

RESEARCH ARTICLE

Geochemical Correlation of Volcanic Rocks and Groundwater Quality in the Todoko-Ranu Complex, Sahu District, West Halmahera, North Maluku, Indonesia

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Abstract

The research area is located in the Mount Todoko-ranu complex and its surroundings, Sahu District, West Halmahera Regency, North Maluku, Indonesia. This area geologically consists of Quaternary volcanic rocks with various petrochemical composition. On the other hand, natural water found in the research area generally physically appears turbid, while people who take water from this sites actually need clean water. As it is known, groundwater quality is influenced by the geochemistry of the aquifer through which it flows, therefore it is important to conduct a study on the geochemical correlation of volcanic rocks and groundwater quality in the research area. Thus, the aim of this research is to examine the geochemical characteristics of Mount Todoko-Ranu complex volcanic rocks, to analyze groundwater quality, and to study the correlation between the geochemical characteristics of rocks and the quality of groundwater in this volcanic complex. Methodology applied in this study was geological mapping, rock samples testing to determine the mineralogy chemical composition, groundwater, and surface water samples testing to identify their quality, and then correlation analysis. The results show that andesitic and basaltic-andesite of calc-alkaline volcanic rock complex is correlative to no dominant cation, but bicarbonate anion, or mixing type of natural water.

Keywords: Geochemistry, groundwater quality, no dominant cation, bicarbonate anion, Todoko-Ranu complex

1. Introduction

Todoko-Ranu is a volcanic complex which no longer active. There is a caldera with a diameter of 2.5 km and a height of ~979 meters above sea level. Apart from that, in this area, there are 2 (two) other eruption centers, namely Mount B'anyo Doi and Mount Uno. The volcano is predominantly constructed by lava, breccia, and tuff (Supriatna, 1980). In this complex, there is also a residential, livestock, and agricultural area, therefore the need for water is relatively extensive volume (<https://id.scribd.com/document/431745834/Rpjm-halbar>).

The large water demand is often faced with water quality in the area being inadequate to meet drinking water needs (Maulana, et al, 2019, Pinning, et.al, 2023). The natural water in the research area physically always appears turbid. It is suspected that the quality of groundwater in the study area is influenced by the volcanic rock chemical composition of these volcanoes. Therefore, it is necessary to conduct research related to the correlation of geochemical characteristics of the volcanic rocks, and groundwater quality of the study a.

The aim of the research is to examine the volcanic petrochemistry of Mount Todoko-Ranu complex, to analyze the geochemical characteristics of the rocks, assessing groundwater quality, and studying the influence of rock geochemical characteristics on the groundwater quality of Todoko-Ranu complex.

The research area administratively is included in several villages, namely Golago Kusuma Village, Sasur Village, and Goro-Goro Village as well as three sub-districts, namely Sahu District, East Sahu District and South Ibu District, West Halmahera Regency, North Maluku Province. It is 14 Km long and 4.5 Km wide. It can be reached about 30 minutes travelling

from the capital city of West Halmahera Regency, Jailolo (Figure 1).

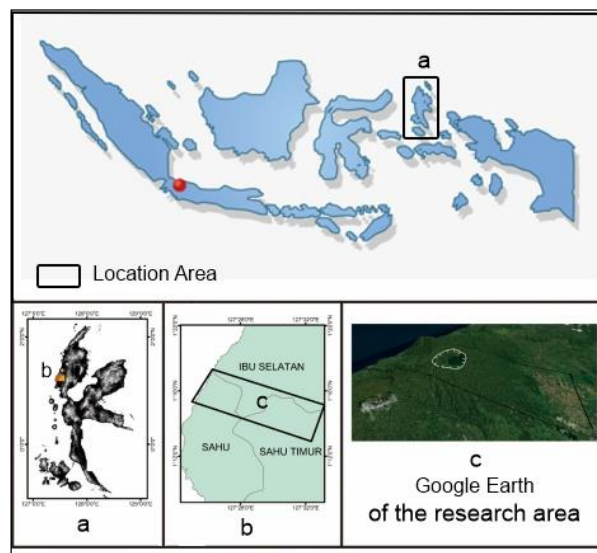


Fig. 1. Location map of the Research area

2. Methods of the Study

The methods applied in this research include surface geological mapping, remote sensing interpretation, geomorphological analysis, hydrochemical analysis, and geochemical studies. Geological mapping was carried out to obtain an overview of the lateral distribution of volcanic

lithology name was done by using petrography analysis (mineral assemblages), while the petrochemistry data was derived from XRF (X-ray Fluorescence) method.

Water samples were also collected, including groundwater and surface water to test the water quality, especially for the chemical aspects. Water sampling was done during dry season. Groundwater sampling was carried out at nine locations representing the research area. Six (6) samples were taken from springs, two (2) samples from surface flows and river, and one (1) sample was from the caldera lake. Testing was carried out physically, biologically, and chemically.

Groundwater quality analysis was carried out, guided by the Regulation of the Minister of Health of the Republic of Indonesia No. 2, 2023 concerning the Standards for Environmental Healthiness (Permenkes No.2, 2023). The hydrochemical test results were then plotted into a Stiff diagram, as well as Piper trilinear diagram, for water geochemistry analysis (Freeze & Cherry, 1979). Comparison analysis between hydrochemistry and rock mineralogy was carried out to ascertain the influence of lithology on groundwater quality in the study area (Maulana, et al, 2019).

2. Results and Discussion

2.1 Geology

Physiographically, the research area is included in the North West Halmahera zone (Setyanta & Setiadi, 2011). In the research area, there are three volcanic eruption centers, namely Todoko-Ranu, B'anyo Doi, and Uno, but currently these volcanoes are no longer active (Setyanta & Setiadi, 2011). These three eruption centers produced lithology that can be grouped into several rock units, as their distribution and description are elaborated in the following discussion.

The lithology that makes up the research area consists of volcanic rock units as the products of the three eruption enters. Volcanic rock of Todoko-Ranu comprises Todoko-Ranu andesite-basaltic lava 1 unit (Tla1), Todoko-Ranu andesite-basaltic lava unit 2 (Tla2), Todoko-Ranu andesite-basaltic lava unit 3 (Tla3), Todoko-Ranu andesite lava unit 4 (Tla4), Todoko-Ranu pyroclastic fall unit (Tjp), Todoko-Ranu laharic unit (TL), and Anak Todoko-Ranu andesite lava unit (Atla).

Volcanic rocks of B'anyo Doi consists of B'anyo Doi basaltic-andesite lava unit (Bla), and B'anyo Doi laharic breccia unit (Bl). On the other hand, volcanic rocks of Uno are composed of Uno andesite-basaltic lava unit 2 (Ula2), and Uno laharic breccia unit (Ul). All the lava belong to lava flows.

Todoko-Ranu andesite lava unit 4 (Tla4) is not only composed of lava but also tuff sourced from the Todoko-Ranu center of eruption. The lava texture is hypocrySTALLINE, medium aphanitic-phaneric, and subhedral, vitrophyric, with mineral composition of plagioclase (andesine, labradorite), pyroxene, hornblende, opaque minerals, and glass groundmass (Figure 3). The rock name is andesite (Streckeisen 1979, LeBas et al, 1986). Tuff texture is poorly sorted, open fabric, subrounded, supported by silic material, ferromagneccian, composition: quartz, plagioclase, hornblende, glass shard, opaque minerals (Figure 4), name: vitric tuff (Pettijohn, 1975).

Pyroclastic fall unit of Todoko-Ranu (Tjp) consists tuff and lapilli. The tuff is glass tuff (Pettijohn, 1975), while the lapilli belongs to lapilli tuff (Fisher 1966).

Todoko-Ranu laharic breccia unit is composed of andesite fragments (Figure 5) and sub-archosic arenite matrix (Pettijohn 1957). Anak Todoko-Ranu (Atla) andesite lava is the product of volcanic activity of the young Todoko-Ranu cone, in the form of lava dome, the rock name is andesite (Streckeisen 1979, LeBas et al., 1986).

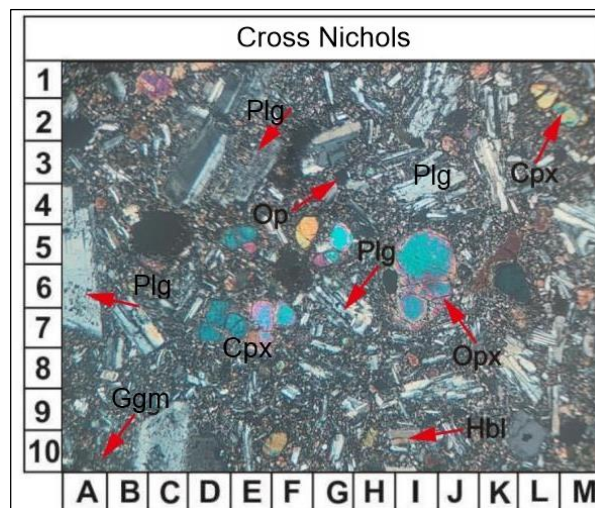


Fig. 2. Petrography of basaltic-andesite lava, showing intergranular texture, plagioclase, pyroxene, hornblende with microcrystalline and glass groundmass

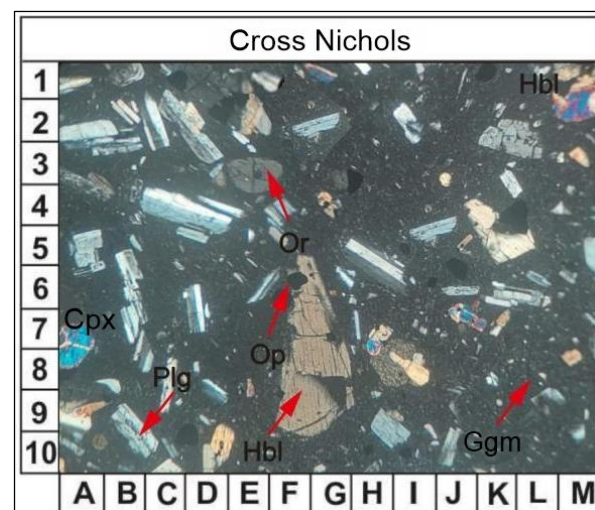


Fig. 3. Petrography of andesite lava, showing vitrophyric texture, plagioclase, pyroxene, hornblende, orthoclase, with glass groundmass

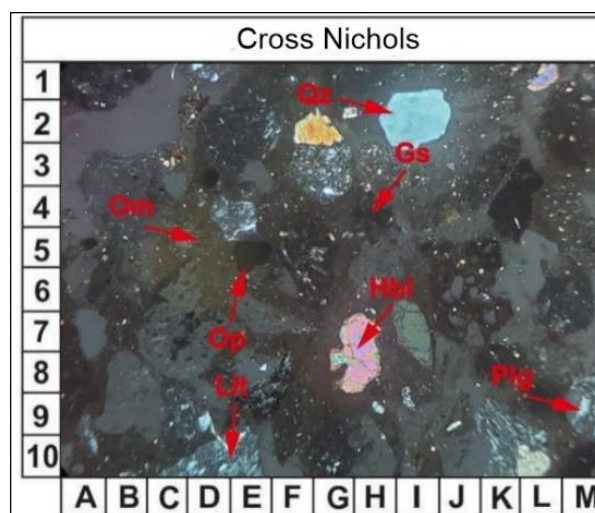


Fig. 4. Petrography of tuff lapilli, showing poorly sorted, open fabric, subrounded, supported by silic material, quartz, plagioclase, hornblende, opaque minerals, and glass shard

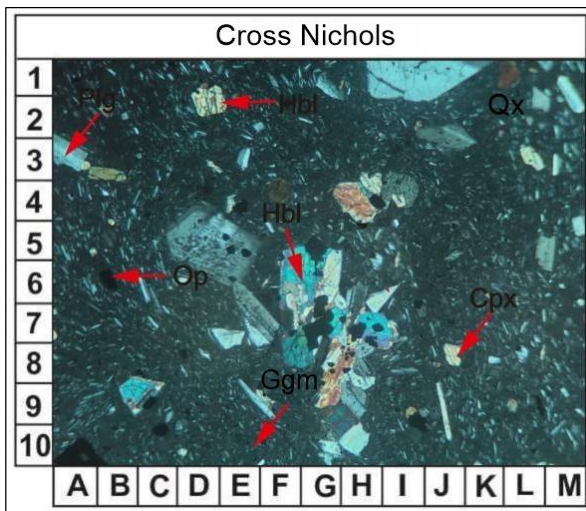


Fig. 5. Petrography of andesite fragment of lahar, showing phylotaxitic texture, plagioclase, pyroxene, hornblende, orthoclase, with microlites and glass groundmass

B'anyo Doi basaltic-andesite lava unit (Bla) is characterized by texture of hypocrySTALLINE, medium aphanitic-phaneric, subhedral, porphyro-aphanitic, phylotaxitic, composition: plagioclase (andesine and labradorite), pyroxenes, hornblende, opaque minerals, microcrystalline and glass groundmass

(Ggm), name: basalt (Streckeisen 1979), basaltic-andesite (LeBas et al, 1986). B'anyo Doi laharic breccia unit (Bl) is polymixed laharic breccia, basalt fragment (Streckeisen 1979), basaltic-andesite (LeBas et al, 1986), andesite fragment (Streckeisen 1979), with subarcose arenite matrix (Pettijohn 1957).

Uno basaltic-andesite lava 2 unit (Ula2) consists of lava from the Uno center of eruption, characterized by texture of hypocrySTALLINE, medium aphanitic-phaneric, subhedral, phylotaxitic, composition: plagioclase (andesine & labradorite), hornblende, pyroxene, opaque minerals, glass groundmass, name: andesite (Streckeisen 1979), basaltic-andesite (LeBas et al, 1986). The basaltic-andesite lava Uno 2 unit (Ula2) texture is hypocrySTALLINE, medium aphanitic-phaneric, subhedral, porphyritic, phylotaxitic, composition: plagioclase (andesine), pyroxene, glass ground mass, hornblende, opaque minerals, name: andesite (Streckeisen 1979), basaltic-andesite (LeBas et al, 1986). Uno laharic breccia unit (Ul) is composed of andesite fragments, and lithic arenite matrix (Pettijohn 1975).

There are normal faults as the geological structures in the research area, with a northwest - southeast and northeast - southwest strikes (Figure 6). The evidences of the fault are the existence of fault planes with slickensides. Besides the normal faults, a ring escarpment can be identified surrounding the Todoko-Ranu caldera. The volcanic stratigraphy of the research area referring to Bronto, 2006 can be seen in Figure 7.

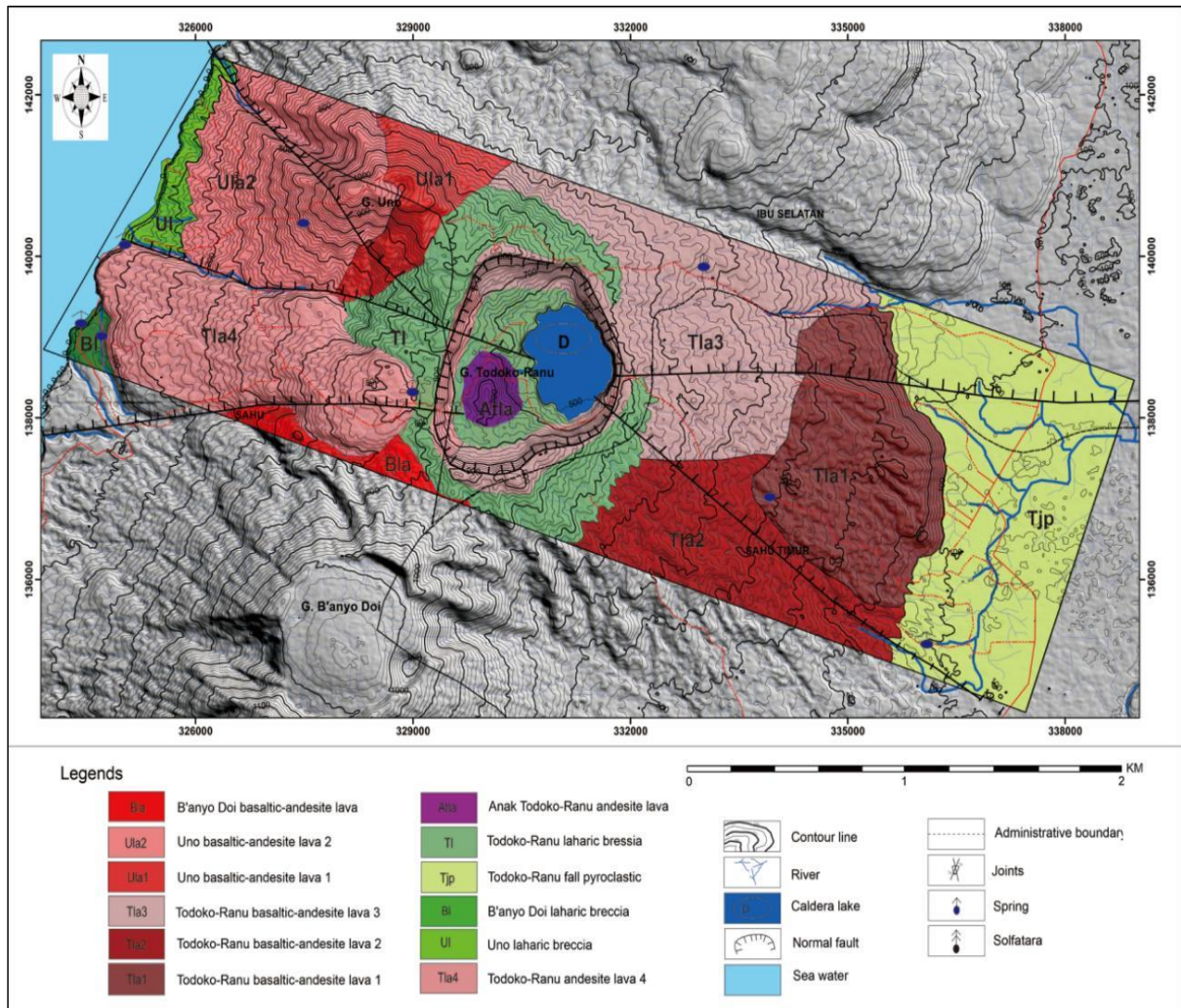


Fig 6. Geological Map of the Research area, showing that there are 3 eruption centers, namely G. (gunung) Todoko-Ranu, G. Uno, and G. B'anyo Doi

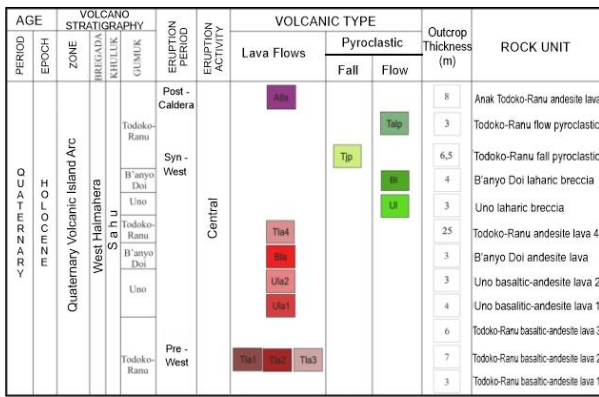


Fig 7. Volcanic stratigraphy of Todoko-Ranu complex, referring to Bronto, 2006

3.3. Geochemical Analysis

Twelve (12) samples have been taken form of lava and breccia fragments in the research area to be tested for whole-rock geochemistry, and peptrography analyses. Various predominant minerals are found in the samples, such as pyroxene, hornblende, plagioclase (labradorite and andesine), and little number minerals of quartz, orthoclase, and muscovite. Opaque minerals are generally present in every sample. The chemical composition of samples in the research area is shown in Table 1.

Based on mineralogical composition mentioned above, it can be affirmed, that magma as the origin of volcanic rocks in the research area is calk-alkaline (Cas & Wright, 1987). It produced basaltic-andesite and andesite rocks types (Eichelberger, 1995, Rompo, et.al, 2023). Calk-alkaline magma affinity generally occurs in convergent tectonic environments

(Eichelberger, 1995, Fisher & Smith, 1991). In the thin sections it is displayed by the presence of phenocrysts which tend to be diverse such as pyroxene, plagioclase and hornblende as well as a slight presence of quartz (Bogie & Mackenzie, 1998, Rompo, et.al, 2023).

Geochemically in the magma differentiation process, it is known that the CaO compound decreases with the increase of SiO₂, which is then followed by the increase in Na₂ O (Fadlin & Wildan, 2018, Fisher & Smith, 1991). These two compounds are known to come from the mineral plagioclase which experiences a change in ions, namely Ca and Na, along with an increase in the SiO₂ compound which is in line with a decrease in temperature (Zulkarnaen, 2008). However, from the low value of the correlation coefficient, it is suspected that there is another process taking place, namely magma assimilation (Cas & Wright, 1987). The decrease in the concentration of Fe₂ O₃, TiO₂ and MgO compounds occurred along with the increase in SiO₂. These three compounds are the main components carried by the mafic minerals of olivine and pyroxene, where if fractionation proceeds normally, their concentration will decrease, while SiO₂ will increase (Zulkarnaen, 2008, Ipranta et al, 2019). The concentration of Al₂ O₃ and P₂ O₅ compounds decrease along with the increase of SiO₂ which was caused by an increase in volatile volume, when the temperature decreases (Eichelberger, 1995). The value of the K₂ O compound increases as the SiO₂ value increases, indicating that the nature of the rock becomes more acidic (Zulkarnaen, 2008).

In the Todoko-Ranu volcanic complex, there are two types of rock namely andesite-basaltic and andesite. This difference can be seen from the composition of the SiO₂ compound, eight (8) rock samples fall into andesite-basaltic and four (4) rocks fall into andesite.

Table 1. Chemical compounds of the volcanic rocks in the research area

Sample Code	Lithology	Major Elements (%)									
		SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	CaO
13	Basaltic-andesit Lava (Tla1)	54,28	1,33	18,36	8,01	0,34	3,79	1,01	1,33	1,11	10,18
29	Basaltic-andesit Lava (Tla2)	54,95	1,28	18,27	7,89	0,23	3,61	1,19	1,03	1,08	11,52
38	Basaltic-andesit Lava (Tla3)	55,59	1,21	18,22	7,77	0,35	3,40	1,48	1,32	1,01	14,19
34	Basaltic-andesit Lava (Ula1)	56,76	1,18	18,15	7,59	0,30	3,33	2,04	1,02	0,93	10,94
29	Basaltic-andesit Lava (Ula2)	55,45	1,14	18,06	7,47	0,25	3,20	2,78	1,65	0,87	4,83
22	Basaltic-andesit Lava (Bla)	56,69	1,05	17,97	7,77	0,30	3,67	2,85	1,32	1,02	8,85
27	Andesite Lava (Tla4)	61,75	0,97	17,88	7,35	0,26	2,90	2,89	1,76	0,78	8,36
36	Laharic Breccia Fragment (TI)	56,70	1,19	18,21	7,81	0,24	3,60	1,07	1,75	1,07	9,92
28	Laharic Breccia Fragment (UI)	57,02	1,12	18,07	7,50	0,26	3,19	2,56	1,12	0,89	11,77
17	Laharic Breccia Fragment (BI)	58,79	0,99	17,96	7,60	0,23	3,50	2,15	1,69	1,04	5,35
11	Pyroclastic Breccia Fragment (Tjp)	55,90	1,19	18,25	7,78	0,20	3,20	2,32	1,59	0,94	10,72
12	Andesite Lava (Atla)	61,87	0,87	17,76	7,27	0,25	2,78	3,45	1,56	0,72	6,15

a. Hydrogeology

Hydrogeological setting of the research area is developed of a moderately productive aquifer system with wide distribution, a lake as groundwater discharges, and a productive aquifers. Based on the type of lithological openings, water-bearing layers can be divided into fractured aquifer, intergranular aquifer, and fractured aquitard.

The fractured aquifer system is composed of basaltic-andesite and andesite lava with joint, vesicular, and sheeting joint structures. The intergranular aquifer system is composed of laharic breccia, lapilli tuff, and tuff, and locally there is a coarse sandstone layer. The fractured aquitard system is composed of basaltic-andesite and andesite lava.

In the research area, some springs can be classified into three types, namely: contact spring, depression spring, and fissure spring (Asdak, 2002). Contact spring is formed due to the

interconnection between two lithologies that have different hydraulic properties. In the study area, it is represented by lava at the bottom and breccia at the top part. Depression spring is developed due to the cutting of the groundwater table by topography. There are two depression springs in the laharic breccia lithology, found in the valley. Fissure springs are non-gravitational springs that result from fissures or joints and fault zones where groundwater flows from the inside out due to pressure differences (Asdak, 2002).

b. Water Quality

As mentioned above, groundwater quality analysis was guided by the Regulation of the Minister of Health of the Republic of Indonesia No. 2, 2023 (Permenkes No.2, 2023). Testing was carried out physically, biologically, and chemically. Chemical analysis of cation and anion of the water

samples was done to determine groundwater facies (Fariz, et al, 2018, Freeze & Cherry,1979).

From the results of the physical analysis (Table 2) it can be seen that among the 9 groundwater samples that were physically tested, the sample taken from the Todoko-Ranu caldera lake exceeded the threshold for clean water.

From the results of the chemical analysis (Table 6), it was found that three samples were chemically unfit, namely samples

30, 2 and sample from the lake, because they exceeded the predetermined hygienic standards. Sample 30 is not suitable due to the fluoride (F) compound. Sample 2 is not suitable due to the fluoride (F) compound and Detergent compound (NaC₁₂H₂₅SO₄). The lake sample is not suitable because it also contains fluoride (F) compounds.

Table 2. Physical properties of water samples

Sample code	Lithology	pH	TDS (ppm)	Parameters		
				Odor	Taste	Temperature
2	tuff	6.48	98	-	-	30
5	lapilli, tuff	6.17	55	-	-	32
9	basaltic-andesite lava	7.4	28	-	-	35.6
23	laharic breccia	7.5	30	-	-	40
27	andesite lava	7.55	67	-	-	35.7
30	basaltic-andesite lava	6.91	45	-	-	33.8
38	Basaltic-andesite lava	7.1	26	-	-	31.3
44	Andesite lava	6.52	23	-	-	29
Lake	Laharic breccia	7.1	86	Smelly	tasty	27

In order to analyze water quality in the research area, the concentration of the hydrochemical composition of the samples, with the cations of Ca, Mg, Na+K (ppm), and the anion compounds of Cl, SO₄, HCO₃+CO₃ (ppm), which are then plotted into trilinear Piper diagram and Stiff diagram. Based on the trilinear plot, the nine water samples fall into several sub types of cations and anions, and draw into three different types of water facieses, namely sodium chloride, calcium sulfate, and calcium bicarbonate (Figure 8).

Based on the result of Stiff diagram plot (Figure 9), it can be seen, that each groundwater sample has different pattern for cation and anion chemical compounds. This shows that the water quality of each sample location contains different

chemical compounds concentrations. As it has been elaborated above, that each water sample was taken from different lithology. It is interpreted that the water interact with the lithology will influenced by the chemical composition of the rock (Kusumayudha, 2005). Rock or petrological chemical composition of rocks is defined by their mineral composition (Fariz, et al, 2018; Kholqi, et al, 2018) of each constituent rock that is passed through by groundwater.

Biological testing was done to detecting e-coli and coliform content of the samples. Results of the biological tests (Table 3) on nine water samples, 5 samples were not suitable and 4 samples were suitable for clean water. Types of water in the research area are detailed in Table 4.

Table 3. Biological properties of the water samples

Sample Code	Lithology	E-Coli (CFU/100ml)	Coliform (CFU/100ml)
2	tuff	200	32
5	lapilli, tuff	36	4
9	basalic-andesite lava	0	1
23	pumice	0	0
27	andesite lava	1	0
30	Basaltic-andesite lava	1	2
38	Basaltic-andesite lava	0	1
44	Andesite lava	0	1
Lake	Laharic breccia	164	24

Table 4. Water types of the research area based on hydrochemical Piper plots

Sample Code	Lithology	pH	TDS (mg/l)	Cation	Anion	Water Type
2	Tuff	6.48	98	No dominant	Bicarbonate	Mixed
5	Lapilli, Tuff	6.17	55	Magnesium	No dominant	Mixed
9	Basaltic-andesite lava	7.4	28	No dominant	Bicarbonate	Mixed
23	Pumice	7.5	30	No dominant	Chloride	Mixed
27	Andesite lava	7.55	67	Sodium + Potassium	Chloride	Sodium-chloride
30	Basaltic-andesite lava	6.91	45	No dominant	Bicarbonate	Mixed
38	Basaltic-andesite lava	7.1	26	No dominant	Bicarbonate	Mixed
44	Andesite lava	6.52	23	No dominant	No dominant	Mixed
Lake	Laharic breccia	7.1	86	Magnesium	Bicarbonate	Magnesium-bicarbonate

3.4. Correlation of Volcanic Rocks Petrochemistry and Groundwater Quality

Referring to the geochemical discussion of the chemical composition of the rock, it is known that the CaO value decreases with the increase of SiO₂ followed by an increase of the Na₂ O value. These two main compounds are identified to be the constituents of plagioclase (Ipranta & Irzon, 2019). The

geochemistry also shows that Fe₂ O₃ , MnO, and MgO compounds decrease along with a rough increase of SiO₂ . The carriers of the three compounds mentioned are olivine and pyroxene. The K₂ O value increases as the SiO₂ value increases, indicating that the rock becomes more acidic in the differentiation process (Mesker & Dirk, 2008; Fadlin & Wildan, 2018). A comparison between volcanic rock petrochemistry and hydrochemistry in the research area can be

seen in Figure 10. Based on these figures it can be concluded that the correlation between the geochemistry of the main elements of rocks and the chemistry of groundwater in the research area is that, there is an interrelated between the chemical elements in rocks and the elements in groundwater. The mineral elements in rocks are subjected to dissolution, hydrolysis, and ion exchange (Freeze & Cherry, 1979) The mineral elements in rocks are subjected to hydrolysis by meteoric water and groundwater, so that some chemical compositions release, dissolve, or carried with water, and some precipitate with the rock (Maulana, et al, 2019).

The minerals that greatly contribute to determining the concentration of chemical elements in groundwater are

plagioclase, providing Ca, Na and K cations, while mafic (pyroxene, hornblende) minerals release Mg and Fe which are then dissolved in groundwater (Freeze & Cherry, 1979, Suganda, et al, 2021).

The dominant bicarbonate in groundwater is thought to come from the interaction between meteoric water and air, especially CO₂ in the rain precipitation process and CO₂ found in soil and rocks in aquifers. The mineral elements in rocks are subjected to hydrolysis by meteoric water and groundwater, so that some chemical compositions release, dissolve, or carried with the water, and some precipitate with the rock.

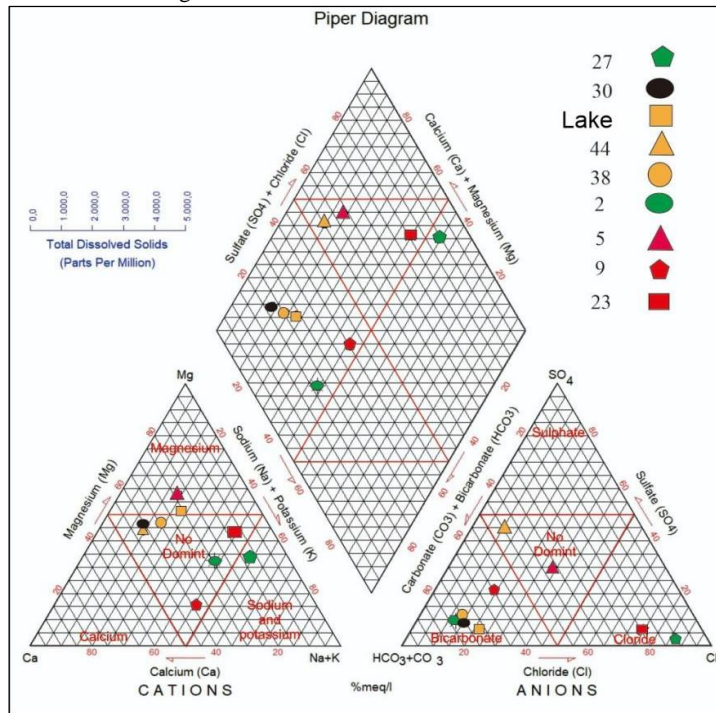


Fig. 8. Piper diagram plot of the hydrochemistry, showing sodium-chloride, magnesium-bicarbonate, and mixed types

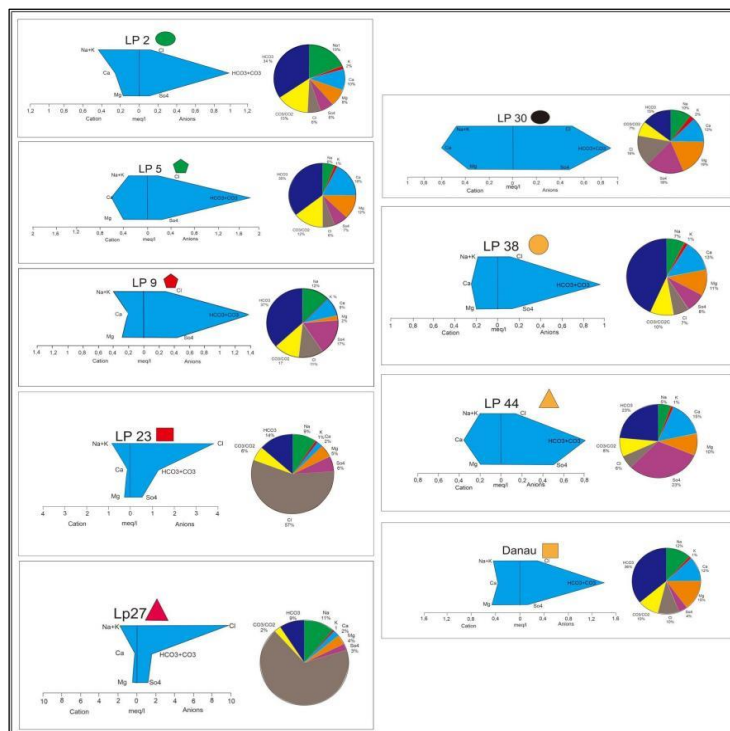


Fig. 9. Stiff and pie diagram plots, showing the distribution of cation and anion dissolved in the groundwater



Fig. 10. Comparison of petrochemistry, hydrochemistry, and mineral composition of the lithology where the groundwater sample were taken

4. Conclusions

The conclusions of this research are as follows:

1. Lithology of the research area is divided into twelve rock units, namely Todoko-Ranu basaltic-andesite lava unit 1, Todoko-Ranu basaltic-andesite lava unit 2, Todoko-Ranu basaltic-andesite lava unit 3, Todoko-Ranu andesite lava unit 4, Anak Todoko-Ranu andesite lava unit, Uno basaltic-andesite lava unit 1, Uno basaltic-andesite lava unit 2, B'anyo Doi basaltic-andesite lava unit, Uno laharic unit, B'anyo Doi laharic unit, Todoko-Ranu pyroclastic fall unit, and Todoko-Ranu laharic unit.
2. Geochemistry of the main elements of volcanic rocks in Todoko-Ranu volcanic complex is estimated to be sourced from a mixture of melted rocks from continental and oceanic crust in a subduction zone, represented by basaltic-andesite and andesite.
3. The hydrogeology of the research area is divided into two water bearing layers, namely aquifer and aquitard. The aquifer system is divided into two parts by lithological arrangement, namely the fractured aquifer system and the

intergranular aquifer system. The aquitard in the research area is a fractured aquitard system.

4. The groundwater types can be divided into three types, namely: Sodium chloride, magnesium bicarbonate, and mixed, which from the results proves that the chemical element content of groundwater is related to the chemical elements of rocks.
5. The quality of the groundwater in the research area refers to the 2017 Ministry of Health Regulation No. 37 concerning hygienic water, from the physical, chemical, and biological parameters, several water samples are suitable, while some samples are not suitable for clean water.
6. The correlation between the geochemistry of the main elements of rocks and the chemistry of groundwater in the research area can be stated that there is an interrelation between the chemical elements of rocks and the elements of groundwater. The chemical elements of rocks are subjected to hydrolysis, dissolution, and ion exchange with meteoric water and groundwater, so that parts of the chemical compositions release and some bind with minerals of the rock.

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