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Analysis of Cobalt Distribution and Co-Ni Correlation in Nickel Laterite Zonation in Tropical Region

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Abstract

Cobalt is a key metallic element required in the manufacture of lithium-ion batteries in the electric car industry, which has led to increased demand for cobalt globally. Cobalt is found associated with laterite nickel deposits but generally at lower levels. This study aims to analyze the distribution of cobalt in the laterite zone, determine cobalt-rich zones, determine cobalt-forming minerals in the limonite, saprolite and bedrock zones. As well as determining the average cobalt content in each nickel laterite zone, and determining the correlation between Co and Ni in the laterite zone. The research methodology was carried out by conducting petrographic analysis on bedrock samples to determine cobalt-forming minerals. Furthermore, X-Ray Diffraction analysis was carried out on limonite and saprolite zone samples to determine the mineral content and cobalt-forming minerals. Furthermore, conduct X-Ray Fluorescence analysis at 12 drill points to determine the percentage of cobalt elements in each laterite zone. Based on the research results, it is known that the distribution of cobalt at 12 drill points has levels in the limonite zone ranging from 0.05-0.12% Co, saprolite zone 0.02-0.05% Co, and the bedrock zone ranges from 0.01-0.04% Co. So it can be concluded that the highest cobalt distribution is in the limonite zone and the average cobalt content in the limonite zone is 0.082%; saprolite zone is 0.029%; and bedrock zone is 0.02%. The mineral identified as the cobalt-forming mineral in the bedrock samples in the study area is the mineral antigorite. The Co-Ni correlation coefficient values range from 0.01 to 0.22.

Keywords : Distribution of Cobalt; Laterite Nickel; Limonite; Saprolite; Bedrock

1. Introduction

The world's technology leads to environmentally friendly industries, and one of the trending industries today is the electric car industry. Cobalt is the main metal element needed to produce lithium-ion batteries in the electric car industry. So the global demand for Cobalt is also increasing significantly, with a growth rate of 7-13% per year to reach 390 thousand tons by 2030 (Dias et al., 2018). Currently, most Cobalt is produced from stratiform copper-cobalt deposits in the central part of the African continent (Dias et al., 2018). In addition to these types of deposits, Cobalt is also associated with nickel laterite deposits but generally at lower grades. Cobalt laterites most commonly form over ultrabasic

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igneous rocks that have undergone varying degrees of serpentinisation. Globally, 15 percent of known Ni-Co laterites developed from the weathering of komatites and layered mafic-ultramafic intrusions, and 85 percent developed from dunites, harzburgites and peridotites in terranes (Elias, 2006).

Indonesia is the largest archipelago in the world with five major islands, namely Sumatra, Java, Kalimantan, Papua and Sulawesi. The five islands have their uniqueness, especially Sulawesi which is tectonically very complicated (Satyana et al., 2011). Indonesia also has the largest nickel-cobalt laterite potential globally, with total resources reaching 2.9 billion tons of ore or equivalent to 4 million tons of cobalt metal (Geological Survey, 2019). However, until now cobalt resources have not been optimally utilized due to the unavailability of processing and refining facilities that can produce cobalt in the country (Prasetiyo, 2015).

Previous research by Anbiyak and Cahyaningrum(2021), discussed the identification of Cobalt-rich zones in nickel laterite deposits in Indonesia but did not specifically discuss the distribution of cobalt elements in each nickel laterite zone and the Co-Ni correlation in the laterite zone. The Pomalaa area is one of the largest producing areas of nickel laterite deposits in Indonesia and is located in the tropics. Based on these conditions, it is necessary to conduct further research to analyze the distribution of cobalt in each nickel laterite zone, determine the minerals that form cobalt and determine the correlation between Co-Ni in laterite zones in the tropics in general and the Pomalaa area in particular.

2. Location and Geological Setting

The research area is located in Dawi-Dawi Village, Pomala Sub-District, Kolaka District, Southeast Sulawesi Province. The research area is about 180 kilometers from Kendari City (the capital of Southeast Sulawesi Province). Based on the local geological map, the Pomalaa area consists of ultrabasic rocks, including peridotite, harzburgite, dunite and serpentinite (Kusuma et al., 2015).

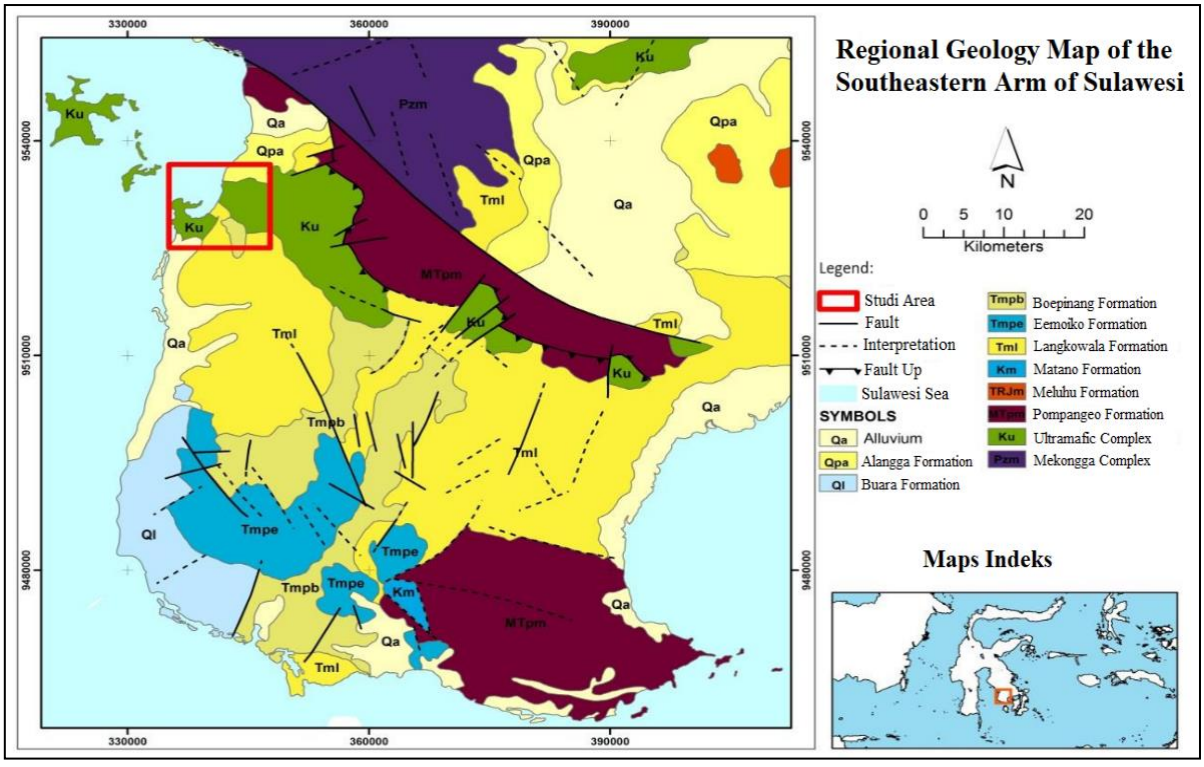


Fig.1. Regional geology of the southeast arm of Sulawesi (Simandjuntak et al., 1993).

An ophiolite rock complex known as the East Sulawesi Ophiolite (OST) developed in the eastern arm and continued into the southeastern arm of Sulawesi. The complex is dominated by large-bodied

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ophiolites that have been disturbed and subjected to tectonic events. The OST is geographically separated into northern and southern segments. The northern segment occurs in the eastern arm of Sulawesi and contains complete ophiolites despite having undergone tectonic events. In the southern segment, only fault contacts are found with crystalline rocks, mainly harzburgite and certified harzburgite.

Outcrops of ultramafic rocks in the eastern and southeastern arms of Sulawesi come in three forms (Leeuwen and Pieters, 2011), namely:

a. As massive bodies with irregular shapes that reach hundreds of kilometers. The largest are large lake areas covering several hundred square kilometers of ultrabasic area.
b. The imbrication layer follows the general pattern of the subduction mélange zone structure.
c. In the form of small, irregular, and isolated ultramafic bodies that generally appear in a limited way that extends following a northeast-directed regional trajectory such as in Sua-sua, Pao-pao, and Pomalaa (Fig. 1).

3. Sample and Analytical Methods

The researcher collected drilling data from 12 drill point samples at the observation stage and representative field activities. The analytical method used was petrographic analysis of 2 bedrock samples to determine the mineral content of the bedrock and determine the cobalt-forming minerals. Then X-Ray Diffraction (XRD) analysis was carried out on 2 samples each representing the limonite and saprolite zones to determine the main mineral composition in the limonite and saprolite zones and determine the cobalt-forming minerals in the limonite and saprolite zones. Then, X-Ray Fluorescence (XRF) analysis was conducted on 12 drill point samples to determine the cobalt content in the limonite, saprolite and bedrock zones. According to Jamaluddin and Adiantoro (2012), XRF is used to analyze elements in materials qualitatively and quantitatively. The resulting X-rays combine a continuous spectrum and a specific energy spectrum (discrete) derived from the target material that is collided by electrons (Sari et al., 2018). After the XRF analysis, the distribution of cobalt in each zone will be analyzed and the lateral and vertical distribution of cobalt will be mapped. Then, a correlation analysis is carried out to determine the relationship between Co and Ni. The laboratory used to analyze petrography, XRD, and XRF is the Laboratory at the Department of Geological Engineering, Hasanuddin University, Makassar, Indonesia.

3. Results and Discussion

3.1. Petrographic Analysis

In this study, petrographic analysis was carried out on two bedrock samples from nickel laterite deposits in the study area, to determine the minerals that make up the bedrock and to determine the Cobalt-forming minerals. Petrographic analysis can also be performed to microscopically identify mineral textures (Ahmed et al., 2023). Cobalt-forming minerals are common, and concentrated in minerals such as olivine, spinel and chlorite which are the main sources of important elements in lateritic and hydrothermal deposits (Smith, 2001).

1. Sample 1 (BR35)

A thin section of ultramafic rock with sample code BR35 has a brown and white color on PP appearance and brown on XP appearance. PP is the appearance of minerals with parallel nicol conditions, while XP is the appearance of minerals in cross nicol conditions. The mineral conditions in the sample have been completely altered or teralterated, with a fine to medium texture, having holocrystalline crystallinity, fine afanite grains, anhedral crystal shape, crystal size 0.01- 0.1 mm, allotriomorphic equigranular relationship, this incision is composed of serpentine minerals (antigorite),

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chromite, and orthochromite (enstatite). The following is a picture of the microscopic appearance of the bedrock samples in the study area (Fig. 2).

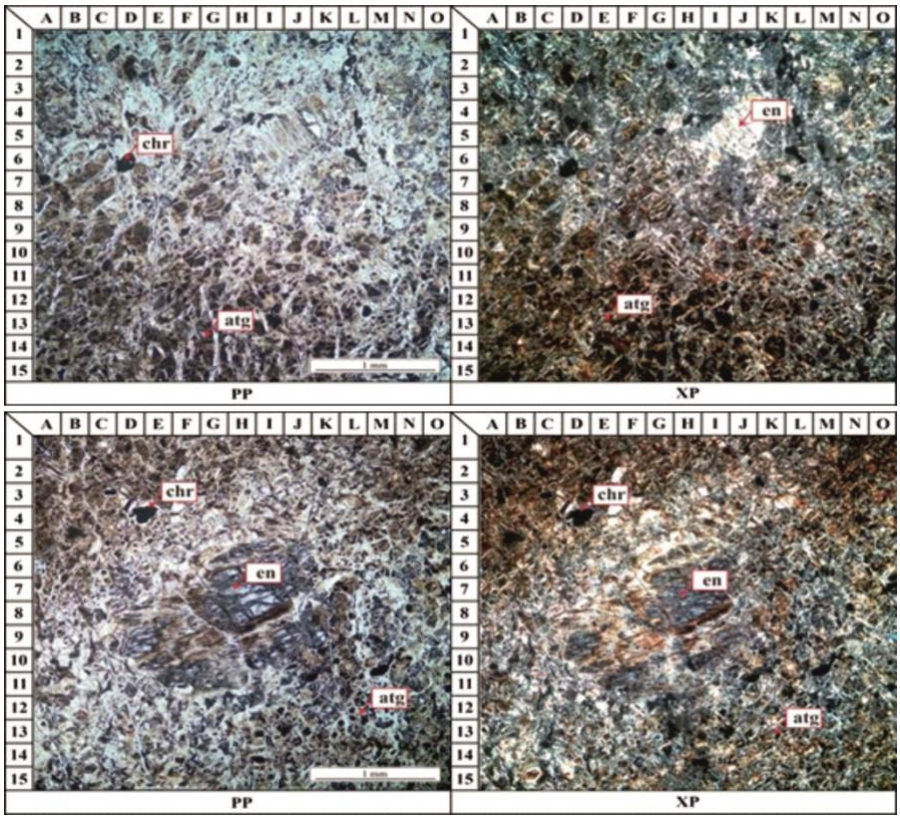


Fig. 2. Result of petrographic analysis of sample 1 (BR35)

In Fig. 2, the presence of the primary mineral enstatite (en) 8% can be identified; which is present as a remnant of the enstatite mineral because the original mineral has been completely transformed by serpentine minerals so that the mineral boundaries are faint but still have parallel dark angles. The secondary mineral is antigorite (atg) 87%; which is an altered mineral from olivine so it is a cobalt-forming mineral. The accessory mineral is chromite (chr) 5%; which is present as an irregular black coloured accessory.

2. Sample 2 (BR32)

A thin section of ultramafic rock with sample code BR32 has black, brown and white colors in the appearance of PP and green, black, grey and brown in the appearance of XP with conditions that have been fully altered or teralterated, with fine to medium texture, has holocrystalline crystallinity, fine afanitic granularity, anhedral crystal shape, crystal size 0.1-0.5 mm, allotriomorphic equigranular relations, has a special metamorphic texture, namely the mesh structure caused by the serpentinisation process in the rock is not perfect, in some parts it is also still clearly visible olivine in the antigorite mineral core, this incision is composed by minerals including serpentine (antigorite and lizardite), olivine (fayalite), clinopyroxene (augite) and chromite.

Figure 3 identifies the presence of primary minerals viz: augite (aug) 3%; which is present as a phenocryst mineral whose mineral boundary has merged with antigorite, has a parallel dark angle and has an exsolution lamellae microstructure. Also identified is the presence of the mineral fayalite (fa) 5%; which is present as a remnant of the altered olivine mineral. The secondary mineral found is antigorite (atg) 74%; which is present as the most dominant mineral in this incision, an altered mineral from olivine that has been fully altered so that this mineral is cobalt-forming. There is also the presence

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of lizardite (lz) 8%; which is present as a veinlet in the mesh structure that fills the incision, is colorless and low relief. For accessory minerals, the mineral chromite (chr) 10% was found; which is present as an accessory mineral associated with the mineral antigorite.

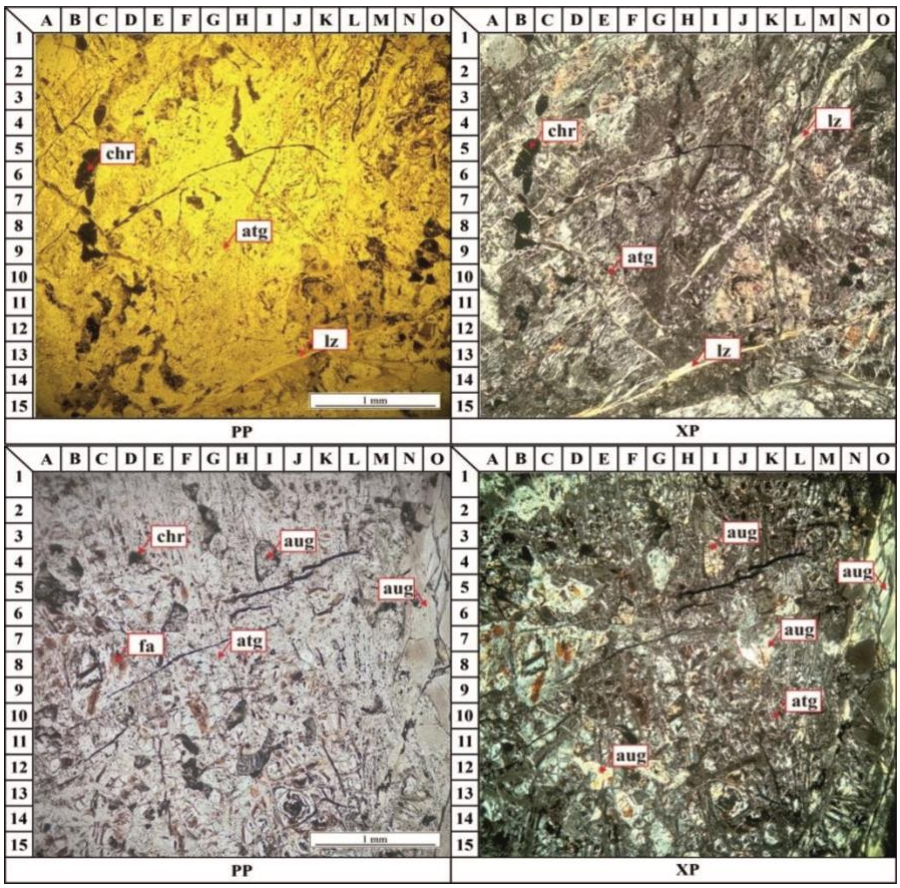


Fig. 3. Result of petrographic analysis of sample 2 (BR32)

3.2. X-Ray Diffraction (XRD) Analysis

XRD analysis was conducted to determine the mineral content of the saprolite and limonite zones; and also to determine the cobalt-forming minerals. XRD can show the mineralogical composition and mineral percentage of a sample (Mustafa et al., 2023). The measurement result obtained is the amount of intensity per step (time step) by carrying out time series statistical analysis. The measurement results per step are converted into a graph of intensity peaks which is also called a diffractogram (Karlinasari et al., 2023). Two samples were selected for XRD analysis, one representing the limonite zone and one representing the saprolite zone at drill point IDH-28.

1. Sample 1 (IDH-28 Limonite)

In sample 1, the minerals detected in the diffractogram were 5 minerals which can be seen in Fig. 4; These minerals are quartz minerals marked with a blue peak, olivine with an orange peak, magnetite with a grey peak, hematite with a green peak, and chromite with a yellow peak. Figure 4 is the diffractogram of sample 1 (limonite zone).

Based on the diffractogram results of the limonite zone samples, the minerals found have mineral values of quartz 7.9%, olivine 90.6%, magnetite 0.1%, hematite 1.3% and chromite 0.1%. Thus it can be known that the cobalt-forming mineral in the limonite zone sample is olivine. Mineral percentages can be obtained by determining the content of various phases using XRD from peak areas. Then determine the chemical formula and calculate the elemental composition. We can also use certain

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software/applications to make it easier to get the percentage of each mineral. The percentage values of these minerals can be seen in Table 1.

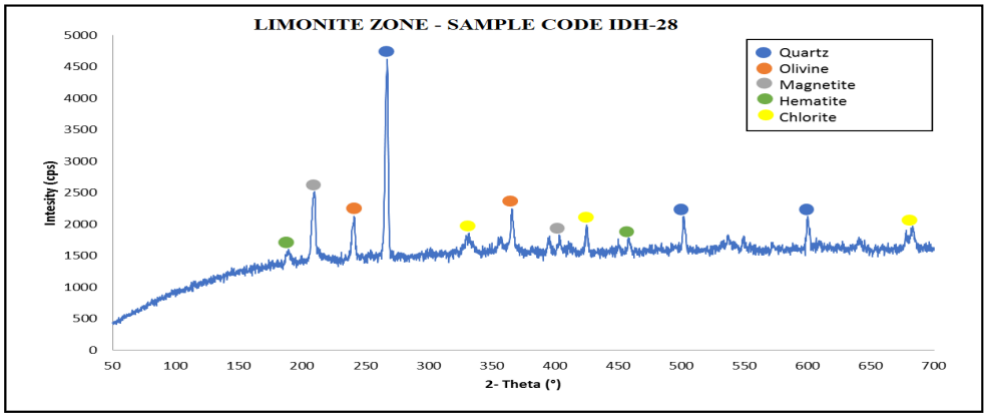


Fig. 4. Difractogram of sample 1

Table 1. Mineral content of limonite zone samples

No.	Mineral Name	Chemical Formula	Percentage (%)
1	Quartz	SiO_2	7.9
2	Olivine	$FeMgO_4$	90.6
3	Magnetite	Fe_3O_4	0.1
4	Hematite	Fe_2O_3	1.3
5	Chromite	$AlO.2Cr_2O_3$	0.1

2. Sample 2 (IDH-28 Saprolite)

The minerals detected in the diffractogram of the saprolite sample are 4 minerals which can be seen in (Fig. 5), These minerals are quartz minerals characterized by black peaks, olivine with blue peaks, lizardite with grey peaks, and liebenbergite with orange peaks.

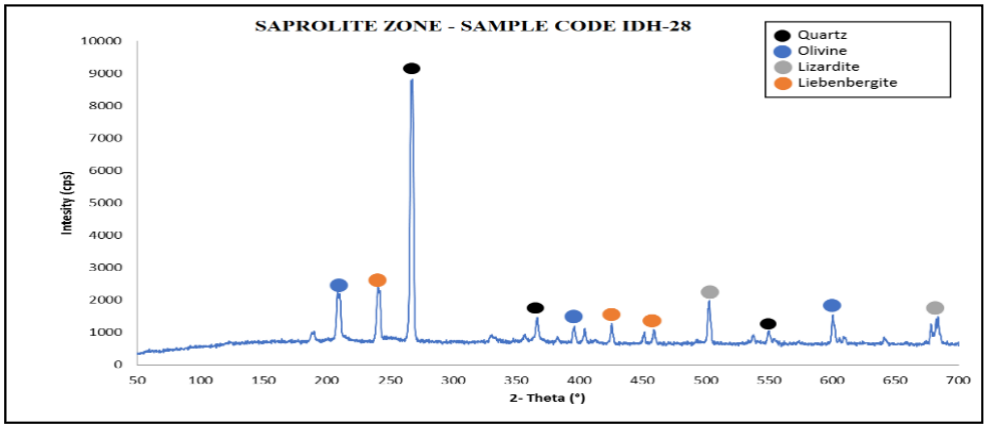


Fig. 5. Difractogram of sample 2

Based on the diffractogram of sample 2 (saprolite zone), the minerals found have values of quartz mineral 90.7%, lizardite 6.5%, olivine 0.8%, and liebenbergite 2.0%. Then it can be known that the cobalt-forming mineral in the saprolite zone sample is olivine. The percentage values of these mineral occurrences can be seen in Table 2.

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Table 2. Mineral content of saprolite samples

No.	Mineral Name	Chemical Formula	Percentage (%)
1	Quartz	SiO_2	90.7
2	Lizardite	$Mg_3Si_2O_5(OH)_4$	6.5
3	Olivine	$FeMgO_4$	0.8
4	Liebenbergite	Ni_2O_4Si	2.0

3.3. X-Ray Fluorescence (XRF) Analysis

XRF analysis was conducted to determine the value of Co grade in the samples in each nickel laterite zoning. For (XRF) The rock samples were ground and crushed to powder (Alrawi et al., 2023). XRF analysis was carried out as many as 12 drill points in the research area. The following is the value of Co grade from the results of XRF analysis on each zoning of 12 drill points.

3.3.1. Cobalt grades in the Limonite zone

In the saprolite zone, the nickel grades vary between 1.5 and 2.6% Ni, while in the limonite zone, it ranges between 1.1 and 1.8% Ni. The average cobalt grade in the limonite zone is 0.082% Co (Table 3). The following are the XRF results from 12 drill points in the study area.

Table 3. Average grades of Co in the limonite zone

Drill Hole	Depth (m)	Co grade in limonite zone (%)
IDH-25	7	0.05
IDH-26	6	0.05
IDH- 26 R	9	0.06
IDH-27	7	0.07
IDH-28	5	0.12
IDH-29	7	0.08
IDH-30	3	0.11
IDH-31	5	0.08
IDH-32	4	0.09
IDH-33	6	0.06
IDH-34	3	0.1
IDH-35	12	0.08
Average		0.082

The limonite zone in the study area contains residual iron enrichment in the laterite profile, mainly consisting of hydrated iron oxides. The material is very soft and dominated by clay minerals. The top is generally blackish and contains hematite. Nickel may be bound to the goethite structure along with aluminum, manganese and chromium. Laboratory test results at 12 drill points show the range of Cobalt grades in the limonite zone ranges from 0.05 to 0.12, with the thickness of the limonite zone ranging from 3 to 12 meters. The thickness of the limonite zone is influenced by the degree of weathering in an area (Wakila et al., 2019).

Based on Table 3, it can be seen that drill point IDH-28 has the highest grade of 0.12% Co, while IDH-25 and IDH-26 have the lowest grade of 0.05% Co. Elemental cobalt generally comes from the goethite mineral which then leached and oxidized with manganese oxide chunks that accumulate at the base of the limonite zone (Golightly, 1981). The distribution of the highest cobalt grades in the limonite zone is in the northwest and west directions, while the low grades are distributed in the north, northeast, and southeast directions (Fig. 6).

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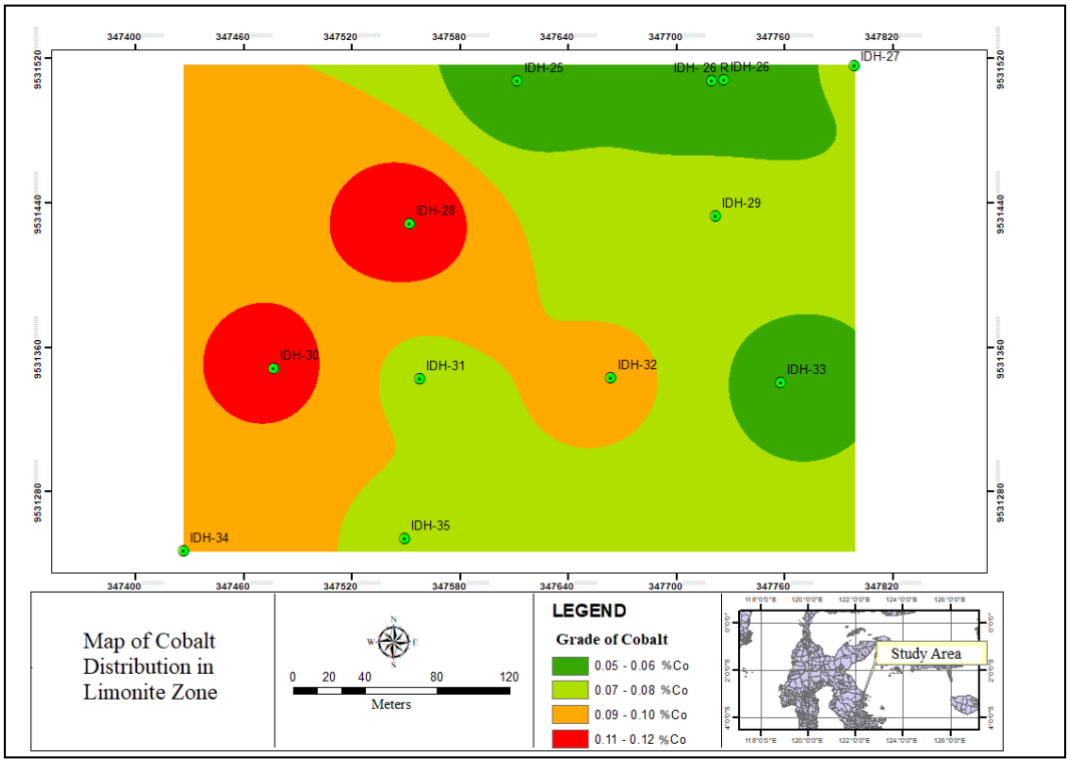


Fig. 6. Map of Cobalt grades Distribution in the Limonite zone

3.3.2. Cobalt grades in the Saprolite zone

The saprolite zone in the study area shows a bedrock texture (rocky saprolite) with fracture zonation filled by garnierite and silica minerals. They encountered silica veins forming a boxy texture that filled the fractures of the original rock structure. The underlying saprolite zone contains 1.5-2.5% Ni and is characterized by low iron and cobalt content (Eramet, 2010). Laboratory test results at 12 drill points show the range of cobalt grades in the Saprolite zone ranges from 0.02 to 0.05. The following are the laboratory test results from 12 drill points in the study area (Table 4).

Table 4. Average grades of Co in the saprolite zone

Drill Hole	Depth (meters)	Co grade in limonite zone (%)
IDH-25	4	0.04
IDH-26	10	0.02
IDH- 26 R	6	0.02
IDH-27	3	0.03
IDH-28	3	0.05
IDH-29	3	0.02
IDH-30	2	0.04
IDH-31	1	0.03
IDH-32	2	0.03
IDH-33	1	0.02
IDH-34	2	0.02
IDH-35	7	0.04
Average		0.029

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Table 4 shows that the highest cobalt grade in the saprolite zone is found at drill point IDH-28 with a grade value of 0.05% Co, and the lowest grade is found at drill points IDH-26, IDH-26R, IDH-29, IDH-33, and IDH-34 with a grade value of 0.02% Co. The thickness of the saprolite zone in the study area varies from 1 to 10 meters. The distribution of the highest grade of cobalt in the saprolite zone is in the northwest direction, and the low grade is distributed in the northwest, east, and southeast directions (Fig. 7).

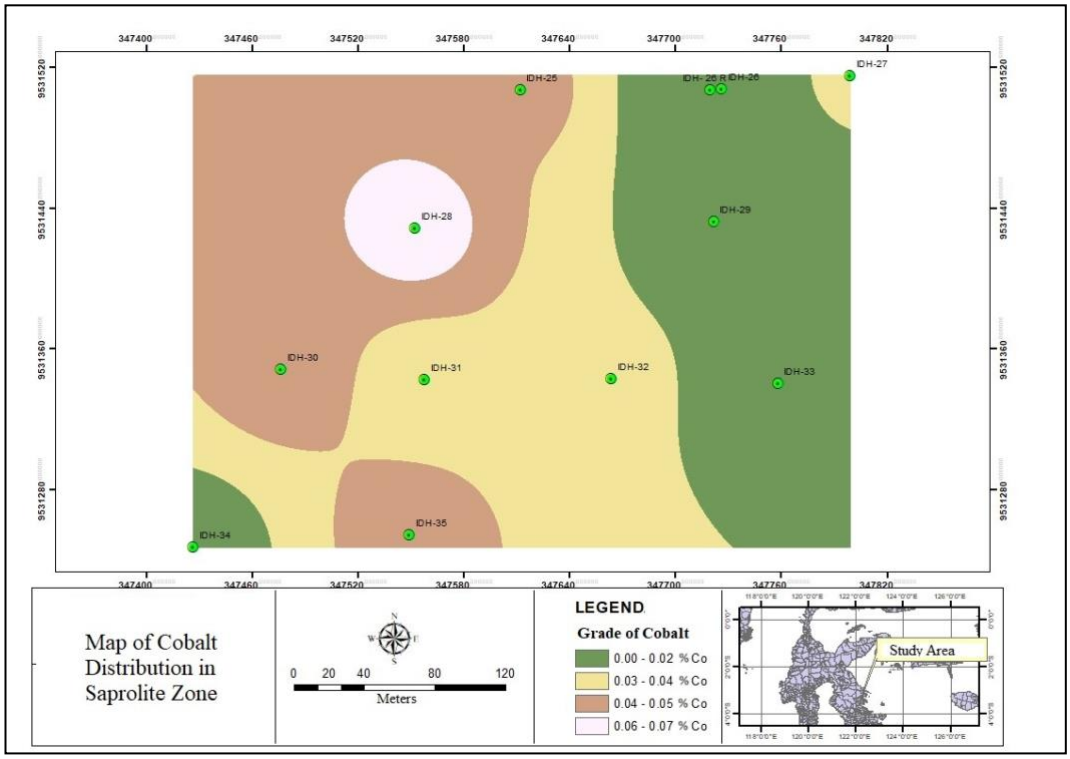


Fig.7. Map of Cobalt grades Distribution in the saprolite zone

3.3.3. Cobalt grade in bedrock zone

The bedrock zone in the study area shows high fracture intensity. It is gray to black, with a rock texture that tends to be coarse, and is composed of olivine, pyroxene, and serpentine. At the top, there are peridotite rocks that have been weathered at the edges. The fractures are irregularly shaped and partly filled in the form of veins by silica and garnierite. In the bedrock zone, cobalt grades range from 0.01 to 0.04, with the highest grade value being at point IDH-32 with a grade value of 0.04% Co. While the lowest grade is at drill points IDH-26R, IDH-28, and IDH-29, with a grade value of 0.01% Co.

The thickness of the bedrock zone in the study area varies from 1 to 4 m. This zone is a zone that has high fracture intensity. Brownish grey, with a coarse rock texture with a mineral composition of olivine pyroxene with serpentine alteration minerals which are ultramafic rocks, namely serpentinite and peridotite rocks.

The fractures are irregularly shaped and partly filled with silica veins and garnierite. From the drilling results, the depth of bedrock from the surface ranges from 25 m to 30 m. This bedrock zone has a nickel content of <0.5% Ni (Kusuma et al., 2019). The distribution of the highest cobalt content in the bedrock zone spreads to the southeast, and the low content spreads to the northeast (Fig. 8).

Based on the results of the study, it is known that the cobalt distribution profile at the 12 drill points above has the same characteristics, namely layers with high cobalt content below the limonite zone or in the saprolite-limonite transition area at the bottom of the redox zone boundary. This is because the presence of cobalt in this zone is associated with Mn oxide minerals. The mobilisation and re-deposition

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of Fe and Mn trigger the absorption of Ni and Co. The cobalt in the goethite mineral undergoes further separation and associates with manganese oxide which accumulates in the limonite zone.

Table 5. Average grades of Co in bedrock zone

Drill Hole	Depth (meters)	Co grade in bedrock zone (%)
IDH-25	4	0.03
IDH-26	4	0.02
IDH- 26 R	3	0.01
IDH-27	2	0.02
IDH-28	3	0.01
IDH-29	1	0.01
IDH-30	3	0.02
IDH-31	1	0.02
IDH-32	2	0.04
IDH-33	1	0.02
IDH-34	2	0.02
IDH-35	2	0.02
Average		0.02

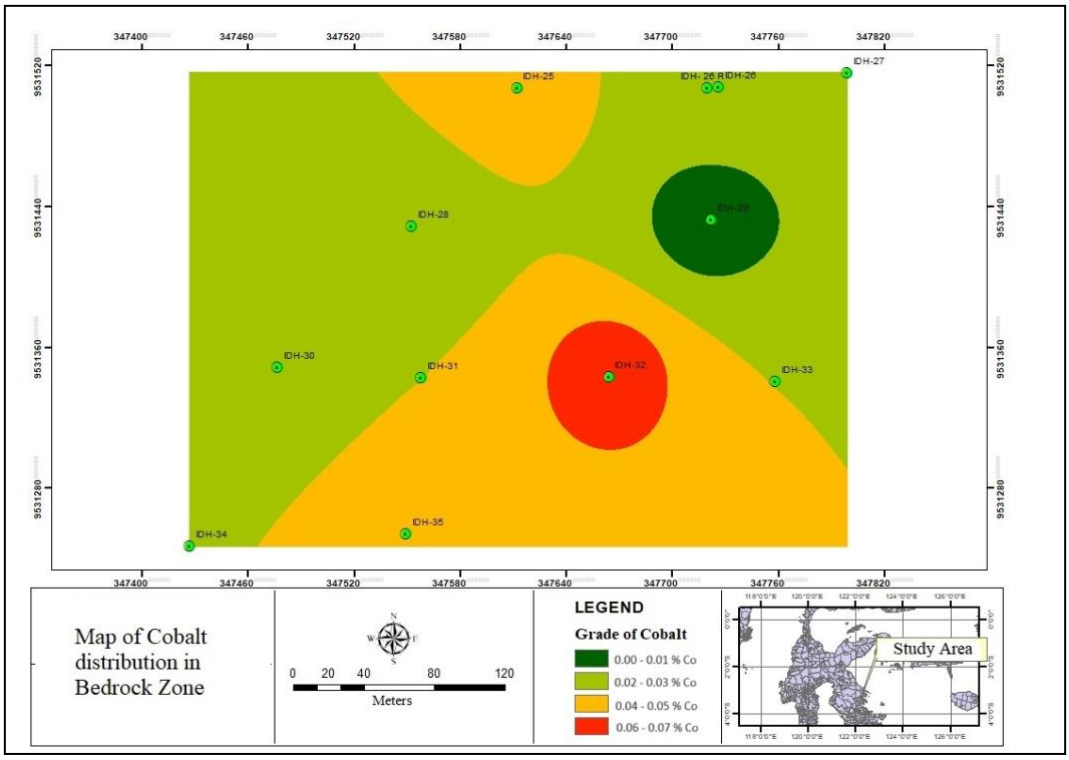


Fig. 8. Map of Cobalt grade distribution in the bedrock zone

The percentage of average Co grade in each nickel laterite zoning can be seen in the diagram below (Fig. 9).

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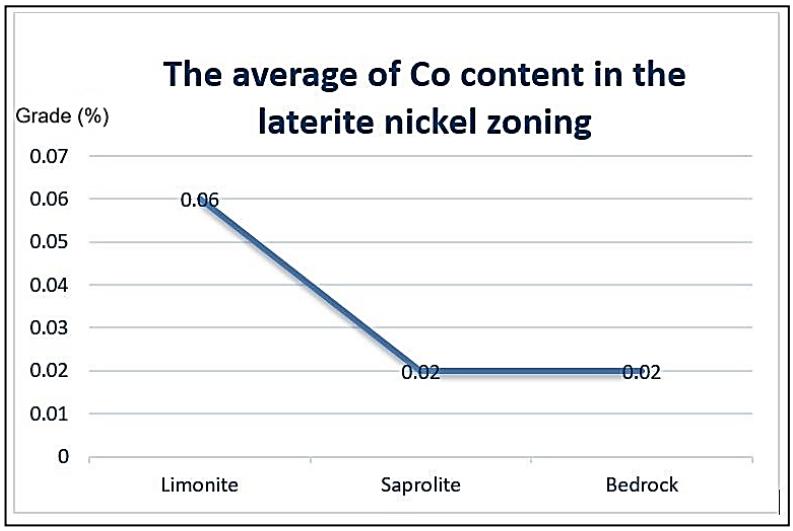


Fig. 9. Comparison of average Co grades in the limonite, saprolite, and bedrock zones

3.3.4. Cobalt (Co) Distribution in the Nickel Laterite Zonation

The geochemical profile of Pomalaa laterite deposits describes a condition in the behavior or tendency of element abundance patterns to the subsurface influenced by the lateritization process. This behavior is influenced by the mobility of elements in the nickel laterite profile, which is known from the degree to which elements are displaced by groundwater flow. Behavior during the lateritization process includes leaching, especially of MgO and SiO_2; supergene enrichment, especially of Ni and Co; and residual elements, specifically Fe, Cr and Al. Minor elements, including Co and Cr_2O_3, show enrichment in the limonite zone and depletion in the saprolite zone. Ni is enriched in the saprolite zone compared to the limonite zone by >2.

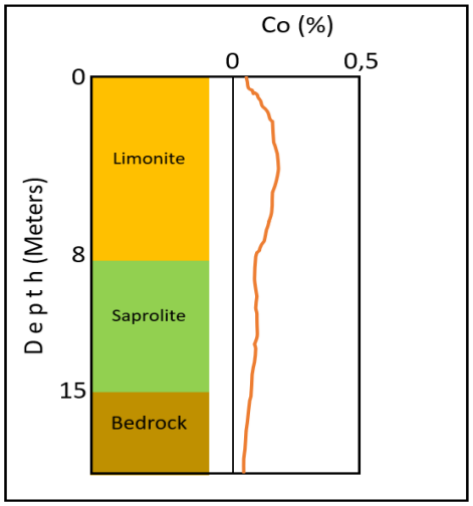


Fig. 10. Laterite zoning, depth, and cobalt grades

The layer with high cobalt grade is at the bottom of the limonite zone and is at the saprolite-limonite transition area at the redox zone boundary. Groundwater levels control the redox zone in laterite deposits during the weathering process. Due to hydrolysis, leaching of ultrabasic bedrock releases nickel and Cobalt from olivine minerals, and some metal elements are absorbed by goethite minerals in the oxide zone. Most of the magnesium and silica are intertwined, causing increased porosity and rock mass loss

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of up to 70% (Butt and Cluzel, 2013). The following is a picture of the laterite zoning, depth, and cobalt levels in each zone (Fig. 10).

3.3.5. Correlation of Co-Ni in laterite zonation

Correlation analysis is a statistical method used to determine a quantity that states how strong the relationship between a variable and another variable is, without questioning whether a particular variable depends on another variable. The more obvious the linear relationship (straight line), the stronger or higher the degree of straight line relationship between the two or more variables (Sekaran et al., 2010). The following is a table of correlation coefficient interval values and their respective relationships.

Table 6. Interpretation of the Correlation Coefficient (Sugiyono, 2017).

Coefficient Interval	Level of Relationship
0.00-0.199	Very Low
0.20-0.399	Low
0.40-0.599	Medium
0.60-0.799	Strong
0.80-1.000	Very Strong

- Correlation of Co-Ni in the Limonite zone

In the limonite zone, the correlation between Co-Ni shows a correlation coefficient of $R^2 = 0.2238$, which means that there is a low relationship between Co-Ni (Fig. 11).

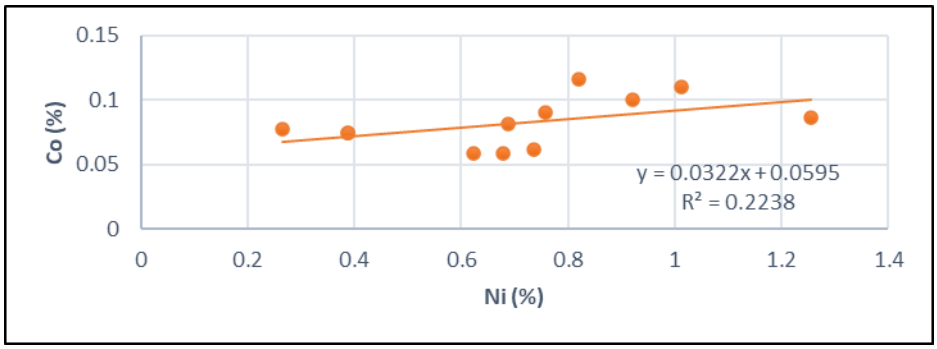


Fig. 11. Scatter Plot between Co-Ni in the limonite zone

- Correlation of Co-Ni in the Saprolite zone

In the Saprolite zone, the correlation between Co-Ni shows a correlation coefficient of $R^2 = 0.0651$, which means that there is a very low relationship between Co-Ni (Fig. 12).

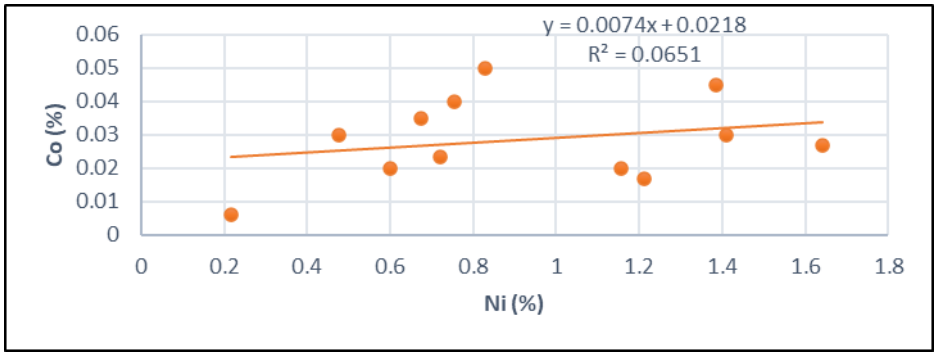


Fig. 12. Scatter Plot between Co-Ni in the saprolite zone

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- Correlation of Co-Ni in the Bedrock zone

In the bedrock zone, the correlation between Co-Ni shows a correlation coefficient of R2 = 0.015, which means that there is a very low relationship between Co-Ni (Fig. 13).

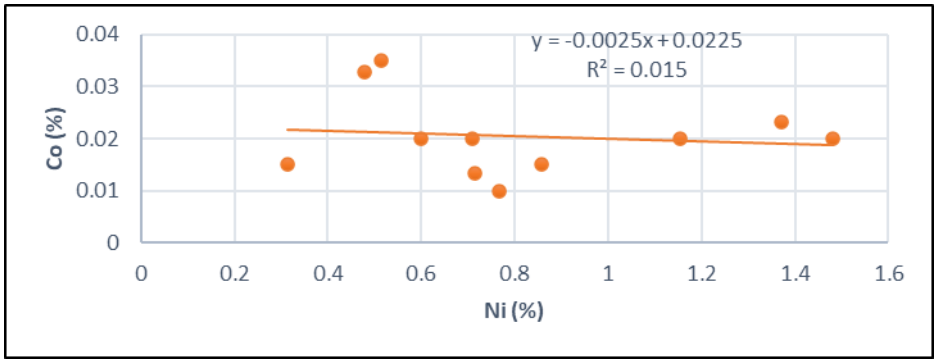


Fig. 13. Scatter Plot between Co-Ni in the bedrock zone

4. Conclusions

The zone with the highest cobalt content is the limonite zone, with an average cobalt content in the limonite zone of 0.06%, saprolite zone of 0.02%, and bedrock zone of 0.02%. Minerals identified as cobalt-forming minerals in bedrock samples in the study area are antigorite minerals and cobalt-forming minerals in limonite and saprolite zone samples are olivine minerals. The correlation between Co and Ni elements in the limonite zone shows a correlation coefficient value $R^2 = 0.22$, which means that the relationship between Co and Ni is low in the limonite zone. For the saprolite zone, the correlation coefficient shows a value of $R^2 = 0.06$, which means that the relationship between Co and Ni is very low in the saprolite zone. For the bedrock zone, the correlation coefficient value $R^2 = 0.01$, means that the relationship between Co and Ni is very low in the bedrock zone.

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