Mineralogy of travertine deposit in Cisolok geothermal field, Sukabumi, West Java, Indonesia

A Firdaus, D T Kurniadi, D N Sahradani and Supriyanto
Geoscience Study Program, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok 16424, Indonesia

Corresponding author’s email: dyahnindita@ui.ac.id

Abstract. Travertine is a geothermal surface feature that forms by the deposition of carbonate from discharging supersaturated thermal bicarbonate fluid. This study was conducted to determine travertine rocks mineralogy found in Cisolok geothermal area, Sukabumi, West Java. Petrographic, diffraction, and elemental analysis were performed on several recent and paleo-travertine samples. The petrographic and diffraction method confirms the presence of calcite and microcrystalline. The paleo-travertine deposit showed a more diverse texture through chemical elemental analysis. The analysis showed that the abundance of calcite minerals and the absence of aragonite indicate the intermediate low temperature geothermal system in Cisolok.

Keywords: Travertine, mineralogy, Cisolok, geothermal manifestation

1. Introduction
Travertine deposits are surface carbonate rocks associated with thermal springs discharging that is rich in calcium bicarbonate (CaCO₃) originating from deep carbonate geothermal reservoirs [1, 2]. Calcium bicarbonate solution can reach the surface due to fractures, subsequently depositing travertine after the release of CO₂ dissolved once reaching the atmosphere, which leads to CaCO₃ supersaturation [1]. The presence of travertine deposits can help determine the geothermal system and the changing of geothermal systems in an area [3]. Information on geothermal system type can help the development of a geothermal area. A comparison between recent and paleo-travertine deposits helps to predict the possible diagenesis process [4].

In previous research, Mandradewi et al. stated that Cisolok geothermal field is characterized and dominated by travertine deposits and silica sinter [3], but this study did not examine in detail the travertine characteristics. This mineralogical study for Cisolok travertine is a fraction for further travertine research in West Java, and this paper can support and complement the travertine-related database in the Cisolok geothermal field. The aim of this study will examine the physical characteristics, mineralogy, and composition using petrographic, diffraction, and fluorescence methods to better understand the evolution of the Cisolok geothermal system.

Geothermal Cisolok is located in Sukabumi Regency, West Java, and is approximately 140 km away from Banten (figure 1). The regional geology of Cisolok is part of the Oligocene Cikotok formation consisting of lava, tuff, and volcanic breccias [5] (figure 2). Following the Early Miocene Cipumag and Citarete formations, conglomerates and breccias controlled the Cimapag Formation, while the Citarete formation consisting of tuff and limestone [5]. Dacitic and andesitic intrusion from the Middle to
Late Miocene is found in the southern section of the research area. Overall, quaternary rocks of basaltic lavas, andesite, and pyroclastic deposits dominated the geological condition of Cisolok [3].

The Cisolok geothermal system model is a hot water-dominated system and considered as a moderate enthalpy geothermal system [6]. Surface manifestations such as travertine deposits, spouting springs, and silica sinters can be found in the Cisolok Geothermal area (figure 3). This area is generally controlled with the main faults trending NE-SW, NW-SE, and N-S [6]. Based on geochemical analysis for the thermal water, Cisolok has bicarbonate water associated with Cl water and dominated by limestone [7].

Figure 1. Research location; (a) map of West Java, Banten, and Special Region of Jakarta; (b) sampling location in the Cisolok geothermal field. The black square is showing the research location, green dots represent sampling location distribution.

Figure 2. Simplified geological map of the studied area [3].
2. Materials and method

Ten travertine samples were collected from around the geothermal manifestation of Cisolok Geothermal, Sukabumi, West Java. The locations for sampling are at the proximity of spouting spring, floor river, pool, and rock vein. All travertine sample deposits are cataloged and characterized based on their recent and paleo occurrence. The samples were first described based on their appearances, color, and texture. Following hand specimen description is petrographic, diffraction, and elemental analysis to determine the physical characteristics of the travertine texture and mineralogy. The petrographic analysis was conducted in the Geological Science Study Program, Universitas Indonesia using a petrographic microscope Leica DM750P. Some fraction of travertine samples were crushed and grinded in order to meet the requirements for XRD and XRF analysis. Diffraction and elemental analysis were conducted by Research Laboratorium UPP IPD FMIPA Universitas Indonesia. Diffraction analysis completed using PAN Analytical X’Pert Pro (CuKα 1.54 Å) with a 2θ range of 5° – 90°.

3. Results and discussion

Recent travertine samples were taken from the active spouting spring (CSL 7) and pool (CSL 9) (figure 4a). Sample CSL 7 is composed of white calcite, composed of alternate heteropachous laminates consisting of micrite and sparite. The porosity of this rock is the intercrystalline type. The CSL 9 sample is composed of alternate homopachous laminates consisting of different textures with a coarser texture in the center 1 cm thick and scattered micrites. This sample has intercrystalline and fenestral porosity.

Paleo-travertine in CSL 3 (figure 4b) sample is taken from the river floor. This sample has alternating homopachous lamination between large calcite crystals with 1 cm thick yellowish calcite crystals and small white crystals. At the top, there is a slightly brownish micritic fibrous calcite. The porosity of this rock is the intercrystalline type. In comparison paleo-travertine in the CSL 8 (figure 4b) sample has a fresh white color and is composed of alternate heteropachous laminations between white calcite with a thickness of 1 cm and brownish micrites. There were traces of microbe in this sample, and this rock tends to be calcareous and not as hard as other samples. This phenomenon is likely to occur because the rock does not undergo cementation due to a fast and continuous precipitation process.

The textural component of travertine is generally dominated by micrite, sparite and more complex dendrites [1]. Petrographic analysis revealed the presence of calcite in all samples and microcrystalline or micrites in some samples. Based on petrographic images, most travertine samples have a combination of textures made up of micrites and sparites. Furthermore, no complex textures such as dendrite or fan
crystals were found on Cisolok travertine samples; the presence of dendritic and fan crystal is usually related to precipitation from fluid with higher temperature as in Reshuitang thermogenic travertine in China [8]. Based on the comparison between the crystal's length and width (ratio of length to width), Cisolok travertine has an equant calcite texture, which can be euhedral-anhedral [1].

Apparently, calcite crystals found in paleo-travertine were more extensive and diverse, whereas recent travertine crystals were smaller and uniform in size (figure 5). Recent travertine with small and simple crystals is generally formed due to the precipitation of hydrothermal fluids with a more balanced medium-low temperature, slow CO$_2$ release rate, steady hydrodynamic state, or influence of tended microbes [9]. While the larger calcite crystals in paleo-travertine are formed due to a diagenesis process such as recrystallization in the form of a micrite change to sparite, this process allows the crystals to rearrange and combine with other minerals to form larger crystals [1]. Other factors that affect the crystal shape are the location and intensity of rainfall. High intensity of rainfall can cause hydrothermal fluid temperature fluctuation and affect the CO$_2$ release rate, which leads to smaller size deposited crystals [8]. In comparison, the location of fluid output such as spouting springs and floor river also affects the fluctuation of hydrothermal fluid output, affecting the saturation level, precipitation rate, and crystal growth rate [1, 9].

![Figure 4. Hand specimen of (a) recent travertine, and (b) paleo-travertine deposit in Cisolok, West Java.](image)

![Figure 5. Thin section photomicrograph of (a, b) recent travertine, and (c, d) paleo-travertine in Cisolok, West Java, which comprised of calcite (c) and micrite (m).](image)
On some thin sections, laminations of minerals are generally composed of small and simple crystals (micrite, sparite) with larger crystals (sparite). Rainfall intensity [8] and fluctuations of deposition rate is thought to influence the formation of alternating lamination in travertine rocks over a certain period [1].

Diffraction analysis proves the presence of namely calcite, clay (dickite and montmorillonite) with traces of corundum as shown in diffractogram (figure 6). Feldspar, hematite, and quartz were also present in few travertine samples. The dominance of calcite in travertine is likely because calcite is thermodynamically stable at ambient temperature [10]. The intensity of dickite found in recent travertine was slightly higher than paleo-travertine, and this is due to the weathering process occurring on paleo-travertine samples. The mineral dickite indicates a weak acid hydrothermal fluid type [11].

In samples, traces of corundum were also found with very little intensity and probably originated from sedimentary materials resistant to weathering [12].

The presence of feldspar and quartz at a lower intensity in the travertine samples is thought to be derived from the andesite lithology hosts at the study site. Meanwhile, hematite’s presence is thought to come from the precipitation of thermal water fluids containing Fe-oxide, whose concentration increases with increasing salinity and acidity [11].

If recent and paleo travertine are compared, recent travertine contains more accessories material in terms of peak number and intensity. These materials may result from CO$_2$ evasion or degassing, which made the pH vary, or as a consequence of oxygen transport, which modify the redox-potential. Moreover, the precipitation environment occurs over rapid pressure, evaporation, and temperature drop [1].

Elemental analysis carried out on all samples was presented as a percentage weight of each element and element oxides (figure 7). Ca-oxide dominates the composition of travertine ranging from 53.82–96.68 %, followed by other element-oxides such as Al-oxide, Fe-oxide, Mn-oxide. In the two samples, the concentration of Cl exhibits a higher concentration than the other samples. All samples contain Mg-oxide ranging from 1.28–3.5 %, where Mg-O is higher for paleo-travertine samples. Higher Mg concentrations in paleo-travertine indicated near-surface reactions to leaching Mg from the andesitic Cisokol host lithology and dilution through groundwater, which contains Mg-rich [11]. The presence of Mg-oxide was also confirmed by the diffraction analysis with alteration minerals such as chlorite and montmorillonite.

Moreover, Al-oxide traces in all samples were found from the results of aluminum precipitation from the acid waters through rock leaching [11]. In contrast, the concentrations of Fe-oxide trace were deficient in recent and paleo-travertine due to precipitation from fluid with ferrous iron concentration, which decreases with decreasing salinity and acidity [11].

![Figure 6. Diffraction analysis for travertine deposit.](image)
Figure 7. Elemental analysis chart for selected travertine samples with slightly anomaly value of their element-oxides.

From a hydrology point of view, recent travertine deposits show more saline and acidic water when compared to the minerals composed in the paleo-travertine deposits. The presence of Al-oxide and Fe-oxide, confirming the presence of clay minerals (dickite) and traces of corundum. Traces of Cl were found very little in the travertine samples; this is due to low Cl levels in waters, which indicate groundwater dilution reaction. The Manganese is a trace constituent that is rarely found in geothermal water; generally, Mn-oxides are deposited from hot springs [11].

The results of the thin section, diffraction, and elemental analysis confirmed the absence of aragonite in the travertine rock samples. The absence of aragonite crystal in all travertine deposits from Cisolok suggests CO₂ loss in the subsurface. Aragonite is usually formed when CO₂ loss occurs very rapidly [11]. Rapid CO₂ loss can occur immediately when subsurface boiling occurs in a higher temperature geothermal system [1]. If such conditions are not met, calcite is a more preferred stable state. Based on mineralogical findings, it is suggested that the Cisolok geothermal field lies within the intermediate or low-temperature geothermal system. However, fluid analysis and geothermometer calculations are required to support the determination of the type of geothermal system.

4. Conclusion
The mineralogy of travertine deposits in the Cisolok geothermal field consists mostly of calcite with micrites and trace oxides. Paleo-travertine deposits show sizes and shapes that are more diverse and larger than recent travertine; this is influenced by the diagenesis process and the reaction of CO₂ with the atmosphere. The percentage of Mg-oxide is relatively high compared to other trace elements. The abundance of calcite minerals and the absence of aragonite indicate the intermediate-low temperature geothermal system in Cisolok.

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