

# Mineralogical and geochemical characterization of the Wonosari formation limestone at Gunungkidul Indonesia as preliminary investigation of Portland cement raw material

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**Abstract**. Mineralogical and geochemical investigations were carried out to determine the characteristics of limestone in the Wonosari Formation and to suggest its depositional environment and a preliminary study for the properties of Portland Cement. The study was conducted at Ponjong Area, Gunungkidul Regency, Daerah Istimewa Yogyakarta, Indonesia. The outcrop in this study area is composed of Wonosari layered limestone. Based on the facies interpretation in the research area, there are three depositional units: packstone, wackstone, and grainstone. This area's depositional environment is the back reef lagoon and sand apron zones that are not related to the open sea. According to XRF data, limestone showed a reasonably high composition of CaO compounds, about 53.78% - 59.09%. Most limestone samples were classified as good quality as Portland Cement Raw Material due to CaO content >49%. The MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>, K<sub>2</sub>O, Na<sub>2</sub>O, TiO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub> compounds also fulfil the Indonesian National Standard (SNI-15-2049-2004). Geochemical content shows limestone has a higher grain percentage than the matrix. The utilization of limestone in research area are expected to be a reference for the development of natural resources in the future that pay attention to the environment for mutual sustainability.

#### 1. Introduction

One of the material components that are indispensable in infrastructure development projects is Portland cement. Portland cement is an adhesive material or aggregate in making concrete [1]. The chemical composition of raw material used play as important role to the quality of Portland cement. The primary raw material used for manufacturing Portland cement is limestone. According to [2], the characteristics of cements comprise several compounds that are affected by the particle size distributions and the chemical-mineralogical compositions of the limestone. Limestone's mineralogical and geochemical composition significantly impacts whether it is high-quality or low-quality as a raw material for Portland cement [2].

This research was carried out at Ponjong Area of Gunungkidul Regency, Daerah Istimewa Yogyakarta, Indonesia (Figure 1). Although studies of limestone geochemistry are highly significant in comprehending the depositional condition of a limestone formation, they were not given as much attention in the studies of the Wonosari Formation, which was the subject of this study. Geochemistry and its implications for the provenance of limestone are just two examples of previous geochemical studies conducted in many parts of the world. They demonstrate the significance of geochemical

research for understanding limestone depositional conditions [3]. However, depending on the limestone facies in which it is found, the limestone itself has varying properties.

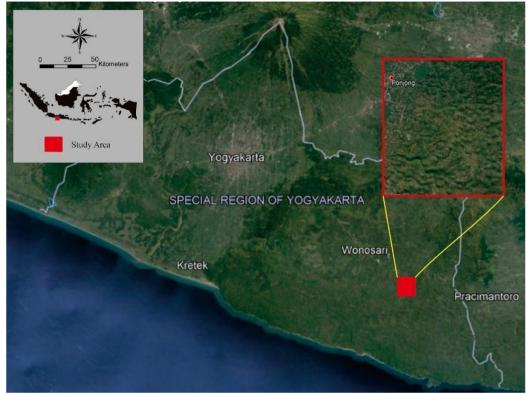


Figure 1. Research Area in Ponjong Area, Gunungkidul Regency, Daerah Istimewa Yogyakarta

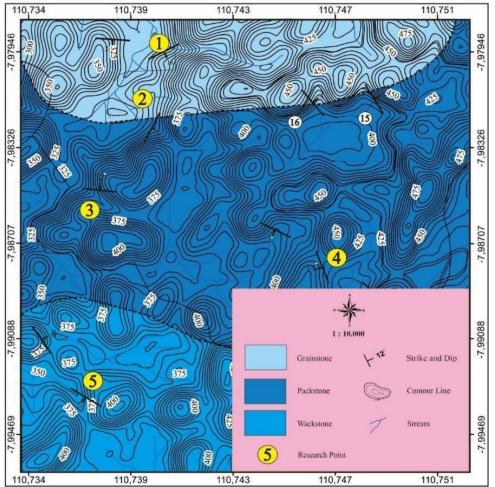
Limestone as the basic material for cement is the main material up to 70% while the other 30% is clay. So, the chemical composition of limestone is very important [4]. This study analyzes the limestone properties and geochemical content to ease the investigation of Portland cement raw materials. Mineralogy and geochemical components, such as the major oxide compounds (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, and Na<sub>2</sub>O) present in the Wonosari Formation limestone, will be used to determine the characteristics of the limestone in the Wonosari formation. The factors would be used to interpret its depositional environment and conduct a preliminary investigation of the raw materials for Portland cement [5]. Therefore, this study might be helpful for better reconstruction and understanding of the Wonosari Formation's characteristics.

#### 2. Geological Condition

According to a regional geological map of Java's Surakarta-Giritontro Quadrangle at a scale of 1:100,000 [6], the Semilir and Wonosari Formation makes up the study area. The Semilir Formation consists of tuff, dacitic pumice breccia, tuffaceous sandstone, shale, limestone, marly-tuffaceous limestone, conglomeratic limestone, tuffaceous sandstone, and siltstone are all parts of the Wonosari Formation, where it was unconformably deposited above Semilir Formation. The research location on the study region's geological map is directly within the Wonosari formation (Figure 2).

Carbonate rocks such as layered limestone and reef limestone dominate the Wonosari Formation, with marl as an insert. This formation is well exposed in the Wonosari area and its environs, generating the Wonosari sub-zone landscape and the Gunung Sewu sub-zone karst topography, 1992). The Wonosari Formation is Middle Miocene-Pliocene in age, based on the occurrence of macro and micro foraminifera fossils such as Lepidocyclina sp. and Miogypsina. This formation's thickness is believed to be more than 800 m. Its stratigraphic position at the bottom intersects with the Oyo Formation, while

it intersects with the Kepek Formation at the top. Simultaneously, the depositional environment is a shallow sea (neritic). The presence of tuff in this formation, especially in the east, indicates that there were still signs of volcanic activity at that time. The study area has packstone, grainstone, and wackestone limestone units [7]. The geological characteristics of the study is dominated by limestone in the karst area.



**Figure 2.** Geological map of the research area showing the distribution of lithology units in the research area and the sampling location for this study

# 3. Methods

This research begins with a literature review, then field observations using geological mapping methods, including geomorphological mapping, structural geology, and lithology. Petrographic and geochemical analyses were carried out for the data analysis stage. At the end, the research concludes the mineralogy and geochemical characterization as preliminarily investigation of Portland cement raw material as shown in Figure 3.

Petrographic analysis was carried out to determine the mineralogy and facies of limestone, then geochemical analysis to determine the chemical content and its percentage. Geological mapping was carried out on 17 observation stations and 5 research point for petrographic and geochemical sampling. Geological mapping was carried out to provide an overview of lithology distribution and structures in the research area. The rock sample collecting for this study was not carried out from a measuring section, but the outcrop sampling was based on the colour and texture difference of the limestone.

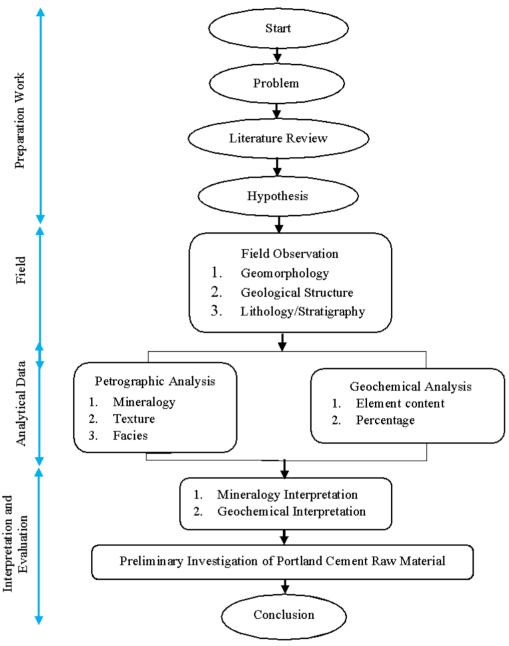


Figure 3. Research Flow Chart

In the laboratory analysis, rock thin section was observed using a polarizing microscope to identify the existing limestone facies. Chemical content analysis was carried out using the X-ray Fluorescence method. The X-Ray Fluorescence method is a non-destructive instrumental method of qualitative and quantitative analysis of chemical elements based on the measurement of the intensity of the X-ray spectral lines emitted by secondary excitation [8]. The X-Ray Fluorescence method was chosen because this method is easy, fast, inexpensive, and has sufficient precision to determine the chemical content of the rock under study [9]. At last, Facies and quality analyses were carried out on five limestone samples at the study site. Determination of the quality of limestone as a cement raw material is based on the classification of limestone quality based on the CaO content of Indonesian Cement Industry by [10][11] and [12] as shown in Table 1 and Table 2

Table 1. Classification of innestone quality by indonesian Cement industry						
No.	Geochemistry Symbol	Cement Raw Material	Cement Raw Material			
		Standard (%) [10]	Standard (%) [11]			
1	CaO	49.8 - 55.6	50 - 55			
2	$SiO_2$	0.76 - 4.75				
3	MgO	0.30 - 2.00	Max. 2			
4	$Al_2O_3$	0.71 - 2.00	Max. 0.95			
5	$Fe_2O_3$	0.36 - 1.47	Max. 2.47			

Table 1. Classification of limestone quality by Indonesian Cement Industry

Table 2. Classification of limestone	quality based on Indonesian	National Standard [12]
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No.	Description	Portland Cement Type (%)				
		Ι	II	III	IV	V
1	SiO <sub>2</sub> . Minimum	-	20	-	-	-
2	A1 <sub>2</sub> O <sub>3</sub> , Maximum	-	6	-	-	-
3	Fe <sub>2</sub> O <sub>3</sub> , Maximum	-	6	-	6.5	-
4	MgO, Maximum	6	6	6	6	6
5	SO <sub>3</sub> , Maximum if					
	$C_3A < 8.0$	3	3	3.5	2.3	2.3
	$C_3A > 8.0$	3.5	-	4.5		
6	Disappearance, Maximum	5	3	3	25	3
7	Insoluble Part, Maximum	3	1.5	1.5	1.5	1.5
8	C <sub>3</sub> S, Maximum	-	-	-	3.5	-
9	C <sub>2</sub> S, Minimum	-	-	-	4.0	-
10	C <sub>3</sub> A, Maximum	-	8	15	7	5
11	$C_4AF + 2C_3A$ or $C_4AF + C_2F$ , Maximum	-	-	-	-	25

According to Indonesian Nation Standard, chemical limitation requirements based on calculations for a particular potential compound do not necessarily imply that the oxide of that potential compound is in a pure state [12]. Therefore, the potential compounds must be calculated using The Bogue calculation based on its oxide composition as follow.

- $C_3S = 3CaO.SiO_2 = (4,071 \text{ x } \% \text{ CaO}) (7,600 \text{ x } \% SiO_2) (6,718 \text{ x } \% \text{ Al}_2O_3) (1,430 \text{ x } \% \text{ Fe}_2O_3) (2,852 \text{ x } \% \text{ SO}_3)$
- $C_2S = 2CaO.SiO_2 = (2,867 \times \% SiO_2) (0,7544 \times \% C_3S)$
- $C_3A = 3CaO. Al2O3 = (2,650 \times \% Al2O3) (1,692 \times \% Fe_2O_3)$
- $C_4AF = 4CaO. Al_2O_3.Fe_2O_3 = (3,043 \text{ x }\% \text{ Fe}_2O_3)$

### 4. Results

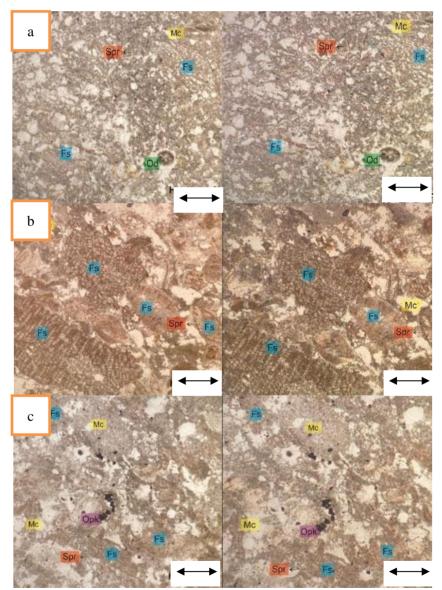
# 4.1. Mineralogy and Deposition Environment

Petrography observation of limestone samples P1, P3, P5 are shown on Figure 4. The mineralogical calculation refers to a normative calculation for sedimentary rocks [11]. Generally, petrographic identification on plane polarized light (PPL) and cross polarized light (XPL) of the limestone samples exhibits almost similar petrographic characteristics, and they can be termed as wackestone, packstone, grainstone by referring to the classification [7].

The research point P5 has a brown colour on PPL observations and brownish gray on XPL observations, 0.2mm to 0.9 mm grain size, angular to very rounded grain shape, moderate sorting, open packing, and intraparticle porosity. The composition comprises allochem in the form of Ooid and foraminifera 30 wt. %, sparite in the form of 3% carbonate mud, and micrite in the form of classic microsparite 65 wt. %. The presence of mineral quartz, feldspar (plagioclase) is in very small quantities of 2 wt.%, Based on its texture and composition, P5 is called Wackstone Limestone [7].

The research point P3 has a brown colour on PPL observations and brownish gray on XPL observations, 0.2mm to 1 mm grain size, rounded grain shape, moderate sorting, open packing, and interparticle porosity, The composition comprises allochem in the form of skeletal grain (foraminifera) 55 wt. %, sparite in the form of carbonate mud 3 wt. %, and micrite in the form of microsparite 40 wt. %. The presence of mineral quartz, feldspar (plagioclase) is in very small quantities of 2 wt.%, Based on its texture and composition, P3 is called Packstone Limestone [7].

The research point P1 has a brownish gray colour on PPL observations and dark brown on XPL observations, 0.1mm to 0.9mm grain size, grain supported, angular to rounded grain shape, moderate sorting, open packing, and intraparticle porosity. The composition comprises allochem in the form of skeletal grain (foraminifera) 67 wt. %, sparite in the form of carbonate mud 2 wt. %, and micrite in the form of microsparite 22 wt. %. The presence of mineral quartz, feldspar (plagioclase) is 9 wt.%, Based on its texture and composition, P1 is called Grainstone Limestone [7].



**Figure 4.** Petrographic Analysis: a) Wackstone in PPL and XPL b) Packstone in PPL and XPL c) Grainstone in PPL and XPL. Note: Mc = Micrite; Spr = Sparite; Op = Opaque; Od = Ooid; Frm = foraminifera; Qz = quartz; Fs = feldspar plagioclase.

Based on the results of field observations and petrographic analysis above, the depositional environment of the research location is the back reef lagoon and sand apron zones that is not related to the open sea [7]. The water conditions are calm, the water circulation is limited, and a lot of burrowing organisms live on the bottom. At this location the energy that works is weak energy, the water conditions are calm.

### 4.2. Geochemistry

The major oxide data in Figure 5 show that limestone of Wonosari Formation at research area contains CaO concentration that ranges from 53.78 - 59.09 wt.%, SiO<sub>2</sub> 0.08 - 1.02 wt.%, MgO 1.41 - 1.62 wt.%, Al<sub>2</sub>O<sub>3</sub> 0.03 - 0.12 wt.%, Fe<sub>2</sub>O<sub>3</sub> 0.02 - 0.08 wt.%, TiO<sub>2</sub> <0.0003 - 0.67 wt.%, P<sub>2</sub>O<sub>5</sub> 0.05 - 0.08 wt.%, SO<sub>3</sub> <0.0003 - 0.01 wt.%, K<sub>2</sub>O <0.0003 - 0.01 wt.%, and MnO <0.01 - 0.37wt%. Plotting of major oxide variation (x-axis) versus major oxide concentration of the sample on y-axis uses normalization from PAAS (Post-Archean Australian Shale) [14]. The plotting shows that CaO concentration of white limestone is the highest concentration of all limestone samples. The high composition of CaO in the research area makes the potential and prospect of using Wonosari limestone as a Portland raw material.

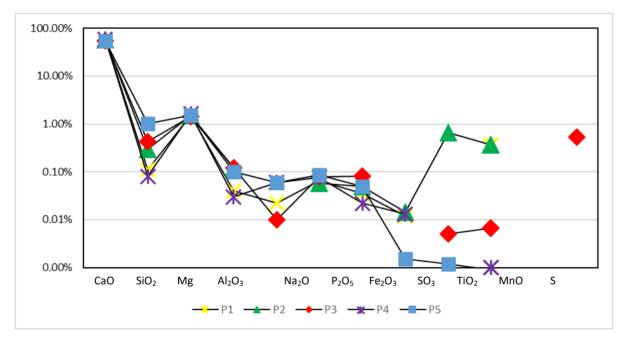


Figure 5. Normalized major oxide diagram for limestone samples of Research Area

### 5. Discussion

Analysis of 5 limestone samples at the study site showed a fairly high composition of CaO compounds, namely 53.78% - 59.09%. The content of MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub> compounds also still meets the Indonesian National Standard [12]. This is interpreted because the characteristics of limestone in the study area are grain supported and low in carbonate mud composition. Most of limestone samples at the study site were classified as good quality limestone because they had CaO content >49%. This value has met the quality standard [10] as well as quality standard classification from Indonesian National Standard [12], Indonesian Cement Industry [11] as a raw material for making Portland cement, which is > 49%. Analysis results XRF at the two research stations is consistent from the previous researchers. The composition of CaO compounds at the research stations was ranged 50.37 - 54.84 % [15].

High amounts of CaO and low levels of MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe2O<sub>3</sub>, SO<sub>3</sub>, K<sub>2</sub>O, and FeS<sub>2</sub> are thought to occur in grain-supported limestones due to the more significant grain percentage than the

matrix. CaO concentration in limestone is derived from limestone grains made up of organism pieces (foraminifera, algae, molluscs, corals, and so on) or cement made up of aragonite or calcite with the chemical formula CaCO3 [14]. The presence or lack of clay minerals and other minerals that constitute the matrix in the limestone influences the levels of MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>, K<sub>2</sub>O, and FeS<sub>2</sub>. On the other hand, the opposite happens matrix-supported limestones. Furthermore, the geochemistry results also demonstrate that the fine-grained limestone has low CaO content and high MgO content. In contrast, coarse limestone has high CaO and low MgO content. This is because the fine-grained limestone contains fewer bioclastic and calcite minerals as consistent as the previous explanation

The utilization of limestone in research area is expected to be a reference for the development of natural resources in the future for the welfare of the community. For this reason, its use must also pay attention to the environment for mutual sustainability.

# 6. Conclusion

From the research that has been done, it can be concluded that the limestone consists grainstone, packstone and wacktone lithology, the sedimentary structure that develops in this location is a layering pattern. The depositional facies belong to the reef core and back-reef lagoon facies zones. The results of the XRF geochemical analysis showed differences in the composition of the constituent compounds. Analysis of the quality of limestone samples at the study site showed that all samples were of good quality with quite varied values according to Indonesian National Standard [12]. CaO compounds in P1, P2, P3, P4 that have many grain-supported rocks such as grainstone and packstone tend to show better quality about 57-59.09%, while CaO compounds in P5 that have matrix-supported texture such as wackstone produce poorer quality limestones to be used as Portland cement about 53.78%. The content of MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub> compounds also still meets the Indonesian National Standard [12].

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