# CHAPTER V

# DOLOMITE AND DOLOMITISATION

Dolomite is a carbonate mineral containing calcium and magnesium occupy preferred sites of rhombohedral structure with the ideal formula $CaMg(CO_3)_2$. The original name dolomite was given by N.T. Saussare, in 1792, in honor of the French geologist Déodat Guy de Dolomieu who first described dolomite rock or dolostones (Zenger and Dunham, 1980, and Warren, 1989). Compositionally, dolostones are of two kinds; (1) calcareous dolostone, carbonate rocks containing 50 to 90 per cent of the mineral dolomite, and (2) a those designated simply as dolostone, carbonate rocks containing 90 per cent or more of the mineral dolomite.

Despite the fact that dolomite is among one of the most studied and yet most poorly understood mineral and rock types. The lack abundant modern dolomite is one of the main reasons that it genesis is so poorly understood. Dolomite is an unusual minerals in the Holocene, yet is common in ancient carbonates.

Throughout the sedimentary sequences of Thailand, it is apparent that almost all carbonate sediments ranging in age from Ordovician to Jurassic periods have been partially or completely dolomitised. Therefore, additional attempt has been made under the present study to propose the dolomitisation processes of carbonate sediments of the Khao Khad Formation at Khao Chan area.

## 5.1 Dolomite in sedimentary sequences at Khao Chan area.

Generally, the field observation of carbonate sediments in the lithofacies of Khao Khad Formation at Khao Chan area reveal diagnostic features of dolomitic limestones. On the weathered surface of the dolomitic limestones, it is commonly show the so-called "elephant skin" or saccharoidal surface texture (Figure 5.1). This surface texture is the result of different solubility of calcite and dolomite under similar chemical weathering processes where the calcite is relatively more soluble than dolomite. With respect to the distribution pattern or geometry of dolomitic limestones in the carbonate sequences, it is obviously not homogeneous, but displaying as patches or banded either in the forms of bedding or lamination. Besides, it is noted that the dolomitic limestones are closely associated with the fine-grained calcarenite or the matrix of the calcirudite.

The dolomitic limestones are present almost throughout the sedimentary sequences of Khao Khad Formation at Khao Chan area, especially in the lower and in the middle parts. In the lower part, dolomitic limestones are recognised in lithofacies I, II, III, and IV whereas in the middle part, dolomitic limestones are found in lithofacies VI and VII. The dolomitic limestone are, mostly, characterised by isolated, euhedral to subhedral, dolomite rhombs scattered in calcareous matrix. The sizes of dolomite crystals vary from a hundred to four hundred microns. The degree of abundance of dolomite rhombs varies throughout the sedimentary sequences, sometimes they form patched or banded dolomitic zones. The patched dolomitic zone is characterised by the irregular shape of small area which dolomite rhombs are relatively abundant than the surrounding area and closely packed (Figure 4.14). The banded dolomitic zone is characterised by the packed zones of dolomite rhombs widely extended, parallel to the bedding plane of sedimentary strata with the thickness varies from few millimetres to several decimetres confine especially in the lithofacies IV (Figure 5.1). The amounts of dolomite in sedimentary sequences of Khao Khad Formation at Khao Chan area are generally low except those in the lithofacies IV where the dolomite content is as high as 88 per cent.


Figure 5.1 The exposure of banded dolomitic limestone interbedded with calcarenite of the lithofacies IV showing the elephant skin texture on weathered surface.

**5.2 Dolomitisation**

Theoretically up to present, the condition of dolomite formation is not clear, there are many unsolved problems and because it is difficult to determine in the laboratory. However, many works on dolomite and dolomitisation have been published as various models and processes, such as, Steidmann (1911), Van Tuyi (1916), Alderman and Skinner (1957), Fairbridge (1957), Adams and Rhodes (1960), Ingerson (1962), Curtis et al. (1963), Sonnenfeld (1964), Von der Borch et al. (1964), Shinn and Ginsburg (1964), Illing et al. (1965), Shinn et al. (1965), Friedman and Sanders (1967), Hsu and Siegenthaler (1969), and Zenger (1972). Under the present study, an attempt has been made to propose the origin of dolomitic limestone at Khao Chan area using the data acquired from lithological and petrographical studies to determine the dolomitisation models of ancient and modern dolomite earlier proposed.

The essential chemical requirements for dolomitisation are the plentiful supply of $Mg^{2+}$ salts from sea water, slightly higher salinity, fairly warm temperature, reduced or elevated $CO_2$ pressure, high pH, reducing conditions, and the presence of organic matter, hydrocarbons, and ammonia compounds (Fairbridge, 1957).

In the marine province, $Mg^{2+}$ ions are provided by sea water which contains on average 1.3 parts per thousand of $Mg^{2+}$, and 0.4 parts of $Ca^{2+}$ (Fairbridge, 1957). Following Clarke (1924), the oceans carry $17x10^{14}$ metric tons of $Mg^{2+}$ with the annual addition of $93x10^{6}$ tons. Chilingar (1956), has determined that the annual precipitation of $Mg^{2+}$ is of the order of $13x10^{6}$ tons. According to present beliefs regarding the solubility of $Mg^{2+}$ ion in the sea water, it is undersaturated, whereas the solubility of $Ca^{2+}$ in warm surface sea water is supersaturated. However, $Mg^{2+}$ and $Ca^{2+}$ concentrations in the sea water may be raised under conditions, such as, increased alkalinity (pH 9 to 10) by means of removal of $CO_2$ and breakdown of bicarbonate (Fairbridge, 1957; Von der Borch, 1965; Berner, 1971, Illing et al., 1965). This reduced $CO_2$ pressure to elevate high pH are obtained in the tide pools during photosynthesis of intertidal zones and probably in buried sediments.

Other than alkalinity condition, the evaporation is also the cause to produce high concentration of $Mg^{2+}$ which commonly occurs in shallow restricted marine, lagoon, and intertidal to supratidal zones, accompanied by precipitation of $Ca^{2+}$ as aragonite and gypsum (Berner, 1971; Deffeyes et al., 1965; Illing et al., 1965).

In the past, there has been some discussions over the direct precipitation, primary, versus replacement origin of dolomite. But, the current view is that primary dolomite is very rare, only forming in certain lakes and lagoons, such as in Coorong and saline lakes of southern Australia (Tucker, 1990), and most of dolomite in the geological record is believed to be replacement origin. The latter class may be subdivided further into the "contemporaneous" or penecontemporaneous", and "subsequent" types with a reasonably slow rate of accumulation, or the times of replacement can take place directly on the sea floor (Fairbridge, 1957)

Since the past, several models of dolomite formation have been proposed, but only seven of them seem to have stood the test of time. They are:

1) Sabkha model
2) Seepage-reflux model
3) Coorong model
4) Mixing-zone model
5) Sulphate-reduction model
6) Burial-stage model
7) Solution-cannibalisation model

Sabkha model is the popularisation of modern evaporative dolomite in the 1963 let the interpretation of many ancient dolomite as supratidal in origin (Curtis et al., 1963).

The typical area is at the Arabian Gulf sabkhas, centred in Adu Dhabi, composed of subtidal, intertidal, and supratidal sediments with contain laminated algal mats. The $Mg^{2+}$ rich, high Mg/Ca ratio, hypersaline fluids seep into the intertidal sediments with the capillary action into the supratidal sediments. Evaporation and evaporative pumping process move the solution through the sediments being dolomitised, usually beneath supratidal evaporite (McKenzie, 1981), produces dolomitised intertidal-subtidal facies.

Seepage-reflux model is very similar in mechanism to the sabkha model, it was first proposed by Adams and Rhodes (1960). This model usually invoked as an explanation of thicker, much larger-scale ancient dolomite. The hypersaline brines usually become heavy enough to displace the connate waters and seep slowly downward through the slightly permeable carbonate sediments at the lagoon floor and dolomitise the sediments.

Coorong model was first documented as an area of primary dolomite deposition by Mawson (1929) and have studied by Alderman and skinner (1957), Skinner (1963), Von der Borch (1965, 1976), Von der Borch and Lock (1979), and Warren (1985, 1986). The dolomite is precipitated as dolomite and not replacing an earlier carbonate materials. They are formed by evaporation of magnesium-rich, mostly, continental groundwater driven to the surface as they float up over a more dense sea water wedge.

Mixing-zone model represents the dolomitising solution formed by the mixing of subsurface sea water and meteoric water. It was first used by Hanshaw et al. (1971) and by Land (1973) to explain dolomite in Quaternary limestone in Florida and Bermuda. An analogous term, "Dorag dolomitization" was coined by Badiozamani (1973). When $CO_2$ saturated meteoric groundwater flowing seawardly by hydrostatic pressure contacts with sea water, the mixed solution may be undersaturated with respect to $CaCO_3$ and supersaturated with respect to dolomite. Thus, dolomitisation can be taken place in the mixing-zone, that dolomite are formed as void-filling cement (Warren, 1989).

Sulphate-reduction model was demonstrated by Baker and Kastner (1981) in the chemical sense which high level of sulphate in sea water inhibits dolomite formation. Form the experiment, the rate of dolomitisation is controlled by the level of sulphate in the dolomitising solution and may not be controlled by the Mg/Ca ratio. This model can be applied to the dolomitisation in the area with abundant microbial reduction in organic-rich sediment, mixing-zone dolomite, and sabkha dolomite that the sulphate can be precipitated respectively before dolomite formation.

Burial-stage model is represented by the dolomitisation found in deep subsurface carbonates and formed by the migration of hot magnesium-rich basinal fluid out of the basin (Zenger, 1983; Warren, 1989).

Solution-cannibalisation model represents the process of dissolving magnesium-bearing limestones and then reprecipitating the magnesium along with some of calcium to form dolomite, such as in the pressure solution seam and stylolites (Logan and Semeniuk, 1976; Wanles, 1979).

In the area of Khao Chan, dolomite are present as small patches and thin bands. Microscopically, the dolomite shows the textures from replacement processes of the Mg-rich fluids on the pre-existing carbonate sediments. It is apparent that the fine-grained carbonate sediments or micrite is most susceptible to the dolomitisation as compared with the skeletal allochems. It is also noted that the petrographic evidences suggest that the dolomitisation is pre-dated the chertification.

It is therefore believed that the dolomite bands associated with limestone of the Khao Khad Formation at Khao Chan area are of contemporaneous or early diagenetic replacement origin. The source of $Mg^{2+}$ is presumably of marine origin in the restricted marine environment. Similar to the seepage reflux model (Adams and Rhodes, 1960).

For the dolomite patches, it is believed that the marine source of $Mg^{2+}$ is probably the magnesium ion released from the transformation of metastable high-Mg calcite to low-Mg calcite during early diagenesis. The proposed dolomitisation is the subsequent type of replacement similar to the burial stage model (Zenger, 1983).

### 5.3 Dolomitisation and chertification

Evidences from the field investigation and detailed petrographic examinations of the Khao Khad Formation at Khao Chan area of approximately 1,285 to 1,857 metres thick reveal that the carbonate sequence with some fine clastics association have been partially dolomitised and chertified. The dolomitisation mainly occurs as dolomite bands in the lithofacies IV, whereas the lithofacies VI, and VII are partially dolomitised as dolomite patches.

For chertification, the lithofacies V has been intensely chertified as chert band, whereas the lithofacies I, III, and VII have been partially chertified as chert nodule, and the lithofacies VIII is least chertified as banded impure chert or porcelanite. Therefore, the dolomitisation can be characterised as band and patch of dolomite, whereas the chertification is characterised as band and nodule of chert depending upon the intensity of dolomitisation/chertification, respectively.

Additional attempt has been made under the present study to determine the calcite/dolomite ratio using the X-ray diffractometry technique (Chave, 1952; Muller, 1967). Altogether 45 samples have been selected from the carbonate sequence of Khao Khad Formation at Khao Chan for this purpose. Besides, quantitative analysis of major oxides of the same samples have been carried out using the X-ray fluorescence spectrometry. The cross-plots between magnesium oxide (MgO) versus silica contents have been made to demonstrate the relationship between dolomitisation and chertification (Figure 5.2). In addition, the distribution pattern of calcite, dolomite, magnesium oxide, and silica contents of carbonate sequence of Khao Khad Formation at Khao Chan has been presented in Figure 5.3.

It is concluded that the chertification and dolomitisation show an antiphatitic relationship. This means that wherever the carbonate sediment has been dolomitised, there is a tendency for the none development of chertification, and vice versa.

The petrographic evidence also confirms that no chert is present in the heavily dolomitised carbonate sequences, i.e. lithofacies IV. Some parts of the carbonate sequences where both dolomite and chert are present together, i.e. the lithofacies VII (Figure 4.14), they are both relatively less abundant. It is quite common for the dolomite rhomb to be embedded in the cryptocrystalline quartz of chert. These petrofabric evidences indicate that the carbonate sediments have been earlier dolomitised prior to the chertification. Therefore, partial dolomitisation of carbonate sediment is pre-dated the selective chertification of the none dolomitised or calcite zones of the rock during diagenesis.

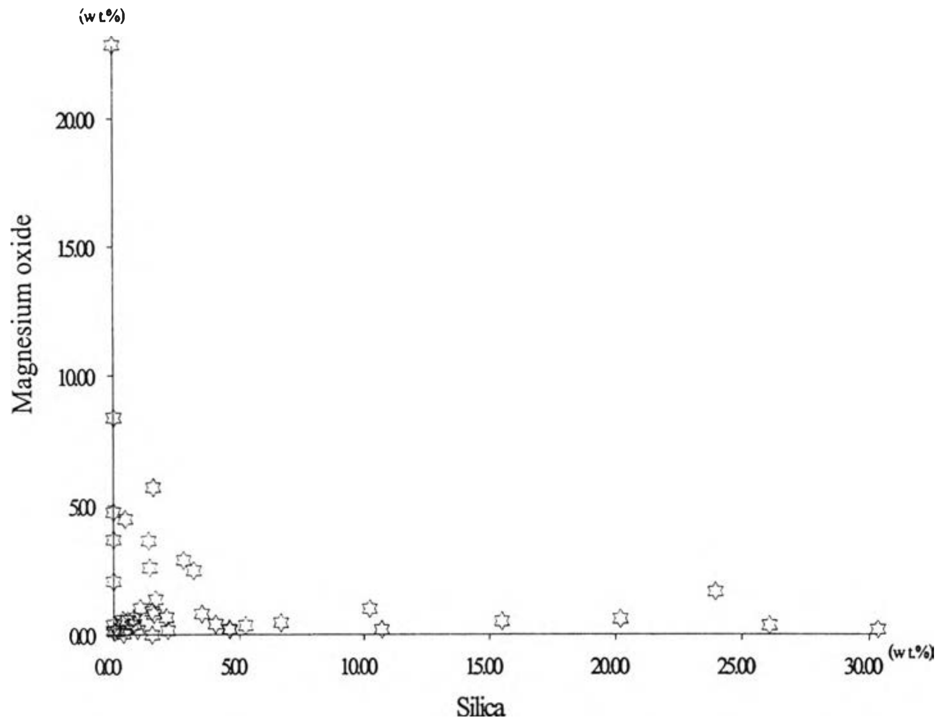


Figure 5.2 The cross-plots between magnesium oxide (MgO) versus silica contents ($SiO_2$).

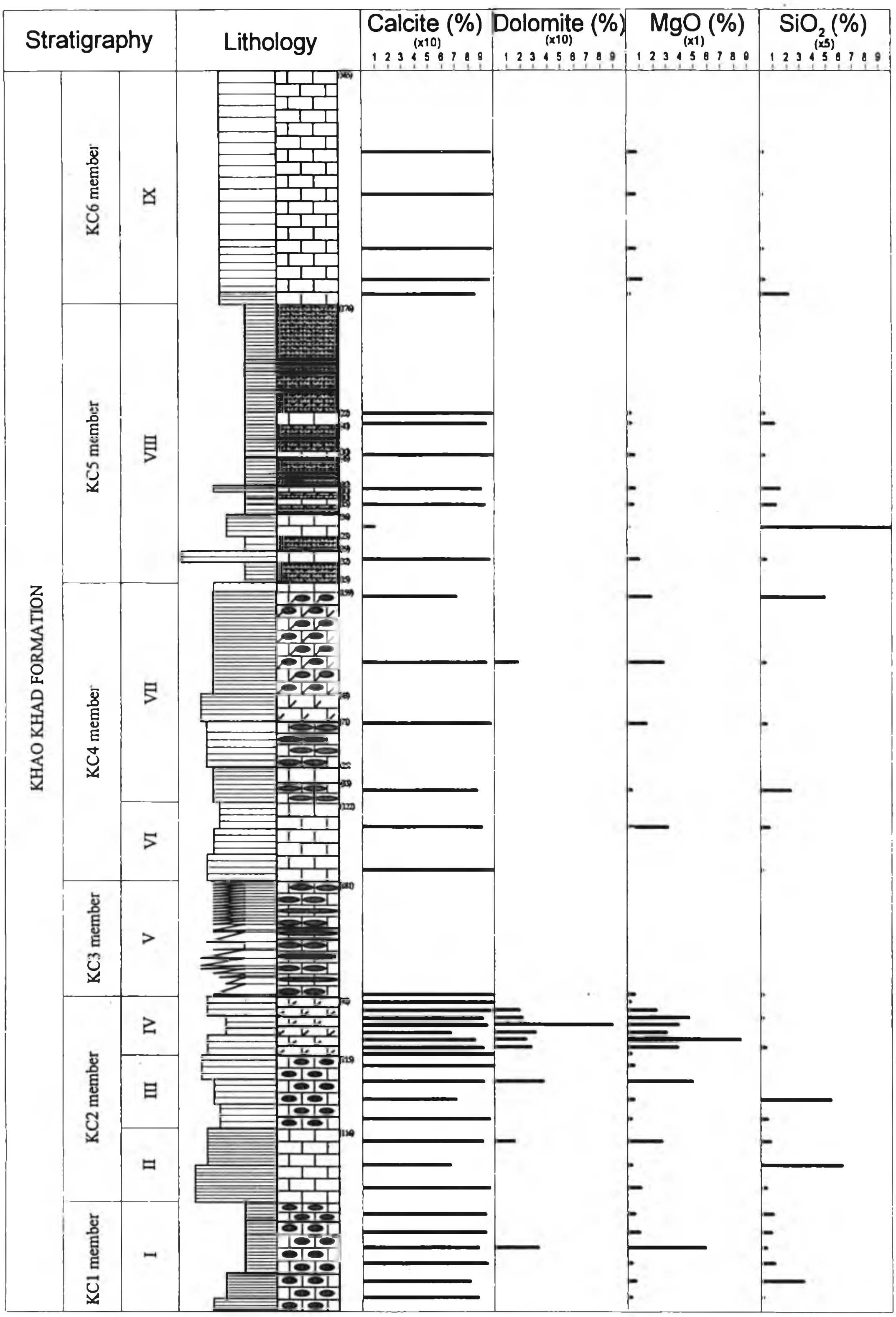


Figure 5.3 The distribution pattern of calcite, dolomite, magnesium oxide, and silica contents of carbonate sequence of Khao Khad Formation at Khao Chan area.