CHAPTER II

LITURATURE REVIEWS

2.1 Paleozoic Rock Studies in Thailand

The first geological report related to the study area was conducted by Lee (1923) on a geological survey across the Kaeng Khoi - Pak Chong area. Since then there were no further work done for several decades. Later, Toriyama and Sugi (1959) conducted a study on Permian Fusulinids of the central Thailand, and Abele and Beeser (1963) reported on the geology of the Muak-Lek area.

Borax and Stewart (1966) conducted a reconnaissance mapping in the area lying west of the Khorat plateau, including the present study area, and reported on several Permian rock-sections in various localities. Generally, the Permian sequence was characterized by interbedding or in part interfingering of limestones, shales, sandstones and conglomerates. The limestones were grey, fine-grained and locally detrital in some areas as they contained beds of limestone-pebble conglomerate. Reef facies were present and boulder beds of reef talus in a matrix of fine-grained limestone were also reported. The measured thickness of the Permian limestones ranged between 452 meters and 2,568 meters. Fossils were recognized almost exclusively in the limestone consisting of fusulinids indicating ages from Lower to Middle Permian.

After that, students of the Department of Geology, Chulalongkorn University made a series of geological maps and reports on the geology of the Muak-Lek - Thap-Kwang area in 1970, 1972, 1983, 1984 and 1985.

Sawata (1985) reported information collected during the field study from 1970 to 1972 with the staff and students of the Department of Geology, Chulalongkorn University. All of illustrations and descriptions were mainly on many sedimentary structures in the Saraburi - Pak Chong area at the south-western corner of north-eastern Thailand.

Hinthong (1974) reported on the geology of the Khao Yai national park and neighboring areas, including parts of Changwat Nakhonrachasima, Changwat Nakhon Nayok and Changwat Saraburi. After that, Hinthong et al. (1985) established the geologic map sheet Changwat Phranakhon Si Ayutthaya, covering the Khao Yai national park and neighboring areas, including parts of Changwat Nakhonrachasima, Changwat Nakhon Nayok, and Changwat Saraburi.

Tittirananda (1976) studied the aspects of stratigraphy and paleontology of the Permian Ratburi limestone of Saraburi, central Thailand, and reported seven rock units with detailed biostratigraphy and some diagenetic features.

Winkel et al. (1983) studied rocks of the Nam Duk Formation (Chonglakmani and Sattayarak, 1978) along the Lom Sak – Chum Phae highway in Petchabun province, and proved that they were a typical pelagic facies of a geosynclinal sequence, and also reported on the boundary of the Lower Permian and Middle Permian strata. The rocks were predominantly built up by allodapic limestone (Meischner, 1964), cherts, shales and clastics which were deposited in a rather deep trough. They also found tuffites of dacitic to rhyodacitic composition which transported by turbidity currents into the basin.

Wielchowsky and Young (1984) conducted a field investigation of the carbonate and siliciclastic lithofacies in Lower and Middle Permian rocks of the

Petchabun fold and thrust belt of north-eastern and central Thailand. They reported several carbonate facies representing six depositional environments, including basin plain, basin margin, outer platform, platform interior, restricted platform and marginal marine; and siliciclastic facies representing deep, shallow and marginal marine depositional environments. In addition, they established three paleogeographic provinces in the study areas during Early through Middle Permian, namely a western carbonate platform, a central mixed siliciclastic-carbonate basin, and an eastern mixed carbonate-siliciclastic platform.

Phothong (1986) studied the structural geology of Changwat Saraburi and concluded that the regional structures of the eastern part of Changwat Saraburi were a limb overturns broad anticline.

Dawson and Racey (1993) reported the biofacies of Permian rocks in Changwat Saraburi area containing abundant fusulinids and algae.

Thambunya (1999) studied the lithostratigraphy and sedimentology of the Khao Khad Formation in the vicinity of Khao Chan, Ban Saphanhin, Amphoe Muak Lek, Changwat Saraburi, and reported nine lithofacies of the Khao Khad Formation deposited in the shallow restricted marine, barrier bar and foreslope.

2.2 Origin of Chert

Theoretically, chert is a sedimentary rock made up of chemically precipitated silica, composed largely or entirely of fibrous microcrystals of chalcedonic quartz or microcrystalline or cryptocrystalline quartz which mostly formed during diagenesis (Berner, 1971). Many authors, including Berner (1971), suggested that the direct chemical precipitation of chert or any other forms of quartz was less likely because of the low silica content in seawater. In fact, however, quartz did precipitate directly from a solution in laboratory done by Mackenzie and Gee (1971). They grew 10 micron-sized subhedral quartz crystals in seawater at 20 degree Celsius in 2 years.

The source of silica during diagenesis is believed to be mainly supplied by the dissolution of siliceous skeletals. During their life processes, the siliceous-secreting organisms are able to remove molecules of silica from undersaturated seawater. The silica is used to construct opaline skeletals (Kling, 1978). After death of those organisms and during diagenesis, the opaline skeletals are dissolved in aqueous solution having dissolved silica contents of about 6 to 120 ppm (Blatt, 1982).

Silica contents of natural water range from about 0.1 ppm in melted snow to 600 ppm in mineral spring water (Table 2.1). However, the contents are less variable than any other major dissolved constituent of natural water

Table 2.1 Average silica concentration in some natural water (Fairbridge, 1972.)

Type of water	Approx. SiO_2 range (ppm)
Groundwater	5-60
Oil field brine	5-60
Rivers and lakes	5-25
Hot spring and geyser	100-600
Sea water	0.01-7

Originally, bedded cherts must have been laid down as some forms of silica. There are two existing possibilities for the source of silica in the bedded cherts. One is an inorganic precipitate from a supersaturated solution, and the other is the accumulation of siliceous skeletal remains.

For normal seawater, inorganic precipitation is impossible since it is undersaturated with respect to amorphous silica. However under some favorable conditions an inorganic precipitation of volcanic-related chert is possible. This is because large amount of silica can be released into solution from volcanic glasses in a restricted basin where submarine volcanism has taken place. This enables a buildup of dissolved silica to saturation in deep water because of the lack of circulation and oxygen. Thus the supersaturated deep seawater, besides being anaerobic and most likely sulphidic as in the Black Sea, can precipitate silica in the form of bedded chert. The common occurrence of bedded cherts in association with black shales and submarine volcanics is a predicted result of the conditions necessary for the formation of inorganic cherts (Berner, 1971).

As for the other possibility for the formation of bedded chert, opaline silica skeletal debris can accumulate in certain areas of the ocean in sufficient high amount that it would form bedded chert if they were recrystallized. The modern oceans contain large numbers of silica-secreting organisms, about 70% of which are diatoms (Lisitzin, 1972). The second important organisms are radiolaria and are followed by silica sponges. Silicoflagellates and higher organisms could also precipitate silica but on a much smaller scale. Most ancient bedded cherts provided direct evidence of a biogenic origin in the form of fossil diatoms or radiolaria (Berner, 1971). In many cases, the fossil evidences may be destroyed by diagenetic alterations and cause confusion to the inorganic origin of the cherts.

The nodular chert also occurs abundantly in sedimentary rocks as fossil replacement. The source of silica for such secondary chert is not as obvious as in the case of bedded cherts. The source of silica is probably the remains of siliceous skeletals in fossiliferous carbonate rocks. Dissolution of the siliceous skeletals, local migration and precipitation or replacement of silica would be involved in the silicification or chertification of carbonate skeletals or nodular formation (Berner, 1971). The nodular cherts can be expected to form along zones of greatest groundwater flux where transport of dissolve silica is most active (Knanth, 1979)

2.3 Occurrences of Cherts in Thailand

Bedded cherts and nodular cherts have been recognized in carbonate successions of Thailand throughout the geological times. For examples, in the Lower Paleozoic era, there were reports of the occurrences of abundant chert nodules in the Tha Manao limestone of Ordovician Chao Nen Group, and the nodular cherts in bedded limestone in Doi Musur Group of Silurian-Devonian periods (Bunopas, 1981).

In the Upper Paleozoic era, cherts were reported in the Phra Woh limestone (Bunopas, 1981) and Khao Plukmu limestone (Bunopas, 1976) of the western provinces. Also abundant nodular and bedded cherts were found in association with carbonate sequences of the Saraburi Group in central Thailand (Bunopas, 1981), particularly in the Phu Phe, Khao Khwang, Nong Pong, Khao Khad, and Sab Bon Formations (Hinthong et al., 1985).

Moreover, the Tak Fa Formation was found to contain nodular cherts in a very thick bedded limestone succession in the vicinity of Changwat Nakorn Sawan (Nakornsri, 1977). In the area of Loei fold-belt, the Nam Mahoran Formation (Charoenprawat et al., 1976, Assavapatchara, 1998) and Pha Nok Khao Formation (Chonglakmani and Satayarak, 1984) were also reported on the occurrences of nodular and bedded cherts in limestone sequences. In the central north, the Pha Huat Formation of Ngao Group was characterized as a very thick-bedded limestone succession with nodular and bedded cherts (Piyasin, 1972; Bunopas, 1981).

In the Sukhothai fold-belt, the Phrae Group of Middle Permian to early Upper Permian age was characterized by a thick flysh with thin limestone assemblages following up to radiolarian chert, thin limestone and ultramafic rocks with pillow lava basalt (Bunopas, 1981). In the eastern part of Thailand, the Sra Kaew Formation of Chantaburi Group was also represented by the radiolarian chert, limestone and composite melange assemblages (Bunopas, 1981).

In the Mesozoic era, the Mae Sarieng Group of Triassic-Jurassic age in the western north was found to consist of shale, sandstone, and intercalations of thin chert beds and limestones (Bunopas, 1981).

2.4 Dolomitization Processes

Dolomite is a carbonate mineral containing calcium and magnesium occupying preferred sites of a rhombohedral structure with the ideal formula $CaMg(CO_3)_2$. The original name dolomite was given by N.T. Saussare in 1791 in honor of a French geologist, Déodat Guy de Dolomieu, who first described a dolomite rock or dolostone (Zenger and Dunham, 1980; Warren, 1989; and Purser et al., 1994). Compositionally, dolostones are of two kinds; (1) calcareous dolostone is a carbonate rock containing 50 to 90 percent dolomite mineral, and (2) that designated simply as dolostone is a carbonate rock containing 90 percent or more of dolomite mineral.

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

Theoretically, up to the present, the condition of dolomite formation is not clear. There are many unsolved problems concerning dolomite formation because dolomite is difficult to synthesize in laboratory. However, various models and processes on the occurrences of dolomite and dolomitizations have been published by many workers, 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), Shinn and Ginsburg (1964), Illing et al. (1965), Shinn et al. (1965), Von der Borch (1965), Friedman and Sanders (1967), Hsu and Siegenthaler (1969), and Zenger (1972).

Essentially, the chemical requirements for dolomitization are the plentiful supply of Mg^{2+} salts from seawater, 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 condition, Mg^{2+} ions are provided by seawater which contains on an average 1.3 parts per thousand of Mg^{2+}, and 0.4 parts per thousand of Ca^{2+} (Fairbridge, 1957). According to Clarke (1924), the oceans carry 17×10^{14} metric tons of Mg^{2+} with the annual addition of 93×10^{6} tons. Chilingar (1956) determined that the annual precipitation of Mg^{2+} was in the order of 13×10^{6} tons. According to the present understanding, seawater is undersaturated with respect to Mg^{2+} ion but warm surface seawater is supersaturated with respect to Ca^{2+} ion. However, Mg^{2+} and Ca^{2+} concentrations in the seawater may be raised under a number of conditions, such as increasing alkalinity (pH 9 to 10) by means of removal of CO_2 or breakdown of bicarbonate (Fairbridge, 1957; Von der Borch, 1965; Berner, 1971, Illing et al., 1965). The reduction of CO_2 pressure to elevate high pH can be obtained in the tide pools during photosynthesis of intertidal zones and probably in buried sediments.

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

In the past, there have been some discussions over the direct or primary precipitation versus replacement origin of dolomite. But, the current view is that the primary precipitation of dolomite is very rare and only forms in certain lakes and lagoons, such as in Coorong and saline lakes of southern Australia (Tucker et al., 1990). Most of dolomite in the geological record is believed to be of 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)

In the past, several models of dolomite formation have been proposed, and 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-cannibalization model

The Sabkha model was popular for the modern evaporative dolomite in 1963 and let the interpretation of many ancient dolomites as supratidal in origin (Curtis et al., 1963). The typical area is at the Arabian Gulf sabkhas, centred in Abu Dhabi, and here are composed of subtidal, intertidal and supratidal sediments with laminated algal mats. The Mg^{2+} rich (high Mg/Ca ratio) hypersaline fluids seep into the intertidal sediments with the capillary action onto the supratidal sediments. Evaporation and evaporative pumping process move the solution through the sediments being dolomitized which is usually beneath supratidal evaporite, and produces dolomitized intertidal-subtidal facies (McKenzie, 1981).

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

Coorong model was first documented in an area of primary dolomite deposition in the Coorong and saline lakes of southern Australia by Mawson (1929) and later studied by Alderman and skinner (1957), Skinner (1963), Von der Borch (1965, 1976), Von der Borch and Lock (1979), and Warren (1985, 1986). This model stated that dolomite was precipitated directly and not replacing earlier carbonate materials. They were formed by evaporation of magnesium-rich, mostly continental groundwater driven to the surface as they floated up over a more dense seawater wedge.

Mixing-zone model is accounted for a dolomitizing solution formed by the mixing of subsurface seawater and meteoric water. It was first used by Hanshaw et al. (1971) and by later Land (1973) to explain dolomite in Quaternary limestone in Florida and Bermuda. An analogous term, "Dorag dolomitization" was reported by Badiozamani (1973). When CO_2 saturated meteoric groundwater flowing seaward by hydrostatic pressure was in contact with seawater, the mixed solution may be undersaturated with respect to $CaCO_3$ and supersaturated with respect to dolomite. Thus, dolomitization could take place in the mixing-zone, by which dolomite was formed as void-filling cement (Warren, 1989).

Sulphate-reduction model was demonstrated by Baker and Kastner (1981) in a chemical sense that high level of sulphate in seawater could inhibit dolomite formation. From the experimental study, they found that the rate of dolomitization was controlled by the level of sulphate in the dolomitizing solution and might not be controlled by the Mg/Ca ratio. This model thus could be applied to the dolomitization processes in the area where abundant reducing microbial organisms occurred, such as organic-rich sediment of mixing-zone and sabkha that the sulphate was precipitated respectively before dolomitization.

Burial-stage model was used to explain the formation of dolomite found in deep subsurface carbonates by which the migration of hot magnesium-rich basinal fluid out of the basin was responsible for the dolomitization (Zenger, 1983; Warren, 1989).

Solution-cannibalization model was 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 seams and stylolites (Logan and Semeniuk, 1976; Wanless, 1979).

2.5 Carbonate Diagenesis

Bustillo and Ruiz-Ortiz (1987) studied the Upper Jurassic carbonate turbidite and reported on the three types of chert, namely bedded, nodular and mottled cherts in the turbidite. Among those, the mottled chert was referred to a weakly dispersed and selective silicification which gave a speckled appearance to the rock. The three types of chert were formed by replacement of limestones and were associated with different calcareous facies. The silicified materials were mainly microcrystalline and cryptocrystalline quartzes with locally chalcedonic quartz. The mottled chert was found in the silicified calcareous breccia beds. The bedded and nodular cherts were interpreted to form as a result of early diagenetic silicification in which the silica was derived during the processes of calcitization and dissolution of radiolarians and sponge spicules. The mottled chert was formed as the consequence of later silicification in a probably Mg-rich environment.

Thériault and Hutcheon (1987) studied the platform carbonate sequence of the Grosmont Formation (Upper Devonian) in northern Alberta and reported on the occurrences of dolomitization and calcitization processes during diagenesis. Three phases of dolomite occurred in the Grosmont Formation; an early sabkha dolomite; dolomite formed during reflux of hypersaline brine, and dolomite related to water expelled from shale during burial. The dolomites were depleted in the heavy isotopes of both carbon and oxygen with increasing degree of dissolution and calcitization. The calcitization was later stage and took place during uplift and the entry of meteoric water along the unconformity.

Smith and Simo (1997) studied the carbonate diagenesis and dolomitization of the Lower Ordovician Prairie du Chien Group, southern Wisconsin. The diagenetic history included syndepositional diagenesis, shallow-burial diagenesis and near-surface weathering. Syndepositional diagenesis was designated as calcium carbonate and dolomite cementation, micritic fabric-retentive replacement of dolomite and anhydrite precipitation. Shallow-burial diagenesis was described as carbonate dissolution and karst development, patchy silicification and dolomitization. The hydrothermal diagenesis was referred to pervasive dolomite cementation and fabric-destructive replacement of dolomite, minor dolomitization and calcite cementation, and patchily Mississippi Valley-type sulfide mineralization. They illustrated some difficulties of interpreting the mechanism responsible for the dolomitization of ancient dolostone, many of which had complicated diagenetic histories including multiple episodes of dolomitization. As found in the Prairie du Chien Group, hydrothermal dolomite had petrographically overprinted on many earlier diagenetic features but did not markedly shifted the bulk-rock $\delta^{18}O$ and $\delta^{13}C$ values from Early Ordovician marine carbonate values.

Reinhold (1998) studied the Upper Jurassic limestone of the eastern Swabian Alb, Germany and found that they were composed of oolitic platform sands with associated microbe siliceous sponge mounts at the platform margins. They were surrounded by argillaceous or calcareous mudstones and marl-limestone alternations, which were deposited in adjacent marl basins. Partial to complete dolomitization was predominantly confined to shallow burial with multiple episodes of dolomite formation and recrystallization. The initial matrix dolomitization occurred during latest Jurassic to early Cretaceous and was related to pressure dissolution during shallow burial at temperature at least 50°C. The source of Mg was believed to derive from seawater that was expelled from adjacent off-reef strata into the mound facies.

Arenas et al. (1999) studied the development of karstic features on the lacustrine deposits of the Ebro Basin in Spain. Several stages of diagenetic processes were found to operate on lacustrine laminated and stromatolitic carbonates. The first stage was syndepositional processes including dolomitization, desiccation and related brecciation, and sulphate precipitation which occurred under progressive evaporation. This was due to the progressive fall of water level in the lake. As such the carbonates were exposed as a supra-littoral fringe surrounding saline mud flats. The second stage was early diagenetic processes including sulphate dissolution and collapse brecciation, dedolomitization, sparry calcite cement and silicification. These processes occurred as a result of meteoric water input and caused a progressive rise of water level in the lake.

Montsant el al. (1999) studied the development of lower Eocene chert in the Corones platform carbonate of the Spanish Pyrenees and found that they were deposited in a restricted brackish- water environments. It was a laminated ostracod-rich facies which contained abundant sponge spicules. Chert occurred as nodular, bedded and mottled varieties. Four types of quartz were found as micro-quartz, length-fast chalcedony, mega-quartz and microspheres. The calcian dolomite was also found disseminated within the micro-quartz and length-fast chalcedony, but it was absent in the megaquartz and the host carbonate. The chert was found closely associated with desiccation cracks and with interstratal dewatering structures. They suggested that the dissolution of sponge spicules and calcitization took place in the carbonate host rocks. Source of silica for Corones chert was derived from sponges during early diagenesis and shallows burial. The silica-rich fluids were migrated due to mechanical compaction and consequently precipitated as chert.

Mukhopadhyay et al. (1999) reported on the fabric development in Proterozoic bedded chert of the Penganga Group in India. The chert was characterized by a wide variety of fabrics, including cryptocrystalline and microcrystalline quartzes, equant mega-quartz and chalcedony. Cryptocrystalline and microcrystalline quartzes were the most common types and occurred mainly as lenses and well-defined laminae. Megaquartz, in contrast, occurred as irregular patches or fenestroids within cryptocrystalline or microcrystalline fabrics, or in complex aggregates and disrupted mosaics. They suggested that those cryptocrystalline and microcrystalline quartzes were formed by maturation of biogenic opal-A to quartz chert through opal-CT stage.

The mega-quartz was formed directly from pore water during the maturation of opal-CT.

Török (2000) studied the Middle Triassic carbonate rocks of the Villány Mountain in southern Hungary. He reported on the occurrence of replacement-type dolomite in the form of rhombs scattering in the rocks and representing the initial phase of dolomitization. The dolomite contained many inclusions and showed very dull luminescent cores and limpid non-luminescent outer zones. The isotopic compositions of those dolomites were similar to the calcitic micrite indicating that dolomitization occurred without the influence of external fluids. The first phase of dolomitization took place during the burial realm in marine water with partly close system. Late-stage was the saddle dolomite precipitation during maximum burial in the Cretaceous.

Kim and Lee (2003) studied the Dongjeom Formation (Lower Ordovician) in eastern central Korea. They reported on the occurrence of radiaxial fibrous calcite cement which was a low-magnesian type and was precipitated in a marine-meteoric mixing zone.