# VARIATION IN CARBONATE CEMENT BY CATHODOLUMINESCENCE MICROSCOPIC ANALYSIS: IMPLICATION ON ENGINEERING PROPERTIES OF OOLITIC LIMESTONE IN FATUMNASI AREA, TIMOR TENGAH SELATAN (TTS) REGENCY, NUSA TENGGARA TIMUR PROVINCE

Herry Zadrak Kotta[1],

[1]*Department of Mining Engineering, Nusa Cendana University, Kupang 85111*

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***ABSTRACT***

*Cathodoluminescence (CL) is generated by visible light of minerals when they are bombarded with a beam of high energy electrons by a cathode gun. There are two types of chatodoluminescence, i.e., cold CL and hot CL. In the cold cathode microscopic equipment, the electrons are generated by an electric discharge between two electrodes under a low gas pressure, whereas in the hot CL microscope, the electrons are generated by heating a filament (2000-3000°C). This research to propose determine the growth of oolitic limestone's cement by cathodoluminescence analysis and it's implication to the engineering properties. Sectoral zoning and chevron-shape growth zoning exist in some coarse-grained calcite aggregates. The sectorial zoning of calcite as reflected by dull to bright CL color indicated as a water level fluctuation during cementation of the carbonate rocks, where the bright color of calcite indicating a shallower depth of water (oxidation) and dull to nonluminescence indicating a deeper level of the water (reduction). The results of this research, oolitic limestone (sample NS-1) showing sectorial zoning (chevron-shape) with at least 6 zonations, and have better engineering properties of other samples, according to SNI. 13-0089-87. Cathodoluminescence analysis is commonly used in the petroleum study, as evidenced in this research can be applied to determine the engineering properties of oolitic limestones in the study area.*

**Keywords:** *Chatodoluminescence, oolitic limestone, calcite, strength, sectorial zoning*

**INTISARI**

*Cathodoluminescence (CL)* terjadi akibat mineral-mineral memancarkan cahaya tampak ketika mineral tersebut di bombardir dengan sinar elektron energi tinggi menggunakan pistol katoda. Ada dua jenis chatodoluminescence, yaitu: CL dingin dan CL panas. Untuk mikroskop katoda dingin, elektron dihasilkan dengan cara mengalirkan energi listrik diantara dua elektroda di bawah tekanan gas rendah, sedangkan pada mikroskop CL panas, elektron yang dihasilkan dengan cara memanaskan filamen (2000-3000°C ). Penelitian ini bertujuan mengusulkan penggunaan analisis cathodolu-minescence untuk mengetahui pertumbuhan semen dan implikasinya bagi sifat keteknikan batugamping oolith. Pertumbuhan zonasi sektoral dan zonasi *chevron – shape* muncul pada beberapa butiran kalsit yang kasar. Zonasi sektoral pada kalsit ditunjukkan oleh warna CL yang kusam – cerah, dan hal ini mengindikasikan fluktuasi air selama sementasi pada batuan karbonat, warna cerah menunjukkan kedalaman air yang dangkal (oksidasi) dan kusam - nonluminescence menunjukkan air yang lebih dalam air (reduksi). Hasil analisis *cathodoluminescence* menunjukkan adanya 6 zonasi pertumbuhan semen pada batugamping oolith (conto NS-1), dan memiliki sifat keteknikan lebih baik dari lima conto lainnya sesuai SNI. 13-0089-87. Hal ini menunjukkan bahwa analisis *cathodoluminescence* yang selama ini digunakan di dunia perminyakan, terbukti dalam penelitian ini dapat diterapkan untuk mengetahui sifat keteknikan batugamping oolith di daerah penelitian.

**Kata Kunci:** *Chatodoluminescence*, Batugamping ooid, kalsit, kuat tekan, zonasi

sektoral

## INTRODUCTION

Petrographic classification of limestones by Folk (1959) indicated that the most common textural elements were micrite (microcrystalline calcite), allo-chems (grain such as ooids, intraclasts, skeletal fragments, and pellets), and sparry calcite (generally as a porefilling cement). Mechanical properties of limestone were strongly influenced by its texture and its composition. Most of limestone and dolostone composed entirely of microcrystalline carbonate were stronger and more brittle than their coarser grained counterparts (Hugman and Friedman, 1979).

A cathodoluminescence (CL) phenolmenon, i.e., emission of light under electron bombardment, was known for a long time and was widely used in nearly all black-and-white, color cathode-ray tubes (Petrov, 1996). There were two types of chatodoluminescence, i.e., cold CL and hot CL. In the cold cathode microscopic equipment, the electrons are generated by an electric discharge between two electrodes under a low gas pressure, whereas in the hot CL microscope, the electrons are generated by heating a filament (2000-3000°C) (Warmada, 2003).

Cathodoluminescence microscopy is a petrographic tool widely used in studies of diagenesis for petroleum study. It is particularly suitable for documenting details of crystal growth in calcite and dolomite cements and for understanding pore evolution in carbonate sequences (Savard, et al., 1995). The intensities of CL in calcites are usually grouped into three categories: nonluminescent (dead, distinguished, or black), dull (brown and very dull), and luminescent (bright yellow, orange, and moderate). Within a single crystal, numerous CL zones can alternate and form features that may not be discernible by conventional light micros-cope or staining. CL features of calcites have generally been attributed to varia-tions in Mn concentrations as the main activator, and to Fe as the main quencher (for a review, see Pierson, 1981; Reeder, Paquette, 1989; Savard, et.al., 1995).

Mn and Fe contents of calcite reflect water (hydrothermal water) chemistry prevailing during carbonate precipitation. Various studies (Grover and Read, 1983; Dorobek, 1987) have suggested that the increasing Fe and Mn contents in the commonly observed sequence of CL zonation from nonluminescent to brightly luminescent to dully luminescent reflects progressive decreese in Eh. The intensity and color of luminescence are also dependent on the relative proportions of Mn and Fe.

In this paper, we would like to presents cathodoluminescence petrography of oolitic limestone from Fatumnasi area, Timor Tengah Selatan District, NTT Province by utilizing a cold CL, as shown in Figure 1. Oolitic Limestone spread quite widely in Timor Island and parti-cularly in the research area. The Oolitic limestone has been mined to commer-cially used as marble. Cathodoluminens-ce application was helpful to know that the cementation phase essentially provide information about it is engi-neering properties. To the best of our knowledge, no prior research using this method to determine the quality of oolitic limestones.


Figure 1. The Map of Fatumnasi Area, Timor Tengah Selatan District, NTT Province

## METHODS

Five-selected samples were collected from Fatumnasi area and analyzed with cathodoluminescence (CL). The Technosym instrument was used for CL studies of double polished thin sections. The CL analyses were carried out by Dr. Adrian Finch in the St.

Andreas Univer-sity, UK. The thin sections of carbonate samples were bombarded with electrons with energy of 15kV accelerating poten-tial and 245μA beam current. This sam-ples were also analyzed by using a PLM (polarized-light microscope) to detailed petrographic analysis of these samples.

**RESULTS AND DISCUSSION**

Oolitic limestone from Fatumnasi area was characterized by clastic texture with an average grain-size range from 0.22 to 6 mm in a bimodal grainsize distribution (0.75 mm and 1.8 mm), poorly sorted, and angular to sub angular form. They composed of peloid, skeletal, and a minor amount of red algae, fossils, detailed in Figure 2.

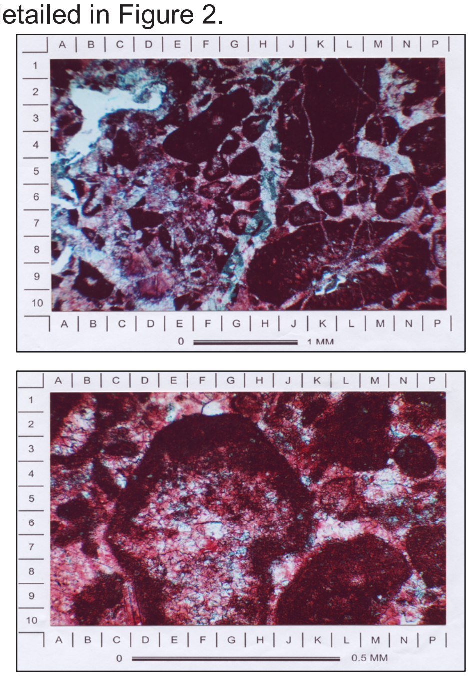


Figure 2. Photomicrograph of oolitic lime-stone in plan-polarized light microscope. Red and blue color due to alizarine red and blue stainning for carbonate mineral determination and and porosity analysis.

Its pore spaces were filled by calcite cement and some dissolu-tion porosity, stilolites and open fractures also existed, but the porosity of this rock was still low (2.5%). Diagenetic features consist of micritization of ooid grains, cementation and neomorphism. Cementation would be divided into three phases: (1) isopachous equant calcite rim ce-ment, (2) sparry calcite intergranular cement, and (3) cementation of micro-fractures. According to Dunham (1962) classification, this limestone was clas-sified as ooid grainstone.

Cathodoluminescence microscopy of the cement of oolitic limestone shows a sectorial zoning with 6 zonations. They show at least two type luminescences, i.e., dull or no luminescence of high Mn calcite, and bright to yellow color of pure calcite. Figure 3 suggested that the luminescence pattern of calcite was controlled by the amount of $Mn^{2+}$. Luminescence intensities varied from dull to nonluminescent (i.e., below the detection limit for the CL device used. If manganese ($Mn^{2+}$) was the activator of luminescence, a minimum amount of $Mn^{2+}$ was required in order to produce a detactable luminescence.

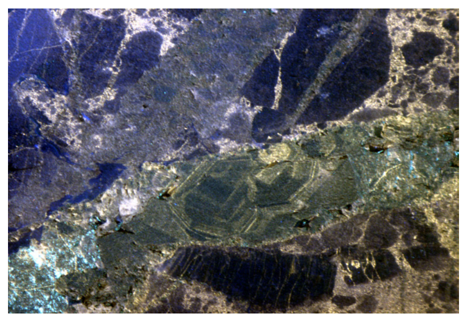

Figure 3. Cathodoluminescence microphotography of the cement of oolitic lime-stone, showing sectorial zoning (chevron-shape) with at least 6 zonations (left figure).

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Pierson (1981) suggested that this minimum amount was close to 1000 ppm $Mn^{2+}$ (0.1 wt.%). $Mn^{2+}$ was generally regarded as the principal activator and $Fe^{2+}$ acted as the main CL quencher in calcite (Spötl, 1991).

Bright calcite was precipitated from meteoric fluids that were slightly reducing to oxydizing condition, allowing only small amount of manganese and lesser amount of iron to be in reduced (2+) valence states and to substitute for calcium in calcite. Dull calcite was precipitated from more reducing fluids than that of bright calcite or nonluminescent, as suggested by high iron or manganese contents. These results were also confirmed by Dorobek (1987); Warmada and Hartati (2006). Sectoral zoning and chevron-shape growth zoning (Reeder and Paquette, 1989) existed in some coarse-grained calcite aggregates. The sectorial zoning of calcite as reflected by dull to bright CL color can be interpreted as a water level fluctuation during cementation of the carbonate rocks, where the bright color of calcite indicating a shallower depth of water (oxidation) and dull to nonluminescence indicating a deeper level of the water (reduction).

As manganese occurs in natural environments in the valence states +2, +3, and +4 (Wolfram and Krupp, 1996) and the higher oxidation states have a strong tendency to hydrolyse and precipitate, transport of Mn in aqueous solutions is generally favored by reducing conditions, and the $Mn^{2+}$ ion, and its complexes, constitute the principal trans-port species. This confirms that the present of significant amount of Mn and Fe as well as trace elements in calcite can effect the cathodoluminescence pat-terns of calcite. Measuring the calcite luminescence can be used to estimate/ interpret the redox conditions during calcite deposition.

Table 1: Compositional variation of oolitic limestone and its mechanical properties (strength).

| Sample No. | Strength (Kg/cm²) | Grain (%) | Matrix (%) | Cement (%) | Replace-ment (%) | Porosity (%) |
|---|---|---|---|---|---|---|
| FT01R | 624.82 | 9.5 | 72.5 | 12.0 | 3.5 | 2.5 |
| NO | 868.28 | 57.0 | 10.0 | 23.0 | 8.0 | 2.0 |
| NS-1 | 1,069.68 | 75.0 | 0.0 | 21.0 | 2.0 | 2.0 |
| NT-B | 357.91 | 69.0 | 6.0 | 21.0 | 2.5 | 1.5 |
| NT-C | 696.63 | 73.0 | 0.0 | 25.0 | 1.0 | 1.0 |
| NT-D1 | 205.54 | 68.0 | 0.0 | 21.0 | 3.0 | 8.0 |
| NT-D2 | 590.39 | 75.0 | 0.0 | 20.5 | 3.5 | 1.0 |
| NT-E | 555.87 | 75.5 | 0.0 | 20.5 | 2.0 | 2.0 |

Note: according to SNI. 13-0089-87: 800 Kg/cm$^2$ is very good properties category for tile with live load > 250 kg/cm$^2$)

Although carbonate-rock textures are often complex, strength and ductility can be predicted from consideration of only a few petrographic properties. Marbles and crystalline limestones are the weakest, most ductile rocks. Limestones with 50% or less sparry calcite behave similarly. Highly micritic limestones are stronger and more brittle, and their ultimate strength is proportional to the content of microcrystalline material, as shown in Table 1.

**CONCLUSIONS**

The CL study of hydrothermal carbonate anable to classify the two carbonate generations, i.e. high Mn calcite with dull or no luminescence, and pure calcite with bright orange luminescence and pure calcite. Sectoral zoning and chevron-shape growth zoning exist in some coarse-grained calcite aggregates. The sectorial zoning of calcite as reflected by dull to bright CL color indicated as a water level fluctuation during cementation of the carbonate rocks, where the bright color of calcite indicating a shallower depth of water (oxidation) and dull to nonluminescence indicating a deeper level of the water (reduction). The strength properties of limestone are controlled mostly by its composition and diagenetic features. Oolitihic limestone (sample NS-1) showing sectorial zoning (chevron-shape) with at least 6 zonations, and have better Engineering properties of other samples, according to SNI. 13-0089-87.

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**BIBLIOGRAPHY**

Dorobek, S.L., 1987. Petrography, geo-chemistry, and origin of burial diagenetic facies, Siluro-Devoni-an Hedelberg Group (carbonate rocks), Central Appalacians. The American Association of Petro-leum Geologists Bulletin, 71: 492-514.

Dunham, R.Y., 1962. Classification of carbonate rocks according to depositional texture: Classifica-tion of carbonate rocks – a symposium. AAPG Memoir 1, pp. 108-121.

Folk, R. L., 1959. Practical petrographic classification of limestones. The American Association of Petro-leum Geologists Bulletin, 43: 1-38.

Grover, G. Jr. and Read, J.F., 1983. Paleoaquifer and deep burial related cements defined by region-nal cathodoluminescent patterns, Middle Ordovician car-bonates, Virginia. The American Association of Petroleum Geolo-gists Bulletin, 67: 1275-1303.

Hugman III, R.H.H. and Friedman, M., 1979. Effects of texture and com-position of mechanical behavior of experimentally deformed car-bonate rocks. The American Association of Petroleum Geolo-gists Bulletin, 63: 1478-1489.

Paquette, J. & Reeder, R.J., 1995. Rela-tionship between surface struc-ture, growth mechaniscm, and trace element incorporation in calcite. Geochimica et Cosmo-chimica Acta, 59: 735-749.

Petrov, V.I., 1996. Cathodoluminescence microscopy. Physics – Uspekhi, 39:807-818.

Pierson, B.J., 1981. The control of cathodoluminescence in dolomite by iron and manganese. Sedi-mentology, 28: 601-610.

Reeder, R.J. and Paquette, J. 1989. Sector zoning in natural and synthetic calcites. Sedimentary Geology, 65: 239-247.

Savard, M.M., Vizer, J., and Hinton, R., 1995. Cathodoluminescence at low Fe and Mn concentrations: A SIMS study of zones in natural calcites. Journal of Sedimentary Research, A65:208-213.

Spötl, C., 1991. Cathodoluminescence of magnesite: Examples from the eastern Alps. Geology, 19: 52-55.

Tucker, M. (ed), 1988. Techniques in Sedimentology. Blackwell Scienti-fic Publications, 394p.

Warmada, 2003. Ore mineralogy and geochemistry of the Pongkor epithermal gold-silver deposit, Indonesia. Ph.D. Dissertation, Papierflieger Verlag GmbH, Clausthal-Zellerfeld, 107pp.

Warmada, I W. and Hartati, R., 2006. Chatodoluminescence microscopic analysis to interpret the redox condition during the formation of carbonate vein. Proceedings of 35th IAGI Annual Convention and Exhibition, 21 – 22 November 2006, 5p.