LREE along with depletion in HFSE and HREE. However, there are some significant distinctions between these two categories that distinguish Ponelo volcanic rocks from CA NSA basalt-andesite researched by Polvé et al. (1997) and Rangin et al. (1997). Several distinctions between them are LREE/HREE ratio in CA NSA basalt-andesite type is higher ($5 < (La/Yb)_N < 10$) than that of the generally flatter Ponelo volcanic rocks ($(La/Yb)_N = 2.15-2.37$) and LILE&LREE more depleted of Ponelo volcanic rocks. We suggest that the difference of geochemical signatures among the Ponelo volcanic rocks and CA NSA basalt-andesite show the different magma source/storage of them in the same subduction process. Geochronology and isotope studies are needed in the future for more detailed information about this volcanic rocks.

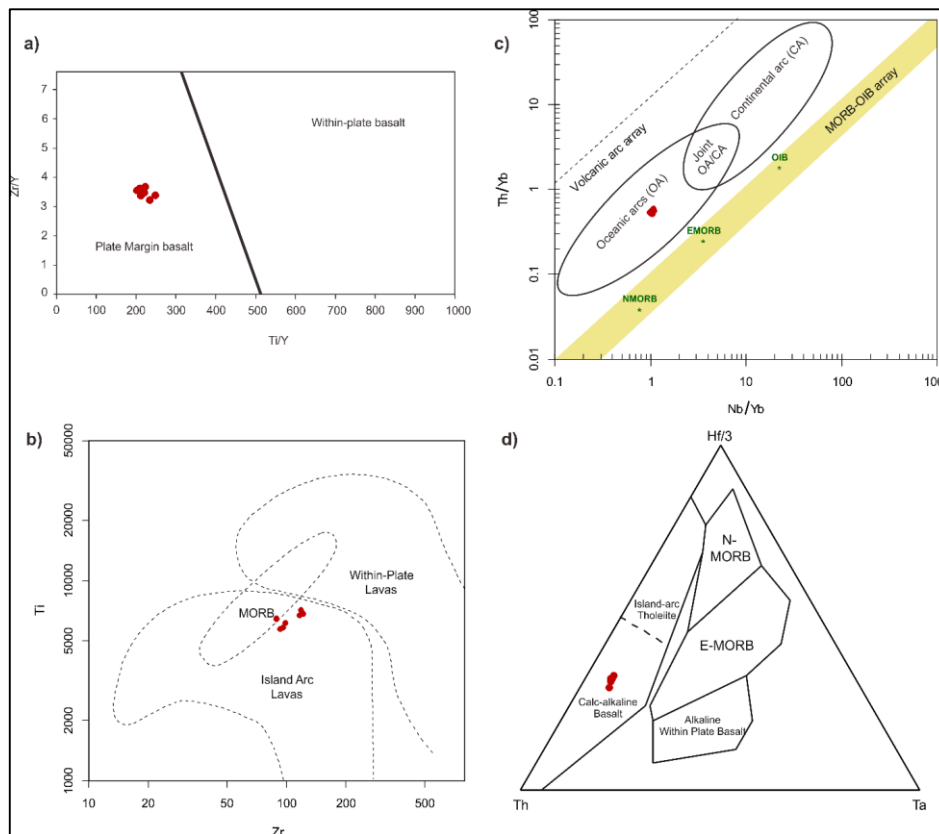


Fig 7. Tectonic settings discriminant diagrams for Ponelo Basalts. (a) Ti/Y-Zr/Y diagram (Pearce and Gale, 1997) to distinguish between basalts formed at the plate boundary and formed within-plate. (b) Zr-Ti diagram and (c) Nb/Yb-Th/Yb diagram (Pearce, 1982) shows the island arc/oceanic arc tectonic setting. (d) WOOD 1980

6. Conclusion

The new trace and rare element geochemical analyses of volcanic rocks in Ponelo Island imply the following conclusions:

- Ponelo island volcanic rocks are composed of basalt-basalt andesitic with calc-alkaline affinity.
- Ponelo basalts were generated by fractional crystallization, ~5% of spinel lherzolite mantle sources partial melting metasomatized by slab-derived fluids and cryptic crustal contamination.
- Tectonic settings of Ponelo volcanic rocks are characterized by Island arcs with enrichment in LILE&LREE and depletion of HFSE&HREE.

Acknowledgements

The author would like to acknowledge the Indonesia Education Scholarship (BPI) under the Education Financing Service Center (PUSLAPDIK), Ministry of Education, Culture, Research and Technology for its scholarship funding support. We thank colleagues for their help during field excursions in Ponelo Island.

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