Chemistry and Cathodoluminescene Properties of the Carbonate Minerals from the Tertiary Sediments, Pohang Area

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1. Introduction

In the Tertiary marine sediments of the Pohang areas, carbonate minerals including calcite and dolomite are present in sandstones as cementing materials and also in the sequence of mudrock as a condensed nodule or nodular bed. Conventionally, Carbonate minerals are easily 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. 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 characterized the mineral and the distribution certain impurities within it. The carbonates from the Pohang area are characterized in detail by cathodoluminescence property compared with chemical analysis. Attention is paid particularly to dolomite.

2. Materials and Methods

Carbonate samples were collected from outcrops and drill cores. 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, 12kV, and 0.6 mA. Chemical compositions of each carbonate mineral were determinined by electron microprobe employing WDS. All analyses were made on polished thin sections.

3. Results and discussion

Calcite occurs as cementing materials in the sandstones. 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 foraminiferal or another organic test. The calcite gives orange-red color luminescence under the cathodoluminoscope. The calcite made up of matrix of the sandstone were chemically analyzed by electron microprobe, and the results are calculated:

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

As poltted within the $CaCO_3$-$MgCO_3$-$FeCO_3$ triangular diagram, the analyses are fall into the ideal region of calcite.

Dolomites are present in sandstones as cementing materials and in the sequence of mudrock as a condensed nodule or nodular bed. The cementing dolomite in the sandstones is colorless and shows mosaic texture with distinct cleavages in the thin section, whereas the nodular dolomite in the mudrock sequences shows sutured texture of anhedral crystals with no cleavage. In addition, the nodular dolomite is sparsely dotted with silt-sized microquartz, woody materials, and pyrites. In the nodular dolomite, there are also some dolomites indicating the presence of microfossils.

Cathodoluminescence microscopy was made on the cementing and nodular dolomite. Cathodoluminescence reveals the outlines of microfossils in the dolomite cements, which are absent in the transmitted light. The relative intensity of the luminescence gives the presence of the foraminiferal test, that is orange-red and orange-yellow in color. Orange-yellow dolomite rhombs, possessing micro-zonation, are also observed in the dolomite cement under the cathololuminoscope. On the other hand, the nodular dolomite gives little or no luminescence.

The intensity difference of the luminescence is produced mainly by the difference in the amount of trace elements such as manganese or iron (Marshall, 1988). Electron microprobe analyses were performed on the dolomite in an attempt to understand the chemistry between orange-yellow, orange-red part, and also on the dolomite without luminescence. The chemical data indicate that the difference of the color is probably attributed to Fe^{2+} and Mn^{2+} contents. The brightly luminescing regions (orange-yellow part) has a relatively small amount of Fe^{2+} and Mn^{2+} compared with the orange-red part. The nodular dolomite has a larger amount of Fe^{2+}. Variation in the cathodoluminescent properties of carbonates are usually attributed to diffrering proportions of manganese (Mn^{2+}) as the most important activator, and iron (Fe^{2+}) as the main inhibitor of luminescence (Pierson, 1981). 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. Consequently, the Yeonil dolomite has a great range of variation in Fe^{2+} , that is responsible for the level of luminescence. As described above, the intense orange-yellow luminescence arises from the vacant parts within the foraminiferal test, whereas orange-red luminescence from the foraminiferal test. Considering sedimentary environments in the Pohang basin, at the initial time of the formation of dolomite, Mg^{2+} may be relatively less substituted by Fe^{2+} because of the high Mg^{2+} content in seawater. Later when Fe^{2+} was plentifullly provided from hinderland, the dolomite in orange-red luminescence may be formed.

Many investigators have worked on the linear variation in the cell dimension of dolomite calculated from X-ray diffraction as the metallic cation content varies (Reeder, 1983). Regression curves were used to measure the compositional variation in dolomite from the Yeonil Group. $CaCO_3$ content ranges from 52 to 55% based on the diagram proposed by Murata *et al.* (1969). $FeCO_3$ content varies between 3 and 9% based on the diagram proposed by Al-Hashimi and Hemingway (1974). Based on X-ray diffraction results, the unit cell dimension of the dolomite from the Yeonil Group was calculated as follows; a=4.815Å c=16.067Å. The unit cell has notably much higher values than the ideal dolomite unit cell. This suggests that the unit cell volume is probably increased by the substitution of Ca for Mg.

Electron microprobe analysis data of the dolomite were illustrated in the triangular diagram $CaCO_3$-$MgCO_3$-$FeCO_3$. The diagram shows very high Ca content, being compatible with the X-ray diffraction data. The dolomite rich in calcium can be compared with protodolomite, which is a synthetic dolomite introduced by Goldsmith and Graf (1958). The dolomite is metastable in the natural state, because it is non-stoichiometric, poorly ordered. If the dolomite rich in calcium was present in liquid at high temperature, it would release the excess Ca and reaches the equilibrium state (Goldsmith, 1958). In these respects, the Yeonil dolomite is interpreted to developed at low temperature, suggesting early diagenesis, and furthermore a geochemical environments with high Fe contents during the early diagenesis.

As mentioned earlier, dolomites of the Yeonil sediment have the higher $CaCO_3$ content relative to those of ideal composition. The calcium-rich dolomite has been known to have poorly to moderately ordered structure, and is an analogue to synthetic protodolomite proposed by Goldsmith (1959). The protodolomites 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. The occurrence of the calcium-rich dolomite has been described at a number of localities that indicate early diagenesis. On the other hand, nodular dolomite has relatively higher Fe content relative to cementing dolomite in the sandstones.

This fact indicates that there was high influx of detrital terrigenious materials at the time of formation of nodules. The microscope reveals that the nodular dolomite contains a lot of minute detritus (mostly microquartz), woody materials, and pyrites. Additionally, the nodular dolomite shows the outline of microfossils in the cathodoluminescence. These textures suggest that the dolomite substituted the siliceous materials in sediments during diagenesis. Murata et al. (1972) has shown that diagenetic dolomites from California and Oregon have unusually high concentration of 13C. 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 13C, they calculate that the diagenetic dolomite was formed at temperatures between 58℃ and 110℃. In these respects, the dolomites of the Yeonil sediment also may be formed at the similar temperature.

4. Conclusion

This study further suggests that the use of cathodoluminescence is a good technique to characterize carbonates, and furthermore interpret the formation of carbonates provided that chemical data is considered.

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