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**RESEARCH ARTICLE** 

# Characteristics of Host Rocks Manganese of The Anabanua Village Barru District South Sulawesi Province, Indonesia

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#### Abstract

One of the prospects for a wealth of geological resources that can be utilized for the benefit of mankind is manganese metal mineral resources. In Anabanua Village, especially at the research location, there is an indication of manganese mineralization, but the type of rock carrying the mineralization is not yet known. The purpose of this study was to determine the chemical elements of metallic minerals, mineralogy, and types of mineralization-carrying rocks in as many as three samples in the form of chunks, which were analyzed using megascopic analysis methods identifying the texture and structure of carrier rocks, XRD (X-ray diffraction) analysis minerals, and XRF (X-ray fluorescence). The characteristics of manganese mineralization carrier rocks consist of metallic elements Mn (0.046%-20.455%), Fe (1.555%-3.673%), and nonmetallic elements SiO<sub>2</sub> (11.403%-48.165%), and K<sub>2</sub>O (0.398%-4.177%). Mineralogy of manganese mineralization carrier rocks are roeblingite (Pb<sub>2</sub>Ca<sub>6</sub>Mn<sub>2</sub>+(Si<sub>3</sub>O<sub>9</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub> 4H<sub>2</sub>O), rhodonite (CaMn<sub>3</sub>Mn[Si<sub>5</sub>O<sub>15</sub>]), diopside (CaMgSi<sub>2</sub>O<sub>6</sub>), calcite (CaCO<sub>3</sub>), kieserite (Al, Ga)<sub>2</sub>(GeO<sub>4</sub>)(OH)<sub>2</sub>), zeolite (Mn<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub>.xSiO.yH<sub>2</sub>O), and palygorskite ((Mg, Al)<sub>2</sub> Si<sub>4</sub>O 10(OH)·4H<sub>2</sub>O). Manganese mineralization host rocks are determined by referring to the SiO<sub>2</sub> (%weight) and K<sub>2</sub>O (%weight) diagrams to produce basalt igneous rock types.

Keywords: Characteristics, host rock, manganese, mineralization, Barru

## 1. Introduction

Manganese metal is currently in 12th place, whose abundance in the earth's crust averages 0.1% (Chatterjee, 2007). Manganese metal is also in 4th place based on its amount after iron, copper, and aluminum. About 92% of the manganese used by the global community is directly related to steel industry products (Das et al., 2015; Sun et al., 2020). Other parts of manganese are used to manufacture dry batteries, chemical industries, and dyes (Pereira et al., 2014). Total production of manganese or Mn metal globally, especially in 2014, reached 17,000 tons (Corathers & Lopez, 2014; Summaries, 2021). The largest percentage of Mn metal production is from South Africa, followed by China, Brazil, Australia, and Gabon (Wilczyński, 2022). Indonesia is not included in manganese-producing countries, but even so, Mn deposits in Indonesia have been reported in several regions, such as NTT, West Java, Manggarai Regency, North Halmahera, Tasikmalaya, Bone and Barru Regencies, and South Sulawesi.

Barru Regency is one of South Sulawesi's regions with unique geological conditions (Wahyuni et al., 2021). (Ariansyah et al., 2020) explained that in Anabanua Village, there are many types of rocks such as sedimentary rocks, metamorphic rocks, and igneous rocks (Wahyuni et al., 2021). The Miocene and Pliocene group of intrusive rocks consists of dacite porphyry, diorite, and trachyte. Diorite rocks and dikes originate as intrusion stocks in the Bulu Maraung area and the Borigint embankment around the northeastern part of the study area such as Sabangnaeri, Palakka, Kaerange, and Bangabangae. Diorite and basalt intrusions are carriers of the mineral barite, gypsum, manganese, and copper. Manganese deposits are found in the Sabangnaeri, Daccipong, and Dengenge rivers (Kaharuddin et al., 2017; Maulana et al., 2020).

Manganese mineralization has been found at the study site but the type of host rock of the manganese ore is not yet known (Eddy & Muksin, 2019). Regarding manganese mineralization carrier rocks, it is necessary to know the characteristics of mineralization-carrying host rocks to be used as a guide to explore these deposits further. So that researchers took the initiative to analyze rock types, chemical characteristics, and mineralogy of manganese mineralization host rocks in the research area, as an initial stage of research using several related analyses.

#### 2. Materials and Methods

In determining the characteristics of manganese mineralization host rocks in the Dengenge River Area, Anabanua Village, South Sulawesi Province using chemical and mineralogical analysis methods Below will be described in detail from each stage of research, which are as follows; The samples used in this study were igneous rocks and manganese ore which were exposed in the study area. Samples were taken from four locations and three samples were analyzed. Hand specimen-sized samples from each site were described macroscopically (Azzaman & Jerniawan, 2023). To determine mineral the texture. structure, and composition microscopically, petrographic analysis was carried out (Azzaman & Jerniawan, 2023). In this analysis, the rock sample is thinly sliced to a thickness of about 0.03 mm and observed under a polarizing microscope. Preparation of thin sections and petrographic analysis was carried out at the Mineral Petrography and Optics Laboratory, Department of Geological Engineering, Hasanuddin University, Makassar. For chemical analysis of the major elements (XRF), the powder samples were made into press pellets and the analysis was carried out using the Rigaku Primus II XRF spectrometer. This analysis involved three rock samples and was carried out at the Central Laboratory of Hasanuddin University, Makassar. Data from the XRF analysis was used to interpret the igneous rock type using The GeoChemical Data ToolKIT (GCDkit) software. Mineralogical analysis using the XRD method using a Rigaku Multiflex diffractometer with CuK $\alpha$  radiation. The operating conditions are as follows: voltage 30kv, current 16 mA, angle 2theta 2 – 70°, scanning time 2° / minute. The diffractogram data was then analyzed using the Match-3 program Results and Discussion

# A. Conditions of the Research Area

The research area, especially in Anabanua Village, Barru District, Barru Regency, South Sulawesi Province, precisely in the 4º 36'16" -5º36'33" LS and 119º43'24" - 119º43'40" BT choordintentions. This is based on geological processes that take place during island formation activities, especially in Sulawesi. Abundant rock types range from igneous rocks to sedimentary rocks, and metamorphic rocks (Ariansyah et al., 2020). Researchers then conduct field activities by looking for outcrops and taking samples that indicate the characteristics of manganese carriers, sampling activities can be seen in Fig. 2.



Fig. 2. Manganese outcrops in the study area



Fig. 3. Description of Station 1 manganese minerals

#### **B.** Chemical Conditions

Station 1 is located at coordinates S  $04^{\circ}27'33.53"$  E 119°42'23.35", megascopically the sample taken is an outcrop of manganese ore, and the appearance of mineral texture with black glass gloss is suspected to be rhodonite (MnSiO<sub>3</sub>). These outcrops have fresh black color and brown weathered color. Has a texture with a black luster, luster (nonmetallic), cleavage not perfect, hackly type fractions. It has hardness number 3

(copper wire), specific gravity of 7.43, and malleable tenacity. The chemical composition of the sample is Mn, with a monocline crystal system, and the mineral name manganese can be seen in Fig. 3.

Station 2 is located at coordinates S 04°27'34.00" E 119°42'30.75", megascopically the sample taken is a rock outcrop, and the appearance of mineral texture with white soil gloss is suspected to be silica minerals, Station 2 found carbonate rock outcrops that have a fresh white color, yellow weathered color. It has a non-clastic texture, with carbonate-forming minerals and a massive or uncoated structure. The mineral composition of the sample is calcite as much as 82%, kieserite 18%, and there are fossils based on microscopic data, and the name of the rock can be known based on the journal by (Indarto et al., 2014), namely calcillitite can be seen in Fig. 4.



Fig. 4. Description of station 2 calcylutite rocks

Station 3 is located at coordinates S 04°27'28.84" E 119°42'43.09", this outcrop is present on the surface with a size of only ±1 meter per outcrop, station 3 is one of the rocks that describes the regional geology of the study area, regionally found the intrusion of igneous rocks of basalt, dacite and diorite types. And megascopically the sample taken is a rock outcrop, the appearance of mineral texture with white soil gloss is suspected to be plagioclase minerals, has a fresh gray color and black weathered color, with textures based on the degree of hypocrystalline crystallization, granularity, or porphyritic (aphanitic) grain size, subhedral crystal shape, relations inequigranular. Have a massive rock structure or not layered, the mineral composition contained is Ca-plagioclase as much as 20%, quartz 10%, and the presence of clay change minerals as much as 5%. Based on the naming of (Travis, 1955) in the journal (Indarto et al., 2014) it is known that the name of the rock is Porphyry Basalt, which can be seen in Fig. 5.



Fig. 5. Description of Station 3 Porphyry basalt

## C. XRF Analysis

This analysis is an analytical technique that can analyze the elements that make up a material. The results of XRF analysis show data based on oxide content (major elements). The results of chemical analysis on each sample showed that the highest Mn values at station 1, Al, Cr, Zn, and Ag values were not found at station 2 and there were few Mn but high Fe, while Zn, Ag were not found at station 3 and high Al.

Concentrations up to 100% were analyzed directly and without dilution, with better reproducibility  $\pm 0.1\%$ . The results of the analysis show data based on oxide content so that in determining the single major element in the sample, a calculation separation of analysis compounds is carried out. The results of the analysis can be seen in Table 1.

Fable 1. The percent	age of element content
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<u> </u>	Percenta	Percentage of element content (%)		
Element	Station 1	Station 2	Station 3	
Mn	20,455	0,046	0,051	
Al	5,039	-	9,397	
Fe	3,673	1,555	1,790	
Cr	0,022	-	0,009	
Zn	0,028	-	-	
Ag	0,009	-	-	

D. Mineralogical Analysis

#### 1. XRD Analysis Station 1

Analysis of XRD station1 is presented in Fig. 6 showing varying results. From the results of XRD analysis, it was found the presence of metal minerals suspected to be manganese-carrying minerals, namely roeblingite as much as 69.4%, rhodonite 18.7%, and diopside 11.9%. (Indarto et al., 2014), explained that mineral roeblingite and rhodonite are the most commonly found minerals, and are metal carrier minerals.



Fig. 6. Diffractogram result in XRD analysis station 1



Fig. 7. Diffractogram result in XRD analysis station 2

#### 2. XRD Analysis Station 2

XRD analysis of station 2 presented in Fig. 7 shows calcitedominant results. The results of XRD analysis found the presence of carbonate minerals, namely calcite at as much as 82.8%, and kieserite at 17.2%, which are the most abundant minerals, and the most stable calcium carbonate minerals (CaCO<sub>3</sub>). For secondary minerals commonly found in sedimentary rocks such as calcite, the results of XRD analysis at station 2 are not sufficient in identifying minor minerals, so petrographic analysis is needed to complement minerals that do not appear in XRD results.

#### 3. XRD Analysis Station 3

Analysis of XRD station 3 is presented in Fig. 8 by showing quite varied results. The results of XRD analysis found the presence of quartz dominant minerals, analcime namely zeolite mineral group, and palygorskite clay mineral group. Quartz was found at 86.2%, analcime at 10.9%, and palygorskite at 2.9%.



Fig. 8. Diffractogram result in XRD analysis station 3

This analysis is an analytical technique that can identify the mineral content that builds a material. The percentage values of the three XRD analysis samples can be seen in Table 2.

Table 2. The percentage of mineral content

Minerals		Percentage of mineral content (%)		
	chemical formula	Statio	Statio	Statio
		n 1	n 2	n 3
Roeblingit e	$Pb_2Ca_6Mn_2$	69,4	-	-
Rhodonite	CaMn₃Mn	18,7	-	-
Diopside	MgCaSi <sub>2</sub> O <sub>6</sub>	11,9	-	-
Calcite	CaCO <sub>3</sub>	-	82,8	-
Krieselite	$Al_2GeO_4(OH)_2$	-	17,2	-
Quartz	SiO <sub>2</sub>	-	-	86,2
Analcime	Na (AlSi <sub>2</sub> O <sub>6</sub> )·H <sub>2</sub> O	-	-	10,9
Palygorskit e	(Mg,Al)₂Si₄O <sub>10</sub> (OH)∙₄H 2O	-	-	2,9

#### E. Microscopic Analysis

#### 1. Mineragraphy Analysis Station 1

Mineragraphy analysis station 1 is used specifically for polished incisions on metals, the minerals found are secondary minerals from manganese mineralization carriers, while the minerals contained in polished incision samples are (Roeblingit = Pb 2 Ca<sub>6</sub>Mn<sub>2</sub>); (rhodonite = CaMn<sub>3</sub>mn); (Quartz =  $_{SiO2}$ ); and (Diopside = MgCaSi<sub>2</sub>O<sub>6</sub>). Roeblingite mineral is a mineral calcium lead sulfate silicate hydroxide hydrate, the elements contained in this mineral are calcium, hydrogen, lead, manganese, oxygen, silicon, and sulfur. It is found with a dark blue glass gloss and euhedral-subhedral texture. (Sukandarrumidi, 2016) explains about mineral rhodonite A red to brown mineral with a triclinic crystal system, and hardness 6, rhodonite with silicate composition has similar physical properties to rhodochrosite, but this mineral is formed as a secondary compound and can be seen in Fig. 9.



Fig. 9. Photomicrograph result of mineragraphic analysis samples 1 (Rb=Roeblingite, Rhd= Rhodonite, Qz=Quartz, Dp=Diopside)



Fig. 10. Photomicrograph result from petrographic analysis samples 2 (Ks=Calcite, Krs= Krieselite

# 2. Petrography Analysis of Station 2

Petrographic analysis of the 2 minerals found to be dominant minerals (calcite =  $CaCO_3$ ) and (cries elite = Al 2 GeO<sub>4</sub> (OH)<sub>2</sub>), calcite minerals are carbonate minerals with unique color features usually found in three colors pink, blue and green on a microscope, system Hexagonal crystals and hardness 3, crieselite is a silicate mineral has a crystal or to rhombic system hardness 5 to 6.5 The naming of rocks at station 2 is conventionally classified according to the grain size, based on the Wentworth grain size scale, station 2 has a grain size of <63 microns so it is called calcylutite or noncarbonate sedimentary rock equivalent to claystone. It can be seen in Fig. 10.

# 3. Petrography Analysis of Station 3

Petrographic analysis of station 3 minerals found to be dominant minerals (quartz = SiO<sub>2</sub>), (analcime= Na (AlSi <sub>2</sub>O<sub>6</sub>) H<sub>2</sub>O,i.e. zeolite mineral group, and (palygorskite = (Mg, Al)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)· <sub>4</sub>H<sub>2</sub>O) clay mineral group, most of these minerals can be said to be secondary minerals. Analcime minerals are white, gray, or colorless. Analcime occurs as the primary mineral in analcime having orthorhombic crystal systems and hardness of 5 to 5.5. Palygorskite minerals are a group of clays or attapulgite is a combination of smectite and palygorskite, white, grayish, yellowish, gray-green monocline crystal system and hardness 2 to 2.5, and the naming of rocks based on the classification of (Travis, 1955) and (Fenton et al., 1940) using the main minerals Ca-plagioclase and porphyritic texture so that the known name of the rock is basalt, can see in Fig. 11.



Fig. 11. Photomicrograph result of petrographic analysis s imperious 3 (Anc=Analcime, Qz=Quartz, Plg=Palygorskit)

F. Rock Naming

Based on the results of megascopic, microscopic, and mineralogical analysis of rocks found from the study, namely 2 types of sedimentary rocks in station 2 samples and igneous rocks in station 3 samples, as for the description of the naming of rocks from both samples, namely:

# A. Sedimentary Rocks

Based on the results of laboratory analysis for sedimentary rock samples then classified based on data on their physical, chemical, and mineralogical properties (Schön, 2015). The classification of naming sedimentary rocks used is the classification by (Grabau, 1904a). The sedimentary rocks found in the study area are carbonate rocks with a grain size of <63  $\mu$ m in Table 3. The (Grabau, 1904b) classification uses three-grain sizes of clastic sedimentary rocks, namely calcarenite-type of limestone grain size >2 mm, calcarenite type of limestone grain size (1/16-2mm), and calcillite type of limestone grain size (1/16-mm).

Table 3. Classification of naming sedimentary rocks (Grabau, 1904a)

Grain Size	Carbonate rock name
> 2 mm	Calcirudite
63 μm – 2 mm	Calcarenite
< 63 μm	Calcilutite

Based on the results of megascopic, microscopic, and mineralogical analysis on the station 2 sample is a type of carbonate sedimentary rock, namely limestone, and analyzed the grain size is smaller than sand < 63  $\mu m$  is a calcilutite type limestone.

# B. Igneous rocks

The naming of igneous rocks is based on the results of laboratory analysis, namely the content of minerals and elements contained. The classification of naming igneous rock types used in this study is (Bas et al., 1986) classification using the percentage of SiO<sub>2</sub> and K<sub>2</sub>O content.

Table 4. The percentage content of SiO<sub>2</sub> and K<sub>2</sub>O

	Percentage element content (%)
Element	Station 3
SiO <sub>2</sub>	48,165
K20	4,177

Based on the percentage content of SiO<sub>2</sub> and K<sub>2</sub>O in igneous rock samples was then plotted in the (Bas et al., 1986) classification with the division of igneous rocks into four groups, namely acidic, intermediate, base, and ultrabasic, and then adjusted to the percentage of SiO<sub>2</sub> and K<sub>2</sub>O. The results of the classification found that the type of igneous rock in the study area was the basalt type (Bas et al., 1986).



Fig. 12. Classification of rock types according to (Bas et al.,1986)

# G. Discussion

In the research area, especially in Anabanua village, many types of rocks were found such as igneous rocks, sedimentary rocks, and metamorphic rocks (Wahyuni et al., 2021). There is manganese mineralization with a large volume of mineralization, but the type of manganese is not yet known.

Based on the results of chemical analysis, it was found that station 1 had Mn levels of 20.455%, Al 5.039%, Fe 3.673%, Cr 0.022%, and Zn 0.028%. Station 2 has Mn content of 0.046% and Fe 1.555%. Station 3 contains Mn 0.051%, Al 9.397%, Fe 1.790%, and Cr 0.009%.

The results of the mineralogical analysis of station 1 found the presence of minerals roeblingite, rhodonite, diopside, and quartz. Station 2 found the presence of calcite and crieselli minerals. Station 3 found minerals quartz, analcime, palygorskite, and plagioclase. Based on the results of chemical and mineralogical analysis, the three rock samples were then classified based on the type of rock to know the name of the rock.

Sample 1 is a type of manganese with the main mineral composition of manganese carriers, Sample 2 is a type of carbonate sedimentary rock and is classified based on its grain size by (Grabau, 1904b) and the name of the rock is calcillutite. Sample 3 is a type of igneous rock and is classified on<sub>Si02</sub> and<sub>K20</sub> diagrams by (Bas et al., 1986), showing igneous rock samples in the Basalt column.

Manganese mineralization in the study area is based on chemical and mineralogical analysis that the carrier rock is a type of Basalt igneous rock that invades side rocks in the form of carbonate sedimentary rocks. And based on regional geology the study site consists of diorite rocks and there are outcrops of basalt.

# 4. Conclusion

The conclusions from the results of the study are: Based on the results of chemical analysis of manganese mineralized rocks consisting of metal elements Mn (0.046%-20.455%), Fe (1.555%-3.673%), and non-metallic elements SiO<sub>2</sub> (11.403%-48.165%), K<sub>2</sub>O (0.398%-4.177%). Mineralogy of manganese mineralization carrier rocks consists of the minerals roeblingite (Pb<sub>2</sub>Ca<sub>6</sub>Mn<sub>2</sub>), rhodonite (CaMn<sub>3</sub>), diopside  $(MgCaSi_2O_6)$ , calcite  $(CaCO_3)$ , kieserite  $(Al_2GeO_4(OH)_2)$ , zeolite (Na(AlSi<sub>2</sub>O<sub>6</sub>). H<sub>2</sub>O), and palygorskite  $(Mg,Al)_2$  $Si_4O_{10}(OH) \cdot 4H_2O$ ). Based on the results of the chemistry and mineralogy of rocks show that rocks belong to the sub-alkaline type of basalt.

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Important input based on this study is that it is hoped that researchers can then know the detailed types of manganese deposits and can find out the distribution of manganese at the location.

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