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# Chemistry and Cathodoluminescence Properties of the Carbonate Minerals From the Tertiary Marine Sediments, SE Korea

# 제3기 해성퇴적층에서 산출되는 탄산염광물의 화학적 및 음극선 발광 특성

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**ABSTRACT** : Carbonate minerals are examined by cathodoluminescence microscopy and chemical analysis to characterize the carbonate materials occurring in the Tertiary marine basin. The microscopic technique with cathodoluminescence gives new informations that are not obtainable by conventional microscopic techniques. The carbonate cements in sandstones appear to be uniform with transmitted light or with crossed prisms, but the inspection with cathololuminescence reveals foraminiferal tests and rhomb crystals in the carbonate cements. The chemical analysis indicates that the intense luminescence depends mainly on the presence of $Mn^{2+}$ and $Fe^{2+}$ as activator ions, but the $Fe^{2+}$ also acts as an important quencher ion when Fe concentration in dolomite is over 10,000 ppm. The dolomites, which are rich in calcium, are formed at the early stage of diagenesis at a temperature of about 60～70℃.

**Key words** : carbonate minerals, Tertiary marine basin, cathodoluminescence, sandstone, dolomite, diagenesis

요약 : 포항지역 제3기 해성퇴적층에서 산출되는 탄산염광물의 특성을 밝히기 위하여 음극선 발광현미경 관찰과 화학분석을 실시하였다. 발광현미경은 보통의 편광 현미경으로는 관찰할 수 없는 정보를 제공해 준다. 사암의 탄산염 교질물 내에서, 편광현미경하에서는 나타나지 않는 유공충의 형태와 마름모꼴로 자란 돌로마이트 형태들이 음금선 발광현미경하에서는 명확히 나타난다. 화학분석 결과, 발광은 탄산염 광물 내의 망간 성분과 철 성분에 의해서 나타난다. 그러나 돌로마이트 내의 철 성분이 10,000 ppm을 넘게 되면 발광은 사라진다. 산출되는 돌로마이트는 칼슘 성분이 많은 것이 특징이며, 60～70℃의 초기 속성작용 단계에서 생성된 것으로 생각된다.

주요어 : 포항지역, 제3기 해성퇴적층, 탄산염광물, 음극선 발광현미경, 사암, 돌로마이트, 속성작용

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## Introduction

The Tertiary marine basin is located around the Pohang city in the southeastern part of the Korean peninsula (Fig. 1). The basin has been investigated mainly with respect to paleontology and bio-stratigraphy, and was named Yeonil Group. The basin was also studied sedimentologically on the coarse-grained formations, and thus the coarse-grained formations are modeled as a fan delta deposit (Hwang *et al.*, 1995). However, the Yeonil Group is, as a whole, a marine sequence of fine-grained clastic sediments which accumulated during Middle Miocene. Many holes have been drilled for hydrocarbon exploration in this basin and revealed that the Tertiary marine sediments are very thin sequences, commonly about 400 m, and dominated by fine-grained mudstones with thinly interbedded sandstones. Indeed, the mudstone beds are easily observed at outcrops prevailed in the Pohang area. The mudstone are composed mainly of randomly interstratified illite-smectite (I-S) with other fine-grained silicate minerals such as quartz and feldspars (Son, 1996).

On the other hand, all the Tertiary marine sediments commonly includes carbonate concretions or nodules, which often form condensed concretionary beds. The origin and formation environments of the carbonate concretions have been recently investigated in detail using textural and stable isotope data (Woo *et al.*, 2003). In addition to concretions, the carbonate minerals including calcite and dolomite are also present in sandstones as cementing materials in the Tertiary marine sediments. Carbonate minerals are conventionally identified by optical properties in polarized light. An additional technique of observing carbonate minerals is to use the property of cathodoluminescence that depend mainly on subtle differences in amounts of different impurities and on crystal defects (Marshall, 1988). When a sample on thin section is bombarded by an energetic electron beam, it responds by emitting light of various wavelengths. The wavelength and intensity of the light emission are characteristic of the minerals and the distribution of certain impurities within it. The objective of this paper is to characterize the carbonate materials by using the cathodoluminescence microscopy as well as chemical analysis. The carbonates from the Tertiary marine sediments in the Pohang area were characterized in detail by the cathodoluminescence property compared with chemical analysis. Attention is paid particularly to dolomite.

## Materials and Methods

Carbonate samples were collected from the cores drilled for hydrocarbon exploration. The drill well is located in the Pohang city (Fig. 1). Carbonate samples analyzed were all from a drill core that penetrated the Miocene marine sediments (Fig. 2). A thick sandstone sequence is predominant at depths of 300~310 m, showing a fining-upward sequence, which is a turbidite channel sequence (Hwang, *et al.*, 1995). The samples were selected from three depth intervals: 126 m, 302 m, and 330 m. The carbonates from 302 m and 330 m occurs in sandstones as cementing materials, whereas that from 126 m is present as a concretion, which can be aware of from hard and dense characters. Numerous concretions are commonly found at the outcrops in the Pohang area.

The specimens were prepared into polished thin sections to observe the occurrence of carbonate minerals as well as the texture of minerals. Polished thin sections including carbonate minerals were examined by using a luminoscope attached to the polarizing microscope. The luminoscope was set at a condition of 40 millitorr, 12 kV, and 0.6 mA. Chemical compositions of each carbonate mineral were determined by electron microprobe employing WDS. The electron microprobe analysis was performed on the polished thin sections using JEOL JCXA-733 electron microprobe. Prior to analysis, areas including carbonate minerals were located and mapped under polarized light to position the exact areas for analysis. X-ray diffraction analysis was also

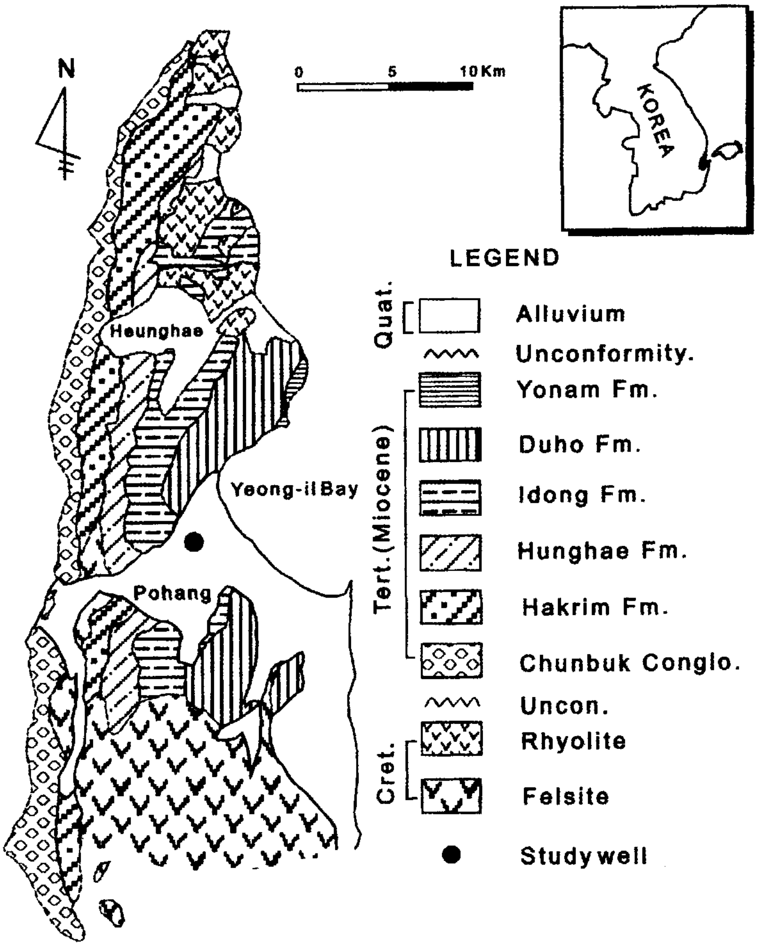

**Fig. 1.** Geologic map and the location of study well.

performed on all the carbonate specimens, and unit cell dimensions were calculated from the X-ray diffraction data.

## Results

### *Occurrence*

Calcite occurs as cementing materials in the sandstones from a depth of 330 m. The mineral has distinct rhombohedral cleavages in conventional polarizing light. Organic tests such as foraminifera are well preserved in the sandstones, indicating that the cementing materials are probably precipitated from the dissolved foraminifera or other organic tests. The calcite is characterized by orange-red color luminescence under the cathodoluminoscope.

Dolomites are present as cementing materials in the sandstones from a depth of 302 m, and also as a condensed concretion in the sequence of mudstones at a depth of 126 m. The cementing dolomite in the sandstones is colorless in the polarizing light and shows mosaic texture with distinct cleavages in thin sections, whereas the concretionary dolomite shows sutured textures of anhedral crystals with no cleavage. In addition, the concretionary dolomite includes sparsely silt-sized microquartz, woody materials, and pyrites. Microfossils are often observed in the concretionary dolomite.

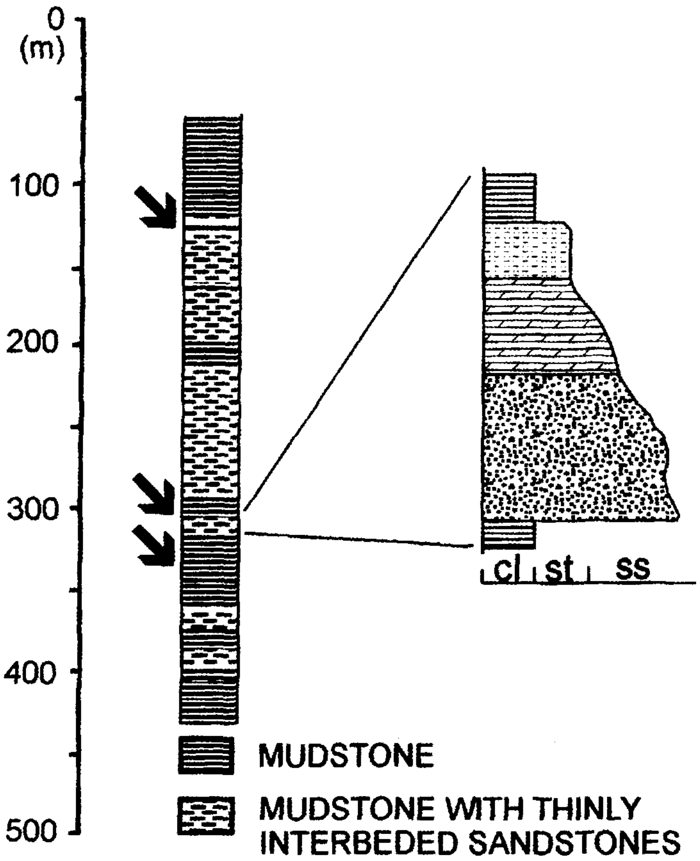

**Fig. 2.** Lithology of the study well. Arrows indicate the depths for sample collection. cl: clay, st: silt, ss: sand.

Cathodoluminescence microscopy shows a completely different image from that in conventional transmitted light. Cathodoluminescence reveals the outlines of microfossils in the dolomite cements, which are never visible with plain polarized light or with crossed polarizing prisms (Fig. 3). The relative intensity of the luminescence shows clearly the presence of the foraminiferal test that is orange-red and orange-yellow in color. Moreover, orange-yellow dolomite rhombs, which possess micro-zonation, are also observed in the dolomite cement under cathololuminoscope (Fig. 4). The micro-zonation of the dolomite rhombs cannot be observed with conventional microscopes, even with crossed polarizing prisms. On the other hand, the concretionary dolomite is lack or free of luminescence. Nevertheless, the concretionary dolomites show that the minerals include foraminiferal tests (Fig. 5).

### *Chemistry*

The cementing calcites in sandstones, which show orange-red color luminescence under cathodoluminoscope, were chemically analyzed by electron microprobe, and the average formula is calculated as follows:

$$(Ca_{1.95}Mg_{0.03}Fe_{0.01}Mn_{0.01})_2(CO_3)_2$$

The analyses fall into the ideal region of calcite as plotted within the $CaCO_3$-$MgCO_3$-$FeCO_3$ triangular diagram.

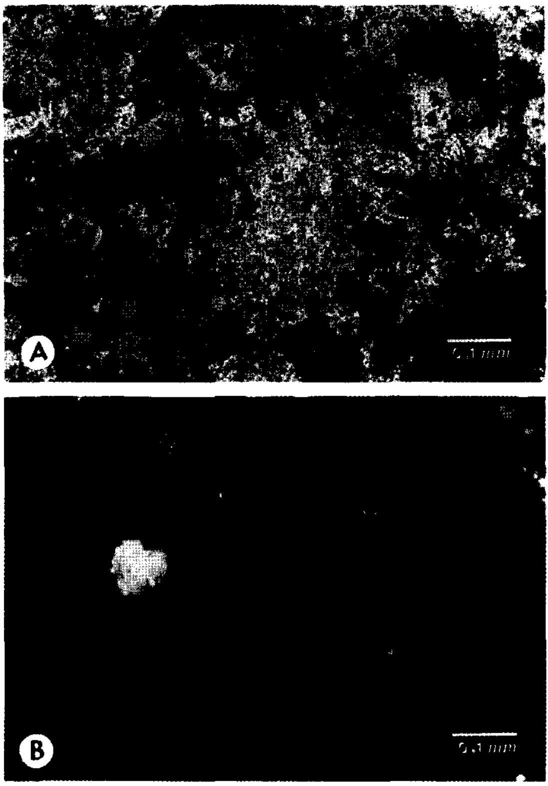

**Fig. 3.** Cathololuminescence reveals a foraminiferal test in dolomite cements that is not visible in conventional polarized light. A: Photo taken by conventional microscope (crossed nicol). B: Photo taken by cathodoluminoscope.

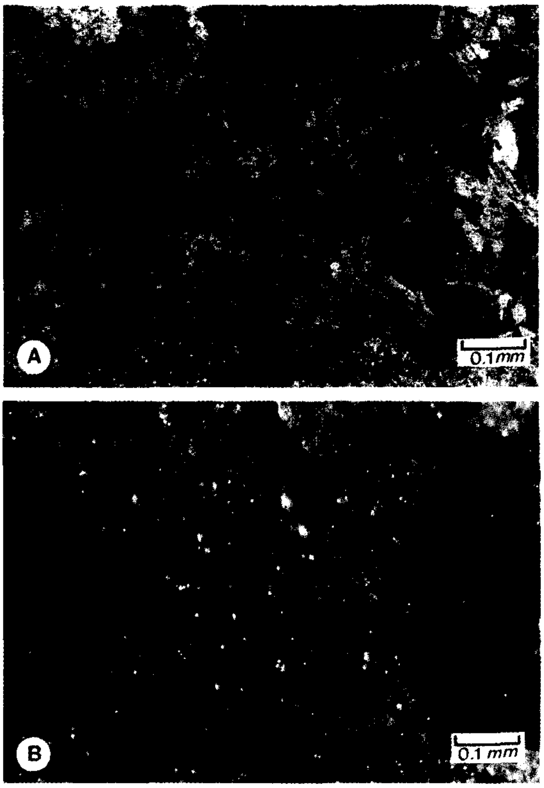

**Fig. 4.** Dolomite rhombs exhibiting micro-zonation which is revealed clearly with cathodoluminescence. A: Photo taken by conventional microscope (crossed nicol). B: Photo taken by cathodoluminoscope.

Dolomite is present in the two different form of occurrence: sandstone cements and concretions. In addition, three different degrees or colors of luminescence are present in the dolomite: orange-red, orange-yellow, and dark black without luminescence. The color is obviously caused by the intensity of luminescence: orange-yellow, orange-red, and dark black (no luminescence) in intense order. The foraminiferal shape is recognized by the difference of luminescent colors: orange-red and orange-yellow, which appear to be uniform in conventional polarizing light, and even with crossed prism (Fig. 3). The areas of orange-red and orange-yellow colors in the Fig. 3 were analyzed by electron microprobe, and the results are shown in Table 1 and 2. The dark black dolomite in Fig. 5 is also analyzed and shown in Table 3. Apparent difference in chemistry appears in the concentration of iron. The dark black dolomite in luminescent color, which occurs in concretionary dolomites, has a high Fe content. In the orange colored dolomites, which occur in sandstone cements, the orange-red part of dolomite has a higher Fe content than the orange-yellow part of the dolomite.

## Discussion

### *Luminescent Intensity vs. Chemistry*

Concretionary dolomite is dark black in color, implying the lack of luminescence. The foraminiferal tests are clearly observed in the dolo-

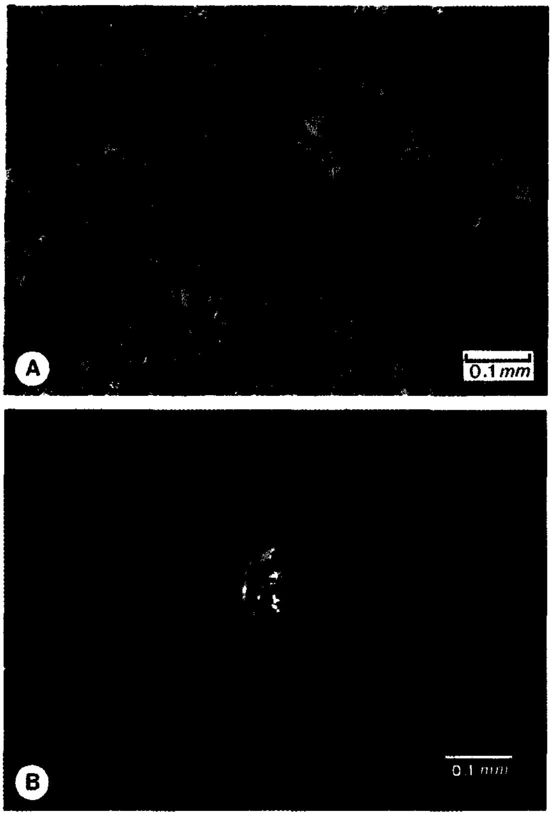

**Fig. 5.** Non-luminescing concretionary dolomites including brightly luminescing foramineferal tests. A: Photo taken by conventional microscope (crossed nicol). B: Photo taken by cathodoluminoscope.

mite cements by the difference of the intensity of luminescence. Luminescence colors is dependant primarily on the intensity of luminescence. Therefore, the electron microprobe analysis was performed on the dolomite cements in an attempt to understand the chemistry between orange-yellow and orange-red parts, and also on the dark black concretionary dolomites to understand why they lack the luminescence. The intensity difference of luminescence has been known to be produced mainly by the difference in the amount of trace elements such as manganese or iron (Marshall, 1988). Therefore, the chemical data by electron microprobe indicate that the difference of color is probably attributable to $Fe^{2+}$ and $Mn^{2+}$ contents. The brightly luminescing regions (orange-yellow part) has a relatively small amount of $Fe^{2+}$ compared with the orange-red part (Table 1). Moreover, the dark black concretionary dolomite is characterized by a larger amount of $Fe^{2+}$ than the cementing dolomites (Table 3). Pierson (1981) proposed that variation in the cathodoluminescent properties of carbonates are commonly attributed to differing proportions of manganese ($Mn^{2+}$) as the most important activator, and iron ($Fe^{2+}$) as the main inhibitor of luminescence. In addition, Pierson demonstrated that very small amounts of manganese, as little as 100 ppm, are sufficent to activate the luminescence but the intensity of luminescence is not proportional to the manganese concentration, and iron begins to quench luminescence as its concentration reaches 10,000 ppm.

The dolomites from the Yeonil Group show a wide range of the concentration in $Fe^{2+}$, that is responsible primarily for the degree of luminescence. When the electron microprobe data are plotted in a diagram that is modified from Pierson's suggestion (Fig. 6), the diagram reveals the relationship between the luminescence intensity and the concentrations of manganese and iron. The brightly luminescing, orange-yellow parts of the dolomite cements have high contents of $Mn^{2+}$ and $Fe^{2+}$. However, the $Fe^{2+}$ contents are less than 10,000 ppm, and thus the orange-yellow dolomites are plotted within the luminescence zone suggested by Pierson (1981). The analyses of the orange-red part of the dolomite cements have enough Mn contents and a higher Fe contents than those of the orange-yellow dolomites. The orange-red dolomites are clustered between luminescence and non-luminescence zones (Fig. 6). On the other hand, the concretionary dolomites with no luminescence have high contents of Mn as well Fe. Accordingly, the concretionary dolomites distinctly fall within the non-luminescent zone. As a result, the lack of luminescence of concretionary dolomites is fundamentally caused by the very high Fe contents, although they have a high content of Mn.

The intense orange-yellow luminescence arises

**Table 1.** Electron microprobe analyses of the orange-yellow luminescing parts in the foraminiferal tests in Fig. 3

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| CaO | 32.92 | 29.59 | 30.04 | 32.05 | 32.81 | 29.91 |
| MgO | 18.52 | 16.31 | 17.16 | 17.53 | 17.36 | 17.04 |
| FeO | 0.03 | 0.19 | 0.03 | 0.00 | 0.00 | 0.44 |
| MnO | 0.08 | 0.09 | 0.07 | 0.13 | 0.10 | 0.28 |
| Total | 51.55 | 46.18 | 47.30 | 49.70 | 50.26 | 47.67 |
| $CaCO_3$ | 58.75 | 52.81 | 53.61 | 57.19 | 58.56 | 53.38 |
| $MgCO_3$ | 38.75 | 34.12 | 35.89 | 36.67 | 36.61 | 35.65 |
| $FeCO_3$ | 0.05 | 0.30 | 0.05 | 0.00 | 0.00 | 0.71 |
| $MnCO_3$ | 0.13 | 0.15 | 0.12 | 0.20 | 0.15 | 0.45 |
| Total (wt%) | 97.68 | 87.35 | 89.65 | 94.07 | 95.02 | 90.19 |
| | Numbers of cations on the basis of 6 oxygens | | | | | |
| Ca | 1.12 | 1.13 | 1.11 | 1.13 | 1.55 | 1.10 |
| Mg | 0.88 | 0.86 | 0.88 | 0.86 | 0.85 | 0.88 |
| Fe | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |
| Mn | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |
| Total | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Mole% | | | | | | |
| $\%CaCO_3$ | 60.14 | 60.44 | 59.79 | 60.80 | 61.62 | 59.19 |
| $\%MgCO_3$ | 39.67 | 39.05 | 40.03 | 38.98 | 38.21 | 39.53 |
| $\%FeCO_3$ | 0.05 | 0.34 | 0.05 | 0.00 | 0.00 | 0.79 |
| $\%MnCO_3$ | 0.13 | 0.17 | 0.13 | 0.22 | 0.16 | 0.49 |

**Table 2.** Electron microprobe analyses of the orange-red luminescing parts in the foraminiferal test in Fig. 3

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| CaO | 30.09 | 30.70 | 29.76 | 30.69 | 29.99 | 29.76 |
| MgO | 17.95 | 17.64 | 17.36 | 17.82 | 17.19 | 17.76 |
| FeO | 0.33 | 1.22 | 0.98 | 0.83 | 0.85 | 0.71 |
| MnO | 0.05 | 0.06 | 0.00 | 0.03 | 0.01 | 0.06 |
| Total | 48.42 | 49.62 | 48.10 | 49.37 | 48.03 | 47.54 |
| $CaCO_3$ | 53.70 | 54.80 | 53.12 | 54.78 | 53.53 | 53.12 |
| $MgCO_3$ | 37.55 | 36.90 | 36.31 | 37.28 | 35.95 | 35.59 |
| $FeCO_3$ | 0.53 | 1.96 | 1.58 | 1.34 | 1.36 | 1.15 |
| $MnCO_3$ | 0.08 | 0.10 | 0.00 | 0.04 | 0.02 | 0.09 |
| Total (wt%) | 91.86 | 93.76 | 91.01 | 93.45 | 90.86 | 89.95 |
| | Numbers of cations on the basis of 6 oxygens | | | | | |
| Ca | 1.09 | 1.09 | 1.09 | 1.09 | 1.10 | 1.10 |
| Mg | 0.90 | 0.87 | 0.88 | 0.88 | 0.88 | 0.88 |
| Fe | 0.01 | 0.03 | 0.03 | 0.02 | 0.02 | 0.02 |
| Mn | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Total | 2.00 | 1.99 | 2.00 | 1.99 | 2.00 | 2.00 |
| Mole% | | | | | | |
| $\%CaCO_3$ | 58.46 | 58.44 | 58.37 | 58.62 | 58.91 | 59.06 |
| $\%MgCO_3$ | 40.88 | 39.36 | 39.90 | 39.90 | 39.57 | 39.56 |
| $\%FeCO_3$ | 0.57 | 2.09 | 1.73 | 1.44 | 1.50 | 1.28 |
| $\%MnCO_3$ | 0.08 | 0.11 | 0.00 | 0.05 | 0.02 | 0.10 |

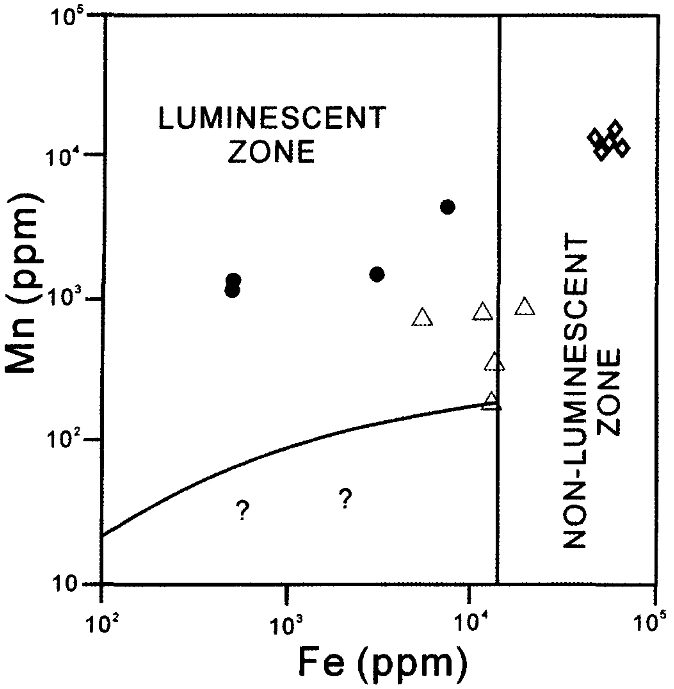

**Fig. 6.** The relationship between luminescence in the Yeonil dolomite and the concentration of manganese and iron. Closed circle: analysis of orange-yellow luminescing parts in Fig 3. Open triangle: analysis of orange-red luminescing parts in Fig. 3. Open diamond: analysis of concretional dolomite with no luminescence in Fig 5. Luminescent and non-luminescent zones are from Pierson (1981).

from the vacant parts of the foraminiferal test morphologically, whereas orange-red luminescence is from the foraminiferal test itself (Fig. 3). Therefore, the orange-yellow part may reflect the earlier pore fluids than those of the orange-red parts. Considering sedimentary environments in the Yeonil sediment, the brightly luminescing orange-yellow cements can be formed at the early stage of the dolomite formation when $Mg^{2+}$ is abundant in seawater conditions. Therefore, $Mg^{2+}$ in the structure of dolomite may be relatively less substituted by $Fe^{2+}$. Later, there would be a change in the chemistry of the pore fluids in sandstones. In other words, $Fe^{2+}$ was plentifully supplied from hinderland, and thus the dolomite with orange-red luminescence may be formed.

### *Formation of dolomite*

The unit cell parameters of dolomite was calculated by refinement of X-ray diffraction data as follows: a=4.815 Å c=16.067 Å (Table 4). These unit cell parameters show much higher values than the ideal dolomite unit cell, suggesting that the unit cell volume should be increased by the substitution of Ca for Mg. In other words, the Yeonil dolmite can be a calcium-rich dolomite. Many investigators showed that the cell dimension of dolomite varies linearly as the contents of metallic cations vary (Reeder, 1983). Similarly, the $CaCO_3$ contents of the Yeonil dolomite are calculated based on the diagram proposed by Murata *et al.* (1969). The calculated $CaCO_3$ ranges from 52% to 55% on the diagram. In addition, $FeCO_3$ content varies

**Table 3.** Electron microprobe analyses of the non-luminescing concretionary dolomite

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| CaO | 29.96 | 28.53 | 31.75 | 30.86 | 29.63 | 29.75 |
| MgO | 15.52 | 14.95 | 15.31 | 15.04 | 15.71 | 15.02 |
| FeO | 2.91 | 3.50 | 2.77 | 3.31 | 3.24 | 3.82 |
| MnO | 0.78 | 1.06 | 0.88 | 0.89 | 0.90 | 0.77 |
| Total | 49.17 | 48.04 | 50.70 | 50.11 | 49.49 | 49.36 |
| $CaCO_3$ | 53.47 | 50.92 | 56.66 | 55.08 | 52.88 | 53.10 |
| $MgCO_3$ | 32.47 | 31.28 | 32.03 | 32.47 | 32.87 | 31.42 |
| $FeCO_3$ | 4.70 | 5.65 | 4.46 | 5.34 | 5.23 | 6.16 |
| $MnCO_3$ | 1.26 | 1.71 | 1.42 | 1.45 | 1.46 | 1.25 |
| Total (wt%) | 91.89 | 89.56 | 94.57 | 93.34 | 92.45 | 91.93 |
| Numbers of cations on the basis of 6 oxygens | | | | | | |
| Ca | 1.10 | 1.08 | 1.14 | 1.12 | 1.08 | 1.10 |
| Mg | 0.79 | 0.79 | 0.76 | 0.76 | 0.80 | 0.77 |
| Fe | 0.08 | 0.10 | 0.08 | 0.09 | 0.09 | 0.11 |
| Mn | 0.02 | 0.03 | 0.02 | 0.03 | 0.03 | 0.02 |
| Total | 1.99 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Mole% | | | | | | |
| %$CaCO_3$ | 58.19 | 56.86 | 59.92 | 59.01 | 57.20 | 57.77 |
| %$MgCO_3$ | 35.34 | 34.93 | 33.86 | 33.72 | 35.56 | 34.18 |
| %$FeCO_3$ | 5.11 | 6.31 | 4.72 | 5.72 | 5.66 | 6.70 |
| %$MnCO_3$ | 1.37 | 1.91 | 1.50 | 1.55 | 1.58 | 1.36 |

**Table 4.** X-ray powder diffraction data of the dolomite from the Yeonil Group

| Hexagonal, $R\bar{3}$ | | | |
|---|---|---|---|
| a=4.815Å | c=16.067Å | V=322.65Å$^3$ | |
| I/Io | d(calc.) | d(obs.) | hkl |
| 2 | 4.036 | 4.033 | 101 |
| 5 | 3.701 | 3.702 | 012 |
| 100 | 2.893 | 2.892 | 104 |
| 10 | 2.678 | 2.677 | 006 |
| 10 | 2.545 | 2.544 | 015 |
| 10 | 2.408 | 2.408 | 110 |
| 30 | 2.196 | 2.196 | 113 |
| 5 | 2.068 | 2.067 | 021 |
| 15 | 2.018 | 2.018 | 202 |
| 5 | 1.851 | 1.851 | 024 |
| 20 | 1.809 | 1.810 | 018 |
| 10 | 1.790 | 1.791 | 116 |
| 5 | 1.569 | 1.569 | 211 |
| 5 | 1.547 | 1.547 | 122 |
| 1 | 1.499 | 1.501 | 1,0,10 |
| 5 | 1.467 | 1.467 | 214 |
| 5 | 1.434 | 1.434 | 119 |
| 5 | 1.415 | 1.415 | 125 |
| 10 | 1.390 | 1.390 | 030 |

between 3% and 9% on the diagram proposed by Al-Hashimi and Hemingway (1974). When the chemical data are plotted in the triangular compositional diagram, the Yeonil dolomites obviously show very high Ca contents that are well compatible with the content inferred from the X-ray diffraction data (Fig. 7). The electron microprobe analysis confirms that the Yeonil dolomite is rich in calcium.

The occurrence of the calcium-rich dolomite has been described at a number of localities at the early stage of diagenesis (Baker and Burns, 1985; Murata *et al.*, 1969). The calcium-rich dolomite can be compared with proto-dolomite that is a synthetic dolomite introduced by Goldsmith and Graf (1958). The dolomite is metastable in the natural state, because it is non-stoichiometric and poorly ordered. The proto-dolomites commonly contain more than 50 mole% $CaCO_3$ in the structure, and the amount of excess $CaCO_3$ in these dolomites is chemically metastable in sedimentary environments. Therefore, if the dolomite rich in calcium was present

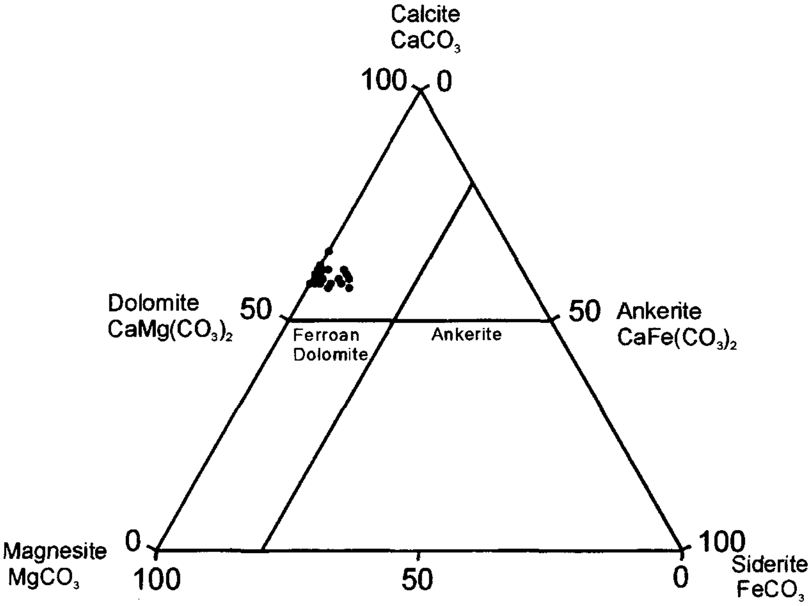

**Fig. 7.** Position of the Yeonil dolomite analyses within the triangular composition diagram $CaCO_3$-$MgCO_3$-$FeCO_3$.

in liquid at a high temperature, it would release the excess Ca and reaches the equilibrium state (Goldsmith and Graf, 1958). On the other hand, concretionary dolomite has relatively higher Fe content compared to cementing dolomite in the sandstones. This fact indicates that there was high influx of detrital terrigenious materials at the time of formation of concretions. The microscope reveals that the concretionary dolomite contains a lot of minute detritus (mostly microquartz), woody materials, and pyrites. Additionally, the concretionary dolomite shows the outline of microfossils in the cathodoluminescence. In these respects, the Yeonil dolomites can be concluded to be formed at low temperatures, and furthermore at a geochemical environments with high Ca and Fe contents.

### *Formation temperature*

Murata *et al.* (1972) showed that diagenetic dolomites from California and Oregon have unusually high concentration of $^{13}C$. They surmise that this results from isotope exchange between carbonate and methane, the methane being produced during the decay of organic material in biogenic sediments. From the concentration of $^{13}C$, they calculated that the diagenetic dolomite was formed at temperatures between 60℃ and 110℃. The Yeonil dolomite would be almost the same dolomite as the dolomite shown by Murata *et al.* (1972) when taking the occurrence and sedimentary environments into accounts. Noh (1998) estimated a maximum burial temperature of 40~60℃ for the Yeonil sediments, based on diagenetic zeolite facies and on the fission track thermochronology suggested by Shin and Nishimura (1994). Son (1996) also proposed that the temperature of the Yeonil sediment is estimated at 50~70℃ based on illite-smectite (I-S) diagenesis and organic maturation data. In these respects, the dolomites of the Yeonil sediment may be formed at the similar temperature. Consequently, the temperature for the dolomite formation is estimated to be about 60~70℃, taken from the lower temperature of Murata *et al.* (1972) and upper value of Son (1996).

## Conclusions

This study suggests that the use of cathodoluminescence is an effective technique to characterize carbonates and to interpret the formation of carbonate minerals provided that chemical data is considered. In the Yeonil sediments, calcite is luminous with orange-red color under the cathodoluminoscope. Foraminiferal tests, which are not visible in a plain polarizing microscope, are detected clearly in dolomite cements with the cathodoluminoscope by the difference in luminescent colors: orange-yellow and orange-red. The difference in colors or luminescing intensity depends strongly on the concentrations of Mn and Fe. Concretionary dolomite in the Yeonil sediment is characterized by the absence of luminescence, which are caused by a high content of Fe, over 10,000 ppm.

The Yeonil dolomites are rich in calcium, implying that the dolomite is an analogue to synthetic protodolomite proposed by Goldsmith and Graf (1959). These Yeonil dolomites are formed at the early stage of diagenesis at a temperature of about 60～70℃ and at a geochemical environment of high Ca and Fe contents.

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