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Models of Dolomitisation - A Literature Review

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Models of Dolomitisation - A Literature Review

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Foreword

This report is the published product of a study by the British Geological Survey (BGS) and was generated as part of the Geochemistry Mineralogy and Hydrogeology Programme's Development of Capability project looking at "Development of Integrated Methods for Characterising Faults and Fractures in Reservoirs and Aquifers". The report provides a review of the literature on dolomitisation.

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Summary

From an economic perspective (e.g. in the hydrocarbon and groundwater industries) one of the main questions relating to dolomitisation is the influence the dolomitisation process has on the nature of the dolomitised limestone’s pore system. To this end, one of the key objectives of the “Development of Integrated Methods for Characterising Faults and Fractures in Reservoirs and Aquifers” project is to understand the nature and distribution of pore-systems within dolomitised limestones and in particular to understand the influence of fractures on dolomitisation and/or porosity distribution, and subsequent fluid-flow pathways.

This document provides a literature review on the current state of knowledge regarding the dolomitisation process. The “dolomite problem” is introduced, and the kinetic inhibitions on dolomitisation from seawater, which ultimately form the crux of the dolomite problem are summarised.

Over the years, various models have been suggested in order to explain the dolomitisation process. Systematic summaries of these models are presented. In essence, each model attempts to provide a mechanism by which the kinetic inhibitions to dolomite formation are overcome (typically through evaporation or dilution of seawater), and a means of pumping large pore-volumes of fluid through the body undergoing dolomitisation.

Following the summaries of the dolomitisation models, the next section contains an introduction into the classification of dolomite fabrics and pore systems. The final sections outline the regional geology of the Lower Carboniferous in the Midlands of the United Kingdom, and describes potential analogue material in Derbyshire and the Bowland Basin.

1 Introduction - The "Dolomite Problem"

Dolomite is a highly ordered mineral that forms as a chemical precipitate associated with limestone deposits. It has the ideal formula $CaMg(CO_3)_2$, although substitution of Mg^{2+} for Mn^{2+} and/or Fe^{2+} is commonly very significant, and other substitutions such as Pb^{2+} and Zn^{2+} may also occur. The "dolomite problem" arises because seawater is supersaturated with respect to dolomite and dolomite should therefore be precipitating readily from seawater at the present day. However, dolomite is only rarely encountered as a precipitate from unmodified seawater and the volumes of dolomite being generated in modern settings are generally considered unlikely to be able to explain the large volumes of dolomitised limestone observed in the geological record.

Development of our understanding of how dolomitisation occurs has been hampered by the fact that in natural dolomites precise stoichiometry and ordering is rarely attained and many natural dolomites are relatively Ca-rich and poorly ordered. Furthermore dolomite composition and degree of ordering are likely to evolve through geological time, hence ancient dolomites tend to have compositions and degrees of ordering closer to that of ideal dolomite than modern day examples.

1.1 DOLOMITISATION KINETICS

As noted above, seawater is saturated with respect to dolomite, and consequently primary dolomite precipitation should be very widespread, however, it has long been recognised that dolomite formation from seawater is largely inhibited due to kinetic effects, summarised as follows:

- **The high ionic strength of seawater** coupled with fast carbonate precipitation rates gives insufficient time for dolomite ordering to be established (although disordered Ca-Mg-carbonates can be generated (Machel and Mountjoy 1986, citing Folk and Land 1975; Lipmann 1973).
- **Hydration of Mg^{2+} ion**. Mg^{2+} is more strongly hydrated than Ca^{2+}, which inhibits the incorporation of Mg^{2+} into growing mineral structures (it is difficult to strip Mg^{2+} of its hydration water). This strong hydration also makes it difficult for the relatively unhydrated **CO_3^{2-}** to get sufficiently close to the surface of the growing mineral to form bonds.
- **Low activity of CO_3^{2-}** (relates to previous point; Machel and Mountjoy 1986 citing Lipmann, 1973).
- **Preferential precipitation of other phases** with less complex (ordered) structures (i.e. calcite).
- **Sulphate concentrations.** Baker and Kastner (1981) showed that small amounts of sulphate could strongly inhibit dolomitisation of calcite, although aragonite can be dolomitised at higher sulphate concentrations than calcite. Sulphate concentrations may be lowered through microbial sulphate reduction, causing dolomitisation. Counter to this hypothesis, Hardie (1987) presented various examples from the literature where dolomitisation had occurred, in-spite of apparently high sulphate concentrations. Therefore the direct effect of sulphate concentrations on dolomitisation remains insufficiently well understood.
- **Influence of organic matter.** Certain organic materials may inhibit dolomitisation (Gaines 1980). In addition, urease-producing and/or uric-acid-fermenting bacteria, and Fe(II) chelates may promote dolomitisation (Machel and Mountjoy 1986 citing Mansfield 1980; Gunatilaka et al. 1985; Mirsal and Zankl 1985).
- Certain **clay minerals** may promote dolomitisation (Machel and Mountjoy 1986 citing Wanless 1979).

- **Precursor mineralogy**. In secondary dolomites, the relative ease with which the different precursor $CaCO_3$ polymorphs can be dissolved will affect the dolomitisation process (Machel and Mountjoy 1986 citing Gaines 1974; Bullen and Sibley 1983; Walter 1985; Katz and Matthews 1977; Mucci and Morse 1983). Aragonite is more readily dolomitised than calcite. Furthermore, precursor mineralogy may influence the rate of diffusion of Ca and Mg ions with the developing dolomite crystal and hence influence degree of ordering.
- **Temperature**. At higher temperatures kinetic inhibitions are reduced (Morrow 1982a).

Thermodynamic (and other) properties of dolomites are further complicated by considerations of stoichiometry and ordering. Hardie (1987) states that "this means that there is not one single dolomite mineral but many dolomites, each with different thermochemical properties depending on degree of ordering and nonstoichiometry". The inference is that disordered dolomites are less stable, but may be easier to precipitate.

In summary, the three main parameters that influence the kinetics of dolomite growth are: Mg^{2+}/Ca^{2+} ratio, salinity and CO_3^{2-}/Ca^{2+} ratio (Morrow 1982a; citing Folk and Land 1975). Most dolomitisation models invoke a mechanism whereby some combination of these parameters are modified either by evaporation, fluid mixing or fluid evolution in response to diagenetic reactions. Finally, the influence of temperature should not be overlooked, and this aspect forms part of the basis for the burial models for dolomitisation.

2 Models for Dolomitisation

This section outlines the various models for generation of extensive dolomite deposits that have been proposed over the years. For each model, the key mechanism by which the model produces dolomite is presented together with some examples and the problems and unresolved questions that have been highlighted by various workers since the model's inception. It appears that many of the models and discussions sought to be able explain all dolomite occurrences by a single mechanism, chosen from a number of competing, mutually exclusive ones. The currently prevailing view seems to be that dolomitisation can occur under various conditions, and within a given sequence the dolomitising mechanism may evolve through time.

In most models (evaporitic, seepage-reflux, mixing zone, and seawater) the source of Mg^{2+} for dolomitisation is taken to be some form of modified seawater (seawater contains Mg^{2+} = 1290 ppm = 0.052 mol l^{-1}). Alternatively, Mg^{2+} may be derived from adjacent basinal mudrocks or precursor Mg-rich calcite by solution cannibalisation (burial model).

2.1 EVAPORATIVE [SABKA OR COORONG]

Sabkha : This model is taken to account for many modern examples of dolomites. Land (1985) calculated that to dolomitise a "typical" recent carbonate sediment (40 % porosity, 6.3 mol% $MgCO_3$) requires *c*.650 pore volumes of sea water. With evaporated seawater at halite saturation, this drops to *c*.30 pore volumes, but significant gypsum-anhydrite should also be precipitated (*c*.20% of the volume of dolomite). Flood recharge during winter storms and high tides, recharges water onto supratidal flats and into saline/hypersaline lakes/lagoons. Heating throughout most of year produces evaporation from the capillary zone above the water table, which may be recharged by evaporative pumping (Tucker and Wright 1990 citing Hsu and Siegenthaler 1969; McKenzie et al. 1980). Dolomite forms in areas with greater amounts of storm recharge in winter (*e.g.* tidal channels.). Machel and Mountjoy's review (1986) suggests that "a continuous spectrum exists from normal-marine subtidal to hypersaline-subaerial dolomitisation" (see section on seawater dolomitisation below).

Coorong lagoon : This can be viewed as a special case of evaporation coupled with a mixed-water / dilution model (see section on mixing zone dolomitisation below). Ephemeral lakes are filled in winter by groundwater seepage and evaporated to dryness in summer (Tucker and Wright 1990 citing Von der Borch 1976; Von der Borch and Jones 1976,). In near coastal settings dolomite may derive Mg^{2+} from seawater, but further inland Mg^{2+} sourced from alkaline groundwater with high CO_3^{2-}concentrations may also contribute.

EXAMPLES:

- Arabian Gulf Sabkhas (Tucker and Wright 1990 citing McKenzie *et al.* 1980; Patterson and Kinsmann 1982).
- West side of Andros Island (Tucker and Wright 1990 citing Shinn *et al.* 1965; Hardie 1987; Shin 1983).
- Coorong (S. Australia) (Tucker and Wright 1990 citing Von der Borch 1976; Von der Borch and Jones 1976).

EXPECT:

- Finely crystalline (1-5µm) dolomite euhedra, associated with other super-supratidal indicators such as fenestrae, microbial laminae, and evaporite mineral pseudomorphs (note: evaporite minerals may not always precipitated or preserved).
- Distinctively cyclic lithologies and structures – dolomite culminating in displacive anhydrite. (Morrow 1982b citing Wood and Wolfe 1969)
- In Coorong Lagoons, dolomite may be finely crystalline/amorphous ("yoghurt-like"; Morrow 1982b citing Von der Borch and Jones 1976).
- Excess Ca (*c*.55 mol % $CaCO_3$) in evaporitic/reflux dolomites, but higher Ca/Mg in Coorong style.

PROBLEMS:

- Some reviews suggest that evaporative pumping is unlikely as a source of significant recharge (Morrow 1982b; citing Hsu and Siegenthalar 1969, Hsu and Schneider 1973; Mackenzie et al. 1980; Patterson 1972 and Patterson and Kinsman 1981).
- Uncertainty as to whether dolomitisation in sabkha environment is a replacive process (dolomite replaces aragonite), or if dolomite is a direct precipitate. The review by Hardie (1987) challenged the view that sabkha dolomitisation proceeds by replacement, and argued on the basis of SEM images that show rhombic dolomite on top of, rather than replacing, aragonite needles that dolomite may be a primary precipitate. Furthermore, Hardie (1987) challenged the mass balance and brine chemistry data that had been used to suggest that dolomitisation was replacive and concluded that the brine compositions could just as easily be explained without invoking dolomitisation at all. Hardie (1987) also suggests that dolomitisation at low temperature will only proceed by direct precipitation requiring supersaturated waters with high Mg/Ca and elevated CO_3^{2-} and HCO_3^- .
- Wright (2000) has recently interpreted the dolomites in the Coorong Lagoons as being microbially mediated (see section on bacterially-mediated dolomitisation).

2.2 SEEPAGE-REFLUX AND EVAPORATIVE DRAW DOWN

This model is a variant of the evaporative model (outlined above), and supposes that the dolomitising fluid is generated by the evaporation of lagoon/tidal flat pore water leading to precipitation of gypsum (Tucker and Wright 1990 citing Adams and Rhodes 1960). This evaporation causes the pore water to become dense relative to sea water and hence warm, alkaline, hypersaline brines with high Mg/Ca ratios infiltrate into the underlying sediments and move seaward by seepage (i.e. reflux) and precipitate dolomite.

EXAMPLES:

- Permian reef complex W. Texas (Adams and Rhodes 1960).
- Zechstein (U. Permian) of Northwest Europe (Tucker and Wright 1990 citing Smith 1981; Clark 1980).
- Edwards Formation (L. Cretaceous), Texas (Tucker and Wright 1990 citing Fisher and Rodda 1969).

EXPECT:

- High $\delta^{18}O$ and trace-element-rich dolomite through formation from evaporated seawater.
- Overlying or encasing evaporite deposits (source of Mg^{2+} rich fluid).
- Mudmounds / reef build-ups may represent palaeotopographic highs that may be more susceptible to reflux / mixing zone dolomitisation after exposure to sea level changes (Morrow 1982b citing Eliuk 1978; Sears and Lucia 1980; Exploration Staff, Chevron 1979).
- Relatively Low Ca/Mg in evaporitic/reflux dolomites.

PROBLEMS:

- It is questionable as to the rate with which fluids flow seawards, and also the duration of flow (seasonal influence). Flow is also likely to concentrated within more permeable horizons and should therefore bypass most of the limestone body (Morrow 1982b; citing Murray 1969).

2.3 MIXING ZONE [DORAG]

This model proposes that mixing of seawater with meteoric water preserves high Mg/Ca ratios, but overcomes kinetic obstacles to dolomitisation caused by the high ionic strength of seawater. An explanation of the mechanism presented by Badiozamani 1973 (cited in Machel and Mountjoy 1986) suggested that mixtures of sea-meteoric water containing *c*.5-50% seawater are undersaturated with respect to calcite, but still oversaturated with respect to dolomite and should therefore precipitate dolomite. This model requires effective movement of fluids and hence a strong palaeogeographic control would be expected. Dolomitisation should occur in more landward parts of platforms, possibly preferentially within more porous facies. The degree of confinement of the aquifer/flow zones will influence extent and shape of dolomitised body. Two subtly different types have been envisaged:

- confined aquifer [inland mixing model], and
- unconfined aquifer [coastal mixing model].

Most examples of thick platform dolomite comprise wedges of regressive carbonate that have been dolomitised by seaward progradation of freshwater aquifers (Morrow 1982b). Mg^{2+} is derived from sea water with circulation of seawater induced by groundwater flow. High dissolved CO_3^{2-} in many continental groundwaters may further drive dolomitisation.

EXAMPLES:

- Hope Gate (Pliocene) and Falmouth (Pleistocene) Formations of Jamaica (Tucker and Wright 1990 citing Land 1973). Dolomite replaces lime mud and high-Mg calcite coralline algal grains. Low Na and Sr contents in the dolomite were taken to infer a dilute-water origin.
- Early-middle Palaeozoic subtidal carbonates of Nevada (Tucker and Wright 1990 citing Dunham and Olsen 1978; 1980). Meteoric waters entered the carbonate package during subaerial exposure during regression, and the distribution of dolomite is interpreted to represent the penetration of the freshwater lenses.

- Devonian, Guangxi, S. China (Xun and Fairchild 1987). In this example dolomitisation is restricted to the platform margin, and stable isotope and trace element data point to dolomitisation by mixed meteoric-marine fluids. This dolomitisation is reported to have occurred during repeated periods of emergence, with fluids likely to have contained high proportions of seawater. Xun and Fairshild (1987) also question Machel and Mountjoys (1986) contention that mixing zone dolomitisation can not produce large volumes of massive replacive dolomite (see below).
- Upper Miocene, Nijar, Spain (Meyers *et al.* 1997). The mixing zone model lends itself to interpretation within a sequence stratigraphic context, as zones of meteoric-marine fluid mixing should reflect relative sea level position through time. Meyers *et al.* (1997) interpret Upper Miocene carbonates from Nijar (Spain) as having been dolomitised in relation to sea level fluctuations. Stable isotope and $^{87}Sr/^{86}Sr$ data suggest mixing of evaporated, and normal seawater with fresh water, shortly after reef formation, during periods of varying sea level. During low-stand times, seawaters were evaporated. As sea levels, then rose again, these evaporated brines were mixed with seawater/freshwater causing dolomitisation.

EXPECT:

- Low trace element content (Na, Sr), light $\delta^{18}O$ and positive correlation of $\delta^{18}O$ and $\delta^{13}C$ due to mixing of two different fluids.
- Possible association with unconformity surfaces, although these may represent a phase of karstification ,which rendered the formation more susceptible to later fluid migration and hence dolomitisation (Morrow 1982b citing Sonnenfeld 1964; Skall 1975).
- Mudmounds / reef build-ups may represent palaeotopographic highs that may be more susceptible to reflux / mixing zone dolomitisation after exposure to sea level changes (Morrow 1982b citing Eliuk 1978; Sears and Lucia 1980; Exploration staff, Chevron 1979).
- Possibly more pronounced on shelf margins which may be exposed during regressions (Morrow 1982b).
- Relatively high Ca/Mg ratios in mixing-zone dolomites. During continued growth dolomites tend towards more stoichiometric compositions and lower trace element contents.

PROBLEMS

- Badiozamani's (1973) model proposed that mixed sea-fresh water solutions containing *c*.5-50% seawater are undersaturated with respect to calcite and oversaturated with respect to dolomite and hence will tend to precipitate dolomite. In it's pure sense this assumes that the only inhibiting fracture on dolomite precipitation is the more rapid precipitation of calcite. However, Machel and Mountjoy (1986) have contended that Badiozamani's model is a purely thermodynamic one and merely implies that "(a) mixed solutions with [<]50% seawater are undersaturated with respect to calcite and should dissolve calcite…; and (b) dolomite should precipitate from solutions with [>]5% seawater" and that dolomite precipitation may still be inhibited due to other kinetic effects.
- Machel and Mountjoy (1986) also note that most recent and ancient coastal mixing zones formed no dolomite, and only few form small amounts of dolomite cement (as distinct from replacive dolomite).
- Hardie (1987) also highlights the fact that original formulation of this model used solubility data for ordered rather than disordered dolomites. When the greater solubilities of disordered dolomite are taken into account, the range of mixing ratios at which Badiodamani's (1973) model would predict dolomitisation is greatly reduced.
- Hardie (1987 and references therein) also notes that there are no well-documented examples of dolomitisation occurring in modern day mixing zones according to this model (and that those cited as examples fall-down under closer scrutiny), and suggests that most accounts of mixing-zone dolomites have been misinterpreted.

- Since the critique by Machel and Mountjoy (1986), Xun and Fairchild (1987) defended mixing-zone dolomitisation, and as noted by Hardie (1987), just because Badiozamani's (1973) model does not provide a satisfactory explanation of why dolomitisation can occur from mixed waters, these fluids are still oversaturated with respect to dolomite and therefore have the potential for dolomitisation.

2.4 BURIAL

This model proposes that dolomite forms in response to the expulsion of Mg-bearing brines from compacting and dewatering basinal mudrocks into platform margin carbonates. Mg^{2+}, along with other ions, are sourced from pore-water [typically some form of modified sea water] and clay mineral reactions. In addition, these brines may be reducing and carry Fe^{2+} and Mn^{2+} in solution, and these ions may aid dolomitisation by increasing saturation in the fluid with respect to substituted dolomite phases such as ankerite and kutnahorite ($Ca(Fe^{2+},Mg,Mn)(CO_3)_2$). Furthermore, kinetic constraints on dolomitisation are reduced due to increased temperatures at depth. Additional effects which can potentially be related to burial dolomitisation are solution / cannibalisation at stylolites and development of tectonic or hydrothermal dolomite (generally fracture-related).

EXAMPLES:

- U. Devonian Miette Buildup of Alberta (Tucker and Wright 1990 citing Mattes and Mountjoy 1980). Dolomite forms a kilometre-wide zone at margin of reef complex with dolomitising fluid interpreted to be sourced from enclosing mudrocks.
- Cambrian Bonneterre Dolomite in SE Missouri (which is also associated with lead-zinc and Mississippi Valley Type [MVT] mineralisation in adjacent sediments; Gregg 1985, 1988). The basal part (*c*.6m thick) of the formation is dolomitised over an area of >16,000km^2. Gregg (1988) suggested that basin-derived brines of original seawater origin were gravity driven through an underlying sandstone aquifer and upwards into the Bonneterre Formation.
- Pendleside Limestone (Dinantian, Bowland Basin, N. England; Gawthorpe 1987). See later section for more details.
- Woo Dale Limestone (Dinantian, Derbyshire; Schofield and Adams 1986). Dolomitisation related to basinal fluids expelled from adjacent Widmerpool Gulf shales and limestone turbidite deposits.
- Presqu'ile, Canada (Qing and Mountjoy 1992, 1994). Significant fluid flow driven by compression to west, with fluid temperatures higher than would be expected for inferred burial depth at time of dolomitisation). Systematic temperature and isotope trends are observed from west to east, reflecting cooling and mixing of the fluids. Qing and Mountjoy (1994) use REE data to infer that the later fracture dolomitisation occurred at high water-rock ratios, whereas the earlier replacive dolomite retains the REE signature of the precursor carbonate, and thus reflects lower water-rock ratios. Note the early dolomite is interpreted to be related to marine fluids.
- Leduc, Canada (Dix 1993; Drivet and Mountjoy 1997). Large scale basin-wide flow drove dolomitisation, with formational fluids (including evaporitic brines) focussed through the underlying Cooking Lake Platform (Drivet and Mountjoy 1997).
- Nisku Fm, Devonian W. Canada Basin. Machel and Mountjoy 1986 (also citing Machel 1984) report that reefs are only dolomitised in their down-dip parts of the system and suggests that faults deflected and funnelled burial compaction fluids from off-reef and underlying shales (Machel and Mountjoy (1986) also cite Jones 1980; Viau and Oldershaw 1984 as other studies supporting influence of faults). *Note this association with adjacent and underlying, rather than overlying, shales.*
- Upper Jurassic, Felsenkalke Formation, Swabian Alb, Germany (Reinold 1998). This example reports partial to complete dolomitisation of sponge mounds, during progressive

burial and ultimately hydrothermal conditions. Reinhold (1998) recognises three episodes of dolomitisation, with the earliest, (low Mg, non-stoichiometric dolomite) associated with pressure solution/stylolitisation during early burial, from slightly hypersaline fluids at temperatures >*c*.50°C. Mass balance calculations suggest that the surrounding shelf carbonate sediments could supply sufficient fluid to account for all the observed dolomite (requires fluid sourced from *c*.70km radius from mound). During later burial, the early formed dolomite was recrystallised (more stoichiometric compositions) at higher temperatures (34-70°C), with high Sr contents in the latest phase of neomorphism attributed to percolating meteoric waters. Late saddle dolomite and ankerite formed from deep-burial hydrothermal fluids focussed along fractures.

- Trenton and Black River Limestones (M.Ordovician, Indiana, USA; Yoo *et al.* 2000). In this example three stages of dolomitisation are reported. The earliest is considered to relate to seawater during shallow burial as overlying shales were deposited (based on isotope compositions that are close to those of Ordovician seawater). As burial progressed, fluid expelled from the overlying shales generated ferroan dolomite as a neomorphic replacement of the earlier formed dolomite (where early dolomite is absent, this second phase of dolomite is also absent; based on isotopic compositions similar to those of the overlying shales). The last dolomite is isotopically similar to the middle generation, but formed from hotter, more saline fluids.

EXPECT:

- Light $\delta^{18}O$.
- Possible association with adjacent evaporite masses.
- Adjacent compacted shales/mudrocks.
- During continued growth dolomites tend towards more stoichiometric compositions and lower trace element contents.
- Significant substitution by Fe and Mn where pore fluids were enriched in these components.

PROBLEMS:

- Distances of fluid transport required,
- Supply of sufficient Mg [mass balance suggests huge volumes of mudrock required to generate significant amounts of dolomite]. Morrow (1982b) suggests that porewater derived from hundreds of volumes of shale would be required to dolomitise one volume of limestone. However, this assertion is based on the assumption that most fluid migrates upwards during shale compaction, and that the released fluid has the composition of seawater. Below *c*.2000m clay transformations will modify composition of pore-fluid, but Morrow (1982b) still considers volumes to be insufficient to produce large masses of dolomite.
- Mudrock compaction also liberates significant Ca^{2+}, which may exceed Mg^{2+} *i.e.* there is little excess Mg^{2+} for dolomitisation (Morrow 1982b citing Boles 1981; Foscolos and Kodama 1974).
- Spatial distribution of dolomite in reefs considered to have dolomitised during burial may resemble distribution of dolomite expected from other processes (e.g. reflux, mixing or thermal convection). Therefore, these processes have to be ruled out using petrographical and geochemical criteria (Machel and Mountjoy 1986).
- Uncertainty as to the amount of "burial" dolomite that represents recrystallisation of earlier formed (*i*.e. surficial) dolomite?

2.4.1 Solution / Cannibalisation and Stylolitisation

Compaction related dissolution concentrates dolomite generated from Mg^{2+} sourced by cannibalisation of pre-existing Mg-calcite potentially along stylolites. This model fails to reconcile the deep burial setting required for stylolitisation with the common pre-burial conversion of high Mg-calcite to low Mg-calcite (Morrow 1982b citing Logan and Semeniuk 1976; Wanless 1979). Mass balance arguments suggest that this mechanism would be unlikely to be the sole source of Mg^{2+} as a sediment solely composed of high Mg-Cc (19 mol% $MgCO_3$) would generate only *c*.30% dolomite (Tucker and Wright 1990). However, Mg-rich calcite may act as a nucleation site (a “half-way house” to dolomite).

Expect: small intraformational dolomite bodies (related to local Mg^{2+} source)

2.4.2 Tectonic or hydrothermal dolomite

In some studies dolomitisation associated with faults and fractures has been described as “tectonic” or “hydrothermal” (Morrow 1982b). However, an association with fractures does not imply hydrothermal conditions and other hydrothermal indicators are required to confirm high temperature conditions, and fracture related dolomitisation may simply reflect the fact that fault and damage zones may enhance fluid and hence dolomitisation at any temperature.

Example: Monterey Formation (Miocene, California; Malone *et al.* 1996). Earlier formed matrix dolomites were recrystallised (including resetting of isotope and other signatures) in response to hydrothermal fluids associated with hydrocarbon migration, which also produced vein-filling dolomites.

Expect:

- Megacrystalline (white or saddle) dolomite (although these have been reported in dolomites considered to have been formed according to other mechanisms). High fluid inclusion homogenisation temperatures, and a possible association with MVT-type mineralisation.
- Significant substitution by Fe and Mn where pore fluids were enriched in these components

Problems: Both Morrow (1982b) and more recently Machel and Lonnee (2002) have taken issue with the widespread use of the term hydrothermal for dolomitisation associated with fracturing where a hydrothermal association is not explicitly proven. Machel and Lonnee (2002) suggest that “a dolomite should be called hydrothermal only if it can be demonstrated to have formed at a higher than ambient temperature, regardless of fluid source or drive”, and that the terms “hydrofrigid”” be used for dolomites precipitated from fluids of lower temperature than their host rock (e.g. dolomitisation from a solution at 150°C introduced into a rock mass of ambient temperature 250°C would qualify as hydrofrigid even thought the fluid is relatively hot). They suggest the term “geothermal” for use where the fluid is at the same temperature as the rock mass.

2.5 SEAWATER

A range of models have been proposed which may enable seawater or only slightly modified seawater to directly dolomitise limestone. These models typically aim to provide an efficient mechanism for passing large volumes of sea water through a formation ([Kahout] thermal convection, reflux, tidal pumping, shallow subtidal models), although organogenesis and microbial activity are also considered important in hemipelagic settings.

2.5.1 [Kahout] thermal convection of seawater

Horizontal density gradients between cold marine water (5-10°C) adjacent to platform and geothermally heated groundwater (>40°C) within platform (Machel and Mountjoy 1986 citing original proposal by Kohout 1967, and elaboration by Simms 1984). This is potentially a long-lived process (on the time-scale of the platform itself), and may include interaction with meteoric waters. Dolomitisation of periplatform oozes has also been reported and may relate to the leaching of Mg from high Mg-calcite grains by inflowing marine water (Tucker and Wright

1990, citing Mullins *et al.* 1984, 1985). This model is intermediate between shallow-subtidal (see below) and burial dolomitisation (see above).

Examples:

- Florida Aquifer (Tucker and Wright 1990).
- Enewetak Atoll (Tucker and Wright 1990 and Machel and Mountjoy 1986 citing Saller 1984).

2.5.2 Reflux

Shallow water on platform becomes slightly more saline than seawater due to evaporation, and refluxes downwards (Tucker and Wright 1990, citing Simms 1984). Requires less dense pore-waters in underlying sediments and no aquicludes. Should form homogeneous bodies that cross-cut formation boundaries (Mattes and Mountjoy 1986 citing Simms 1984).

Example: Bahama Platform (Tucker and Wright 1990 citing Simms 1984).

2.5.3 Tidal Pumping

Precipitation of dolomite from only slightly evaporated seawater, with water pumped through the sediments during spring tides (Tucker and Wright 1990). Seasonal influxes of meteoric water may corrode the dolomite which initially forms very fine crystallites.

Examples:

- Sugar Loaf Key, Florida (Tucker and Wright 1990 citing Carballo *et al.* 1987).
- Ambergris Cay, Belize (Tucker and Wright 1990 citing Mazzullo *et al.* 1987).

2.5.4 Shallow Subtidal

Dolomitisation occurs penecontemporaneously with sedimentation from slightly evaporated seawaters (Machel and Mountjoy 1986 citing Sass and Katz 1982 and Bein and Land 1983). This model essentially represents the sabkha model extended into the shallow-subtidal zone.

Examples:

- Cretaceous Soreq Fm, Israel (Sass and Katz 1982) – penecontemporaneous, shallow marine dolomitisation.
- Permian San Andres Formation (Bein and Land 1983) – dolomitisation from slightly evaporated seawater associated with skeletal moulds, anhydrite, high-Sr-calcite and celestite at T *c*.40-50°*C*. These probably formed as proto-dolomite which recrystallised to better ordered/stoichiometric dolomite (see Machel and Mountjoy (1986) for summary of these occurrences).

2.5.5 Hemipelagic Environments (microbially-mediated dolomitisation)

Formation of dolomite during burial of organic-rich muds possibly influenced by bacterial fermentation (e.g. Teal et al. 2000; Mazzullo 2000). Methanogenesis and late sulphate reduction promote dolomitisation by raising and sustaining high pH and carbonate concentrations, by decreasing hydration of Mg and Ca, and/or by promoting crystal surface reactions. Dolomites generated due to sulphate reduction will be low-Fe due to concurrent pyritisation. $\delta^{13}C$ will depend upon extent of organic reactions and amount of ^{13}C contributed from seawater, but should be low in sulphate reduction dolomite and high in methanogenic dolomite. $\delta^{18}O$ compositions should be more restricted, reflecting pore fluid temperature and salinity. Dolomite in hemipelagic environments is finely crystalline (7µm; Teal et al. 2000), Ca-rich and poorly ordered. Wright (1997, 2000) suggests that the recent dolomite in the Coorong Lagoons is microbially mediated and that many ancient dolomites may have been similarly mediated, due to greater abundances of benthic microbial communities than are found today. This activity facilitates dolomitisation by lowering sulphate activity, increasing pH and carbonate activity, with Mg^{2+} possibly sourced from breakdown of cyanobacterial sheaths and mucilage.

Examples:

- Gulf of California (Tucker and Wright 1990 citing Kelts and McKenzie 1982).
- Holocene, Cangrejo Shoals Mudbank, northern Belize (Teal *et al.* 2000).
- Coorong Lagoons (Wright 2000).
- Cambrian Eilean Dubh Formation, Scotland (Wright 1995).

3 Dolomite Fabrics and Pore Systems

3.1 CRYSTAL FABRIC CLASSIFICATION

Gregg and Sibley (1984) provide a scheme for classification of dolomite fabrics, which attempts to account for differences in nucleation and growth of dolomite under different conditions. Their classification is essentially a refinement of that proposed by Friedman (1965; cited by Gregg and Sibley 1984). Gregg and Sibley (1984) and Sibley and Gregg (1987) suggest that dolomite textures are largely controlled by a *surface roughness factor* which relates the relative surface free energy of a growing crystal to the enthalpy of formation, degree of supersaturation and temperature (Sibley and Gregg 1987 citing Jackson 1958). Thermodynamic considerations imply that below a "*critical roughening temperature*" (CRT), or below a "*critical saturation*", growth occurs by lateral migration of layers or growth spirals (partial filling of new layers is energetically unfavourable). This should generate regular, euhedral (*i.e.* **idiotopic** textures). At temperatures above the CRT, or saturation above the critical saturation, atoms are added to the growing crystal in an essentially random manner. This results in the generation of rough crystal surfaces which lead to a mosaic of anhedral crystals (*i.e.* **xenotopic** fabric). On the basis of comparison of natural and artificially synthesised dolomites, Gregg and Sibley (1984) place the CRT for dolomite as somewhere between 50°c [dolomites formed below this temperature are idiotopic], and 100°c [above which dolomites are xenotopic]. They also suggest that Fe- and Ca-rich dolomites may have lower CRTs, and that calcite has a CRT of <25°c. Where crystals are growing into open pore space, euhedral crystals (i.e. idiotopic) may form at temperatures above the CRT [impurities stabilise crystal surfaces during growth?; Gregg and Sibley (1984)]

Gregg and Sibley (1984) suggest that the controls on dolomite texture are: density of nucleation sites [controls crystal size] and the mechanism of crystal growth [control crystals shape]. Dolomite neomorphism is considered to be driven by a combination of:

- phase change [inversion from unstable phase],
- lowering of surface energy [increasing crystal size], and
- strain recrystallisation. They suggest that the nonstoichiometry and high surface energy (small crystals) of recent supratidal dolomites should make them particularly susceptible to recrystallisation.

Gregg and Sibley's (1984) classification is summarised as follows:

IDIOTOPIC – RHOMBIC SHAPED EUHEDRAL TO SUBHEDRAL DOLOMITE (PLANAR):

- **Idiotopic-E** (euhedral) - almost all dolomite crystals are euhedral rhombs; crystal-supported with intercrystalline area filled by another mineral or porous.
- **Idiotopic-S** (subhedral) - (≡ Hypidiotopic of Friedman 1965) – subhedal to anhedral dolomite crystals with low porosity and/or low, intercrystalline matrix; straight, compromise

boundaries are common and many of the crystals have preserved crystal-face junctions. Possibly the result of grain growth from a sucrosic state, until crystals join along irregular compromise boundaries.

- **Idiotopic-C** (cement), euhedral dolomite crystals lining large pores and vugs or surrounding patches of another mineral such as gypsum or calcite.
- **Idiotopic-P** (≡ Porphyrotopic of Friedman 1965), euhedral dolomite crystals floating in a limestone matrix. The crystals are floating rather then crystal supported.

XENOTOPIC – NONRHOMBIC, USUALLY ANHEDRAL DOLOMITE (NON-PLANAR):

- **Xenotopic-A** (anhedral) – tightly packed anhedral dolomite crystals with mostly curved lobate, serrated, indistinct or otherwise irregular intercrystalline boundaries. Preserved crystal-face junctions are rare and crystals often have undulatory extinction in cross-polarised light. Differentiation of this fabric from idiotopic-s is often difficult, and relies on the recognition of "crystal-face boundaries" in the idiotopic-s fabric (Gregg and Sibley [1984] define xenotopic as fabrics within which less than 30% of the crystals have crystal-face boundaries).
- **Xenotopic-C** (cement) – pore-lining saddle shaped or baroque dolomite crystals characterised by scimitar-like terminations, when observed in thin-section, and sweeping extinction in cross-polarised light.
- **Xenotopic- P** (porphyrotopic) – single anhedral dolomite crystals or patches of anhedral dolomite crystals floating in a limestone matrix. The dolomite crystals usually have undulatory extinction in cross-polarised light.

This classification was slightly refined by Sibley and Gregg (1987), who also include crystal/grain size distributions (unimodal or polymodal), and a description of allochems, matrix and void-fillings, which may be differentially dolomitised.

Other influences on dolomite crystal fabrics include:

- **Crystal size:** is controlled by interplay of nucleation rate and growth rate, which in turn are dependant upon many other factors, including; number/availability of nucleation sites, temperature, degree of supersaturation. Therefore crystal size in itself is not necessarily diagnostic of the conditions of dolomitisation, although Sibley and Gregg (1987) suggest that at higher temperatures [all other factors being equal] dolomite will tend to form coarser crystals.
- **Reactant mineralogy:** rate of dolomitisation should reflect original mineralogy, and surface area of dolomitising host. High Mg-calcite and aragonite commonly preferentially dolomitised relative to low Mg-calcite. Primary fabric retention is commonly better in high Mg-calcite, but this may be as much to do with differences in crystal size as in mineralogy. Reactant mineralogy should only influence dolomitisation if dolomite is actually directly replacing the $CaCO_3$ precursor and not filling pores/dissolution cavities.
- **Saturation state** of dolomitising fluid – where low saturation, certain phases will be preferentially replaced (chemical and crystal size control), and unreplaced $CaCO_3$ allochems may dissolved out later to give mouldic pores.

Other commonly encountered dolomite fabric terminology:

- **Dolomicrite** - finely crystalline direct (early) replacement of aragonite.
- **Sucrose** / **Saccharoidal** - porous "sugary" mosaic of euhedral rhombs (a special case of an idiotopic-E type fabric).
- **Baroque or saddle** dolomite = curved crystal faces, commonly with hypersaline FI and inclusions of gypsum-anhydrite. Can be very Fe-rich (up to *c*.15 mol%).
- **Limpid** - clear, glassy (inclusion-free) rhombic dolomite. Dolomite rhombs commonly have cloudy/inclusion-rich cores, with clear overgrowths. Cores indicate that during early dolomitisation fluids were unable to completely dissolve the Cc precursor. Possibly

recording an evolution from near calcite saturated solutions to calcite undersaturation (Morrow 1982b citing Sibley 1980).

- **Mimic / non-mimic.** Mimic replacement preserves the structure (but not necessarily the form) of the replaced phase. Non-mimic replacement may preserve the form, but not the structure (Sibley and Gregg 1987).

3.2 VOLUME CHANGES AND DOLOMITE PORE SYSTEMS

Various different studies offer apparently conflicting views as to whether dolomitisation is a porosity enhancing, a porosity degrading or a porosity re-distributing effect. Purser *et al.* (1994) suggests that much of the porosity within a dolomite is inherited from it's sedimentary precursor, but that porosity may be improved or reduced through dolomitisation. The dolomitisation process can be considered according to 2 different reactions:

$$2CaCO_3 + Mg2+ \Leftrightarrow CaMg(CO_3)_2 + Ca^{2+} \quad (1)$$

Reaction 1 implies a *c*.10% volume loss (*i.e.* porosity enhancement). Dolomitisation **replaces** Ca^{2+} with an equal number of moles of Mg^{2+} (mole-for-mole replacement). If this reaction represents the dolomitisation reaction, then the question remains as to where does the liberated Ca^{2+} go?

or

$$CaCO_3 + Mg^{2+} + CO_3^{2-} \Leftrightarrow CaMg(CO_3)_2 \quad (2)$$

Reaction 2 implies a *c*.80% volume increase (*i.e.* porosity reduction). Dolomitising components are effectively **added** to the system. Therefore, the degree of porosity change reflects the relative significance of these reactions, and whether components are added to or replaced within the system. This can be summarised according to the reactions:

$$(2\text{-}x)\ CaCO_3 + Mg^{2+} + x\ CO_3^{2-} \Leftrightarrow CaMg(CO_3)_2 + (1\text{-}x)\ Ca^{2+} \quad (3)$$

or

$$(2\text{-}x)\ CaCO_3 + Mg^{2+} + x\ HCO_3^{2-} \Leftrightarrow CaMg(CO_3)_2 + (1\text{-}x)\ Ca^{2+} + H^{+} \quad (4)$$

For volume-for-volume replacement x = 0.11 (aragonite) or 0.25 (calcite).

3.3 POROSITY CLASSIFICATION

A system for porosity classification and description was proposed by Choquette and Pray (1970; Table 1) for carbonate sediments in general (an excellent summary is given in Figures 2, 3 and 4 of the original paper), but this scheme is also partially applicable to dolostones.

Purser *et al.* (1994) provide a more specific review of pore-types in dolomites and recognise five genetically distinct porosity types, each of which has a distinctive character:

- **Fabric-Replacive Porosity.** Primary sedimentary textures and microstructures of grains are perfectly preserved. The fabric and pore system are effectively that of the precursor limestone.
- **Dissolution, Vuggy and Mouldic Porosity.** Purser *et al.* (1994) make the distinction between pre-, syn- and post-dolomite porosity. *Pre-dolomite* pores may result from emersion and exposure to mixed and/or meteoric waters prior to dolomitisation. *Syn-dolomite* porosity is identified on the basis of its restricted occurrence only within dolomitised parts of the sequence. Post-dolomite pores result from dissolution of unstable dolomite and/or evaporitic minerals.
- **Intercrystalline Porosity.** This is the typical pore type encountered in dolomitic hydrocarbon reservoirs and commonly coincides with complete destruction of the primary limestone fabric. Where porosity is abundant, this corresponds with the sucrosic crystal fabric type.

- **Intracrystalline Dolomouldic Porosity.** This results from partial dolomite dissolution, which is typically the result of near-surface telogenetic diagenesis. This will typically preferentially remove ferroan-dolomite.
- **Fracture and Breccia Porosity.** Dolomites are more prone to fracturation than limestones due to their more brittle, crystalline character.

Porosity types:	*Size modifiers*:	*Genetic modifiers:*	*Time of formation:*
interparticle	**Megapore**:	**Process:**	**Primary:**
intraparticle	large (32-256mm)	solution	predepositional
intercrystal	small (4-32mm)	cementation	depositional
moldic	**Mesopore:**	internal sediment	**Secondary:**
fenestral:	large (½-4mm)–	**Direction or stage:**	eogenetic
shelter	small ($^1/_{16}$-½mm;	enlarged	mesogenetic
growth	6.3-50µm)	reduced	telogenetic
framework			
fracture:	**Micropore:**	filled	
channel	(<$^1/_{16}$mm;		
	<6.3µm)		
vug:			
cavern			
breccia			
boring			
burrow			
shrinkage			

Table 1 Porosity classification of Choquette and Pray (1970).

4 Lower Carboniferous Limestones of the United Kingdom

4.1 MIDLANDS

The dolomitised deposits that outcrop in the Midlands (Leicestershire and south Derbyshire; Figure 1) form the basis of this study and are of Dinantian age. They have been described in some detail by Ambrose and Carney (1997 and 1999) and Ambrose and Horton (1998), summarised on Figure 2.

Depostional environments: the limestones and dolostones of the area represent deposition on a marine shelf, with the bedded dolostones considered to represent distal storm deposits, gravity flows and turbidites, with mud accumulations during quieter periods. Within this setting localised mud mound build-ups, comparable to the Chadian Reefs of Derbyshire (Bridges and Chapman 1988), developed. A more detailed summary of the main characteristics of the Dinantian deposits as exposed in Breeden-on-the-Hill and Cloud Hill Quarries, and as recovered from the Ticknall Borehole can be found on Figure 2). To the north of the study area turbidites were being deposited in the deep Widmerpool half-graben. During Permo-Triassic times, the area stood out as an inselberg, being gradually buried by fluvial and aeolian sediments, with the development of a cave system.

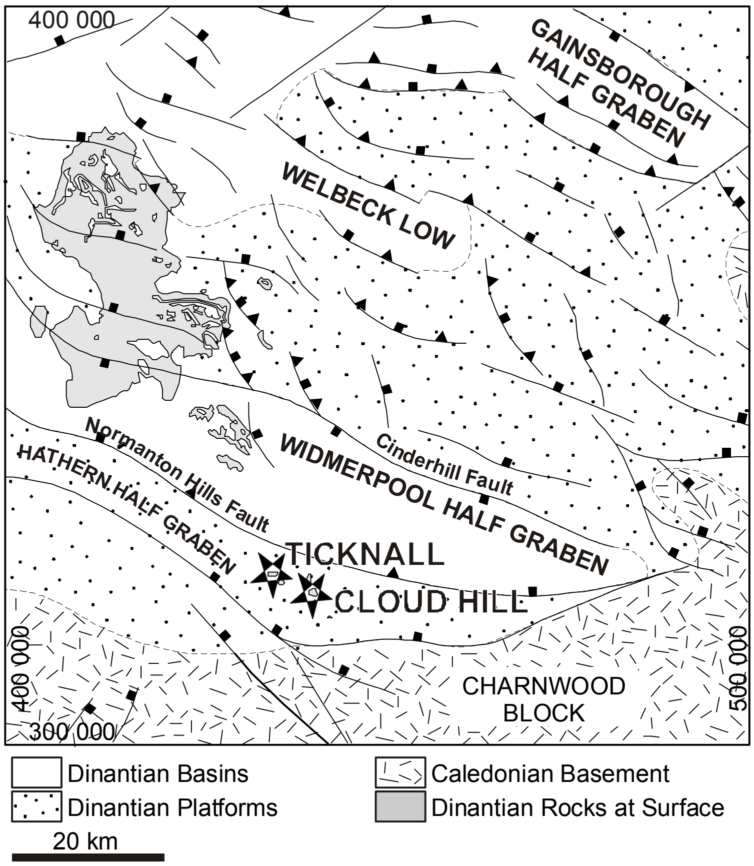

Figure 1 Location map showing the general locations of blocks and basins during Lower Carboniferous times, and the positions of the sites studied as part of the Development of Integrated Methods for Characterising Faults and Fractures project.

4.2 DERBYSHIRE

Hollis and Walkden (1996) and Hollis (1998), present data from the Lower Dinantian deposits from Derbyshire, which represent a potential undolomitised, but similarly fractured analogue to the dolomitised material exposed at Breeden. The Derbyshire limestones contain late burial fracture-related mineralisation (calcite plus galena/fluorite mineralisation and minor [non-economic] hydrocarbons). Hollis and Walkden (1996) recognise 6 principal burial diagenetic calcite cement zones, which are rationalised into early (3A, 3B) and late (4A, 4B, 4C and 4D) generations.

Schofield and Adams (1986) describe dolomitisation of the Woo Dale Limestone Formation, east of Buxton (Derbyshire), and report two phases of dolomitisation. Stage one dolomite is related to Mg-rich fluid expelled from adjacent basinal shales. Stage two dolomite is more Fe and Mn-rich, indicating increased alteration of underlying volcanic deposits by the formation waters expelled from the shales. This dolomite generation is more limited in extent, and is more abundant towards the top of the Woo Dale Limestones, suggesting that dolomitising fluids moved up through permeability channels in phase one dolostone and “spread out” in the overlying limestones. Following dolomitisation, unreplaced limestone was dissolved (?meteoric fluids during uplift), resulting in fracturing and collapse of some dolostones. Within these cavities, some internal (clastic) sediment accumulated, prior to development of zoned pore-filling calcite, during the development of which, minor hydrocarbon emplacement occurred.

		BREEDON ON THE HILL AREA			CALKE ABBEY (TICKNALL) AREA		
		Cloud Hill Quarry	Breedon on the Hill Quarry	Interpretation	Ticknall Borehole	Ticknall Quarries	Interpretation
Ticknall Limestone Formation	Late Asbian [D1]	14m of grey to buff, medium to locally very coarsely crystalline, thickly bedded, nodular dolostone with rare clay partings. Palaeosols are developed within this Formation.			Unit G (6.7m): F2 and F1. Described in more detail in Ticknall Quarries. Unit F (17.7m): calcretes/palaeosols (F5). In the lower part of the unit bioclastic grainstone (F3), comprise buff to grey, fine to coarsely crystalline dolostones and fine-grained ?oolitic/peloidal, bioclastic limestone. Some evidence for karstification of this unit (clastic filled cave/fissure) Unit E (10.0m): nodular, grey, fine-grained, muddy bioclastic limestone interbedded with dark grey, fossilifierous, pyritic mudstone. The interval is predominanty F2, in association with F3. Unit D (17.0m): basal pebbly sandstone overlain by pale to medium grey, fine-grained, dolomitic limestone with sutured stylolites. This is overlain by a fine- to coarse-grained bioclastic (and ?oolitic/peloidal at top) dolostone of F3, with emergence noted by intervals of palaeosol development (F5). Unit C (0.8m): soft, red-brown and mottled silty mudstone (fault gouge or cavity fill?)	Dolostone (4-5m): buff to grey, stained red, yellow or purple, finely crystalline, locally sandy, fine to very fine-grained dolostone. Generally massive with some beeding traces, clay/silt partings and stylolites. Locally fossiliferous. Locally only partially dolomitised. Limestone (up to 6m): grey, muddy, finely crystalline, thickly interbedded limestones with common beds of fissile mudstones. Commonly fossiliferous. Locally dolomitised.	
Cloud Hill Dolostone Formation	Late Asbian [D1]	c.125m thick. Bedded dolostones: Southern end of quarry. Comprises grey, pale reddish grey and pale buff, locally stained, finely to coarsely crystalline, thin to very thickly bedded dolostone. Non-sutured stylolites are common. Bedding planes are undulatory, often with mudstone partings. Evidence that these were originally bioclastic grainstones. Mud mound reef facies: N-Western part of quarry. Buff to grey, locally reddened, finely crystalline massive dolostones which are medium to coarsely crystalline in places. Bedding traces are rare, but fabrics visible include elongate, sub-parallel cavities with sparry calcite fill, and stromatolitic lamination. Generally fossiliferous, but overprinted by dolomite resulting in mouldic porosity.	Only 5m of this Formation is exposed, but is not accessible.	Gradually emerging sequence, but difficult to relate sequences in North and South of Cloud Hill Quarry due to faulting. In the north of Cloud Hill Quarry interbedded carbonates may represent **storm deposits**. Above the Cloud Wood Member, **mud-mound reef** built up, however, extensive dolomitisation obscures the internal makeup of In the south of the quarry, undivided and unstratified carbonates represent possible platform **storm generated carbonates.**	Unit B (29.1m): buff to (pale) grey and off white, fine- to medium-grained limestones and dolostones, with local beds of lime mudstone and micrite F4). Stylolites are common, particularly within limestone. The lower part is a weakly calcareous dolostone, and the upper part is mainly limestone. Bioclastic debris is rare. Calcite +/- pyrite cemented and open veins are common throughout. Bioclast moldic porosity attest to high biocalst content on deposition (F3). Mudstone partings represent "deeper water" sediments. The uppermost beds are mainly fine grained and may be altered sabkha-peritidal carbonates (F4). Unit A (4.3m): structureless, fine- to very fine-grained, probably bioclastic limestones with undulating, locally sandy mudstone partings. 3 emergent cycles are evident with coarser, more bioclastic limestone passing into finer micritic limestone (F3 at base, passing upwards into F4 and F5).		
Cloud Wood Member (Breedon on the Hill Area) Scot's Brook Member (Calke Abbey Area)	Early Asbian - Late Holkerian [S2-D1]	36m thick. Base of mudstone dominated unit pockets of dolostone breccia in contorted mudstone matrix. Overlain by dolostone unit, with 3 sub-units of massive and thinly to thickly bedded, finely to coarsely crystalline dolomite with stylolitic, clay-lined partings.		Mud-deposition in quiet, relatively deep water.	Green-grey, medium- to coarse-grained and pebbly sandstones and argillaceous mudstones, with subordinate mudstone and micritic/nodular limestone, and pedogenic modification.		Layering of these deposits is comparable with alluvial calcretised palaeosols developed under hydromorphic, reducing, conditions. A peritidal setting is inferred for these deposits by their stratigraphic setting.
Main Breedon Discontinuity **Milldale Limestone Formation** Holly Bush Member	Late Chadian [C1]	Above Holly Bush Member: interval of non-dolomitic or partly dolomitised limestone (25m thick in south of quarry, but thins rapidly and passes northwards into dolostones). Comprises grey, fine to coarse grained, thinly to thickly bedded bioclastic and locally oolitic and peloidal limestone. Present in Southern end of quarry. Contains beds of fine to medium grained dolomitic sandstone and sandy dolostone. Below Holly Bush Member: grey to buff, thin to thickly bedded, fine to coarsely crystalline dolostone, with undulating, stylolite-enhanced bedding surfaces with clay-rich drapes. Some chert nodules. Mouldic porosity is associated with faunal debris.	c.380m thick, but incomplete and poorly exposed due to major fault through quarry. West of fault: 70m of buff-grey, finely crystalline, moderately to well-bedded, poorly to fossiliferous, massive dolostone of **mud-mound (Waulsortian) reef facies.** This is overlain by 20m of bedded East of fault: 6 distinct dolostone units. Grey to buff, fine to coarsely crystalline. Some units are **massive,** others are **thinly to thickly bedded** (some laminated beds) and clay/shaley mudstone partings. Variably fossiliferous, with some chert nodules and some	Bedded deposits represent **ramp facies** deposited as distal storm-generated gravity flows (?turbiditic). In quiet periods, mud accumulated forming the interbedded laminated mudstones and siltsones. The deposits at Cloud Hill are probably more proximal than those seen at Breeden on the Hill. This unit indicates that the deposits at Cloud Hill are probably more proximal than those seen at Breeden on the Hill. The massive deposits represent the core of a **mudmound,** with associated laminated deposits probably representing accum-ulation on the flanks of the mound.			

TICKNALL BOREHOLE FACIES SCHEME:

F1 : ***Proximal (to shore) shallow water carbonate facies*** : exclusively dolomitised, with a component of fine-grained quartz sand. Some bioclasts/bioclastic debris. Best seen in the Ticknall Quarries.

F2 : ***Distal shallow water, interbedded carbonates and mudstone facies*** : fine grained muddy limestone and coarser bioclastic limestones, with fossiliferous siltstone and mudstone. Argillaceous beds are commonly stylolitised.

F3 : ***Bioclastic grainstone facies*** : high energy deposition in shallow water. Much of the dolomitised sequence is interpreted as this facies.

F4 : ***sabka-peritidal carbonate facies*** : poorly fossiliferous, very fine grained carbonates and lime mudstones. Birds-eye textures attest to peritidal conditions.

F5 : ***Palaeosol (calcrete) facies*** : nodular carbonates with generally stylolitic contacts, indicating soil formation during emergent conditions. A secondary facies superimposed on facies 2, 3 and 4.

Figure 2 Stratigraphic summary of the Lower Carboniferous Deposits in the Breeden-on-the-Hill area.

4.2.1 Carbonate (Waulsortian Reef) Mud Mound Facies and Architecture

Bridges and Chapman (1988) and Bridges et al. (1995) provide a description of comparable, but undolomitised mud-mound deposits from the Derbyshire Platform where they recognise five mound associated facies:

- **mound core** – massive to crudely bedded wackestones with comminuted bioclastic debris (diverse fauna), in a matrix of clotted micrite, and common small irregular cavities and neomorphic textures. This is interpreted to represent the site of carbonate generation, with micrite precipitation in response to high ammonia levels generated through decomposition of algae/bacteria. These mounds were colonised by a range of organisms, with localised development of stromatolites.
- **mound flank** (coarse) - bedded, moderately dipping packestones and crinoid-intraclast floatstones, with crinoid columnals, micritised algal-encrusted intraclasts, foraminifera and coarse peloids. This facies is interpreted to represent downslope movement of material from the mound core, with some colonisation by crinoids.
- **mound flank** (fine) – bedded, moderately dipping packestones and wackestones, with sponge spicules, ostracods and foraminifera. This facies is also interpreted to represent downslope movement of material from the mound core (more distal extent).
- **intermound** (coarse) – bedded, gently dipping, coarse grainstones or fine-rudstones dominated by intraclasts, peloids and crinoids. Material derived from a range of sources (mound and platform). Plane lamination and graded textures imply density and wind induced flows were active.
- **intermound** (fine) - bedded, gently dipping bituminous packestones and wackestones. Deposition under quieter (?deeper water or storm/turbidite-free) conditions.

Bridges and Chapman (1988) also recognise syn-depositional tension-related features (slope instability) on the mounds.

4.3 BOWLAND BASIN

The Pendleside Limestone occurs in the Bowland Basin (N. England; Fig 1), is of Dinantian age and has been described by Gawthorpe (1987). Limestone and sandstone bodies within a mixed clastic/carbonate/shale sequence, were dolomitised (preferentially at their margins and along more permeable horizons) by fluid expelled from the enclosing mudrocks during intermediate to deep burial. As noted in other examples of burial dolomitisation, early replacive dolomite is separated from a later dolomite cement generation, by a phase of carbonate dissolution (dissolution not observed in undolomitised limestone). In this case, Gawthorpe (1987) attributes the dissolution to expulsion of acidic fluids from the shales, which were generated by the smectite-illite transformation, CO_2 release and organic acid production (citing Curtis 1983; Foscolos & Powell 1979, 1980; Surdam et al. 1984). Towards the onset of hydrocarbon generation pore waters would have become less acidic (carbonate dissolution, decreased CO_2, decreased organic acid generation), and thus able to precipitate carbonates. This is model is supported by minor element chemistry (*e.g.* Fe contents of the dolomites related to relative stability of Fe- and Mg-rich smectite in the mudrocks).

This examples demonstrates the need to look outside the dolomitised limestone mass, into the inferred Mg^{2+} source, in order to constrain the fluid/burial history of the shales.

5 Conclusions

Sea water is supersaturated with respect to dolomite and therefore dolomitisation should be widespread at the present day. However, this is not the case and various kinetic inhibitors of dolomite precipitation have been identified which can be summarised in terms of: Mg^{2+}/Ca^{2+} ratio, salinity and CO_3^{2-}/Ca^{2+} ratio. Furthermore, the volumes of dolomite being generated today are too low to account for the large volumes of dolomitised limestone observed in the geological record. A number of models have been proposed to explain dolomitisation, and the majority of these provide an mechanism by which seawater is modified such that the kinetic inhibitors on dolomite formation are reduced or removed. The main models are:

- **Evaporative (Sabkha or Coorong) –** flood recharge of marine waters which percolates downwards to the groundwater. Evaporation causes the precipitation of aragonite and gypsum, increasing the Mg/Ca ratio of the porewater until dolomite precipitation occurs.
- **Seepage-Reflux and Evaporative Draw Down** –evaporation of lagoon/tidal flat pore water, with precipitation of gypsum in the lagoon. The residual fluid is warm, alkaline, hypersaline and has a high Mg/Ca ratio, and sinks downwards causing dolomitisation in the subsurface.
- **Mixing Zone [Dorag]** –seawater mixed with meteoric water preserves high Mg/Ca ratio, but overcomes the kinetic obstacle to dolomitisation caused by seawater's high ionic strength.
- **Burial** – dolomite forms in response to the expulsion of Mg-bearing brines from compacting and dewatering basinal mudrocks into platform margin carbonates. Additional effects related to burial dolomitisation are solution/cannibalisation and development of tectonic or hydrothermal dolomite (generally fracture-related).
- **Seawater** – various models have been proposed which may enable seawater or only slightly modified seawater to directly dolomitise limestone. These models either provide an efficient mechanism for pumping of large volumes of sea water through a formation ([Kahout] thermal convection, reflux, tidal pumping and shallow subtidal models), or invoke organogenetic or microbially-mediated (sulphate-reducing bacteria) mechanisms.

Gregg and Sibley (1984) defined a classification scheme for dolomite crystal fabrics and suggested that textures are controlled by density of nucleation sites [controls size] and the mechanism of crystal growth ["*surface roughness factor"* controls shape]. Below a "*critical roughening temperature*" (CRT) or below a "*critical saturation*", growth occurs by lateral migration of layers generating regular, euhedral (*i.e.* **idiotopic** or planar textures). At temperatures above the CRT, or saturation above the critical saturation, atoms are added in an essentially random manner, resulting in rough crystal surfaces and anhedral crystals (*i.e.* **xenotopic** or non-planar). Gregg and Sibley (1984) place the CRT for dolomite between 50°c [dolomites formed below this are idiotopic], and 100°c [above which dolomites are xenotopic]. Gregg and Sibley (1984) define a number of subtypes of these fabrics. In addition, a number of other terms such as sucrose/saccharoidal and saddle are widely used to describe specific textures.

The commonly assumed relationship between dolomitisation and porosity creation is dependant upon simple stoichiometric replacement of calcite by dolomite, which should result in increased porosity. However, such situations are likely to be rare in nature with most examples of dolomitisation being accompanied by addition or removal of components from the system and thus dolomitisation may be a porosity destroying, redistributing or creating process. A descriptive scheme for porosity classification was proposed by Choquette and Pray (1970) for limestones, and many of these pore types and modifiers can be apply equally successfully to dolostones. Purser *et al.* (1994) provide a more genetically-based classification specific to dolostones.

The background geology of a number of Lower Carboniferous Limestone deposits from the UK are also summarised. These areas include, in particular, the deposits of Leicestershire and South

Derbyshire, which are the main area of interest for the Development of Integrated Methods for Characterising Faults and Fractures project. These deposits were deposited on a marine shelf, with the bedded dolostones considered to represent distal storm deposits, gravity flows and turbidites, with mud accumulations during quieter periods. Within this setting localised mud mound build-ups developed. Relatively little information on the mechanisms and timing of dolomitisation in the study area was uncovered during this literature review. Potentially comparable deposits on the main Derbyshire Platform and in the Bowland Basin are also summarised.

References

Most of the references listed below are held in the Library of the British Geological Survey at Keyworth, Nottingham. Copies of the references may be purchased from the Library subject to the current copyright legislation.

ADAMS, A.E. and RHODES, M.L. 1960. Dolomitization by seepage refluxion. American Association of Petroleum Geologists Bulletin, v.44, p.1912-1920.

AMBROSE, K. and CARNEY, J.N. 1997. Geology of the Breedon on the Hill area. *British Geoogical Survey Technical report WA/97/42.*

AMBROSE, K. and CARNEY, J.N. 1999. Geology of the Calke Abbey area. *British Geoogical Survey Technical report WA/97/17.*

AMBROSE, K. and HORTON, A 1998. Excursion to Breedon on the Hill Quarry *Mercian Geologist, Vol. 14(3), 145-147.*

BADIOZAMANI, K. 1973. The Dorag dolomitization model - application to the Middle Ordovician of Wisconsin. *Journal of Sedimentary Petrology, v.43, p.965-984.*

BAKER, P.A. and KASTNER, M. 1981. Constraints on the formation of sedimentary dolomite. *Science, v213, 10-07-81, p214-216.*

BEIN, A. and LAND, L.S. 1983. Carbonate sedimentation and diagenesis associated with Mg-Ca-chloride brines: the Permian San Andres Formation in the Texas Panhandle. *Journal of Sedimentary Petrology, v.53, p.243-260.*

BOLES, J.R. 1981. Clay diagenesis and effects on sandstone cementation (case histories from the Gulf Coast Tertiary). *in: LONGSTAFFE, F.J. (ed.) Clays and the Resource Geologists. Mineralogical Association of Canada, Short Course Handbook, v.7, p.148-168.*

BRIDGES, P.H. and CHAPMAN, A.J. 1988. The anatomy of a deep water mud-mound complex to the southwest of the Dinantian platform in Derbyshire, UK. *Sedimentology Vol. 35, 139-162.*

BRIDGES, P.H., GUTTERIDGE, P. and PICKARD, N.A.H. 1995. The environmental setting of early Carboniferous mud-mounds. *International Association of Sedimentologists, Special Publication, v.23, p.171.190.*

BULLEN, S.B. and SIBLEY, D.F. 1983. Dolomite selectivity, an experimental approach. *American Association of Petroleum Geologists Bulletin, v.67, p.433-434.*

CARBALLO, J.D., LAND, L.S. and MISER, D.E. 1987. Holocene dolomitization of supratidal sediments by active tidal pumping, Sugarloaf Key, Florida. *Journal of Sedimentary Petrology, v.57, p.153-165.*

CHOQUETTE, P.W., AND PRAY, L.C. 1970. Geologic nomenclature and classification of porosity in sedimentary carbonates. *AAPG Bulletin (American Association of Petroleum Geologists), Vol. 54(2), p207-250.*

CLARK, D.N. 1980. The diagenesis of Zechstein carbonate sediments. *Contributions to Sedimentology, v.9, p.167-203.*

CURTIS, C.D. 1983. Geochemistry of porosity enhancement and reduction in clastic sediments. *In. BROOKES, J. (ed) Petroleum Geochemistry and Exploration in Europe. Geological Society of London, Special Publication, v.12, p.113-126.*

DIX, G.R. 1993. Patterns of burial and tectonically controlled dolomitisation in an Upper Devonian fringing-reef complex: Leduc Formation, Peace River Arch Area, Alberta , Canada *Journal of Sedimentary Petrology, v.63(4), p.628-640.*

DRIVET, E. and MOUNTJOY, E.W. 1997. Dolomitization of the Leduc formation (Upper Devonian), southern Rimbey-Meadowbrook reef trend, Alberta. *Journal of Sedimentary Research, v.67(3), p.441-423.*

DUNHAM, J.B. and OLSON, E.R. 1978. Diagenetic dolomite formation related to Paleozoic paleogeography of the Cordilleran miogeosyncline in Nevada/ *Geology, v.6, p.556-559.*

DUNHAM, J.B. and OLSON, E.R. 1980. Shallow subsurface dolomitizatlon of subtidally deposited carbonate sediments in the Hanson Creek Formation (Ordovician-Silurian) of Central Nevada *In: Zenger, D.H., Dunham, J.B. and Ethington, R.L. (eds). Concepts and models of dolomitization. SEPM Special Publication, v.28, p.139-161.*

ELIUK, L.S. 1978. The Abenaki Formation, Nova Scotia Shelf, Canada - a depositional and diagenetic model for a Mesozoic carbonate platform. *Canadian Society of Petroleum Geologists Bulletin, v.26, p.424-514.*

EXPLORATION STAFF, CHEVRON STANDARD LIMITED. 1979. The geology, geophysics and significance of the Nisku Reef discoveries, West Pembina area, Alberta, Canada. *Canadian Society of Petroleum Geologists Bulletin, v.27, p.326-359.*

FISHER, W.L. and RODDA, P.U. 1969. Edwards Formation (Lower Cretaceous), Texas: dolomitization in a carbonate paltform system. *American Association of Petroleum Geologists Bulletin, v.53, p.55-72.*

FOLK, R.L. and LAND, L.S. 1975. Mg/Ca ratio and salinity: twocontrols on crystallisation of dolomite. *American Association of Petroleum Geologists Bulletin, v. 59, p.60-68.*

FOSCOLOS, A.E. and KODAMA, J. 1974. Diagenesis of clay minerals from Lower Cretaceous shales of northeastern British Colombia. *Clays and Clay Minerals, v.22, p.319-335.*

FOSCOLOS, A.E. and POWELL, T.G. 1979. Catagenesis in shales and occurance of authigenic lcays in sandstones, North Sabine, H-49 well, Canadian Arctic Islands. *Canadian Journal of Earth Sciences, v.16, p.1309-1314.*

FOSCOLOS, A.E. and POWELL, T.G. 1980. Mineralogical and geochemical transformations of clays during catagenesis and their relation to oil generation. *In: Facts and Principles of World Petroleum Occurrences. Mem. Can. Soc. Pterol. Geol., Calgary, v.6, p.153-172.*

FOWLES, J. 1991. Dolomite : the mineral that shouldn't exist *New Scientist, 26-10-1991*

FRIEDMAN, G.M. 1965. Terminology of crystallization textures and fabrics in sedimentary rocks. *Journal of Sedimentary Petrology, v.35, p.643-655.*

GAINES, A.M. 1974. Protodolomite synthesis at 100degC and atmospheric pressure. *Science, v.183, p.5180520.*

GAINES, A.M. 1980. Dolomitization kinetics: recent experimental studies *In: Zenger, D.H., Dunham, J.B. and Ethington, R.L. (eds). Concepts and models of dolomitization. SEPM Special Publication, v.28, p.81-86.*

GAWTHORPE, R.L. 1987. Burial dolomitisation and porosity development in a mixed clastic-carbonate sequence: an example from the Bowland Basin, northern England. *Sedimentology, v.34, p.553-558.*

GREGG, J.M. 1985. Regional epigenetic dolomitization in the Bonneterre Dolomite (Cambrian), southeastern Missouri. *Geology, v.13, p.503-506.*

GREGG, J.M. 1988. Origins of dolomite in the offshore facies of the Bonneterre Formation (Cambrian), Southeast Missouri *in: Shukla, V. and Baker, P.A. (eds) Sedimentology and geochemistry of dolostones. SEPM Special Publication, v.43, p.67-83.*

GREGG, J.M. and SIBLEY, D.F. 1984. Epigenetic dolomitisation and the origin of xenotopic dolomite texture. *Journal of Sedimentary Petrology, v.54(3), p908-931.*

GUNATILAKA, A., SAHLEH, A. and AL-TEMEEMI, A. 1985. Sulphate reduction and dolomitization in a Holocene lagoon, Kuwait. *Nature, v.311, p450-452.*

HARDIE, L. 1987. Perspectives: Dolomitisation a critical view of some current views. *Journal of Sedimentary Petrology, v.57(1), p.166-183.*

HOLLIS, C. 1998. Reconstructing fluid history: an integrated approach to timing fluid expulsion and migration on the carboniferous Derbyshire Platform, England. *In: J.Parnell (ed), 1998, Dating and duration of fluid flow and fluid-rock interaction. London: Geological Society of London (Special Publication no.144) p.153-160*

HOLLIS, C. and WALKDEN, G. 1996. The use of burial diagenetic calcite cements to determine the controls upon hydrocarbon emplacement and mineralization on a carbonate platform, Derbyshire, England. *IN: P.Strogen, I.D.Somerville & G.Ll.Jones (ed), 1996, Recent advances in Lower Carboniferous geology. London: Geological Society of London (Special Publication no.107) p.35-49*

HSU, K.J. and SCHNEIDER, J. 1973. Progress report on dolomitization and hydrology of Abu Dhabi sabkhas, Arabian Gulf. *In: PURSER, B.H. (ed.), The Persian Gulf, Springer-Verlag, Berlin, P.409-422.*

HSU, K.J. and SIEGENTHALER, C. 1969. Preliminary experiments on hydrdynamic movement induced by evaporation and their bearing on the dolomite problem. *Sedimentology, v.12, p.11-25.*

JACKSON, K.A. 1958. Mechanisms of growth. *In: Liquid Metals and Solidification. Cleveland. Amer. Soc. of Metals., p.174-186.*

JONES, R.M.P. 1980. Basinal isostatic adjustment faults and their petroleum significance. *Canadian Petroleum Geologists Bulletin, v.28, p.211-251.*

KATZ, A. and MATTHEWS, A. 1977. The dolomitization of CaCO3: an experimental study at 252-295degC. *Geochimica et Cosmochimica Acta, v.41, p.297-308.*

KELTS, K. and McKENZIE, J. 1982. Diagenetic dolomite formation in Quaternary anoxic diatomaceous muds of Deep Sea Drilling Project Leg 64, Gulf of California. *Initial Reports of the Deep Sea Drilling Programme, v.64, p.553-570.*

KOHOUT, F.A. 1967. Groundwater flow and the geothermal regime of the floridan Plateau. *Transactions of the Gulf Coast Assoc. Geol. Soc., v.17, p.339-354.*

LAND, L.S. 1973. Contemporaneous dolomitisation of middle Pliocene reefs by meteoric water, north Jamaica. *Bulletin of Marine Science, v.23, p.64-92.*

LAND, L.S. 1985. The origin of massive dolomite. Journal of Geological Education, v.33, p.112-125.

LIPMANN, F. 1973. Sedimentary Carbonate Minerals. Springer, Berlin, 228pp.

LOGAN, B.W. and SEMENUIK, V. 1976. Dynamic metamorphism: processes and products in Devonian carbonate rocks Canning Basin, Western Australia. Geological Society of Australia Special, Pat., v.6, pp.138.

MACHEL, H.G. 1984. Facies and dolomitization o fthe Upper Devonian Nisku Formation in the Brezeau, Pembina and bigoray area, Alberta Canada. in: Carbonates in Subsurface and Outcrop. Canadian Society of Petroleum Geologists Core Conference, 1984, p.191-224.

MACHEL, H.G. and MOUNTJOY, E.W. 1986. Chemistry and environments of dolomitisation. *Earth Science Reviews, v.23, p175-222.*

MACHEL, H-G. and LONNEE, J. 2002 Hydrothermal dolomite—a product of poor definition and imagination**.** *Sedimentary Geology v.152. p.163–171.*

MALONE, M.J., BAKER, P.A. and BURNS, S.J. 1996. Recrystallization of dolomite breccias hydrothermal dolomitization and recrystallization of dolomite breccias from the Miocene Monterey Formation, Tepusquet area, California. *Journal of Sedimentary Research, v. 66(5), p.976-990.*

MANSFIELD, C.F. 1980. A urolith of biogenic dolomite - another clue in the dolomite mystery. *Geochimica et Cosmochimica Acta, v.44, p.829-839.*

MATTES, B.W. and MOUNTJOY, E.W. 1980. Burial dolomitizatlon of the Upper Devonian Miette Buildup, Jasper National park, Alberta *In: Zenger, D.H., Dunham, J.B. and Ethington, R.L. (eds). Concepts and models of dolomitization. SEPM Special Publication, v.28, p.259-297.*

MAZZULLO, S.J. 2000. Organogenic dolomitization in peritidal to deep-sea sediments *Journal of Sedimentary Research, v.70(1), p.10-23.*

MAZZULLO, S.J., REID, A.M. and GREGG, J.M. 1987. Dolomitization of Holocene Mg-calcite supratidal deposits, Ambergris Cay, Belize. *Geological Society of America Bulletin, v.98, p.224-231*

McKENZIE, J.A., HSU, K.J. and SCHNEIDER, J.F. 1980. Movement of subsurface waters under the sabkha, Abu Dhabi, UAE, and its relation to evaporative dolomite genesis *In: Zenger, D.H., Dunham, J.B. and Ethington, R.L. (eds). Concepts and models of dolomitization. SEPM Special Publication, v.28, p.11-30.*

MEYERS, W.J., LU, F.H. and ZACHARIAH, J.K. 1997. Dolomitization by mixed evaporative brines and freshwater, Upper Miocene carbonates, Nijar, Spain. *Journal of Sedimentary Research, v.67(5), p.898-912.*

MIRSAL, I.A. and ZANKL, H. 1985. Some phenomenological aspects of carbonate geochemistry. The control effect of transition metals. Geol. Rundsch. V.74, p.367-377.

MORROW, D.W. 1982a. Diagenesis 1. Dolomite - Part 1: the chemistry of dolomitization and dolomite precipitiation. *Geoscience Canada, v.9(1), p5-13.*

MORROW, D.W. 1982b. Diagenesis 2. Dolomite - Part 2: Dolomitization models and ancient dolostones. *Geoscience Canada, v.9(2), p.95-107.*

MUCCI, A. and MORSE, J.W. 1983. The incorporation of Mg2+ and Sr2+ into calcite overgrowths: influences of growth rate and solution composition. *Geochimica et Cosmochimica Acta, v.47, p.217-233.*

MULLINS, H.T., HEATH, K.C., VAN DUREN, H.M. and NEWTON, C.R. 1984. Anatomy of modern open-ocean carbonates: Northern Little Bahama Bank. *Sedimentology, v.31, p.141-168.*

MULLINS, H.T., WISE, S.W., GARDULSKI, A.F., HINCHEY, E.J., MASTERS, P.M. and SIEGEL, D.I. 1985. Shallow subsurface diagenesis of Pleistocene periplatform ooze: northern Bahamas. *Sedimentology, v.32, p.473-494.*

MURRAY, R.C. 1969. Hydrology of south Bonaire, N.A. - a rock selective dolomitization model. *Journal of Sedimentary Petrology, v.39, p.1007-1013.*

PATERSON, R.J. 1972. Hydrology and carbonate diagenesis of a coastal sabkha in the Persian Gulf. *Ph.D. Thesis, Princeton University, Princeton, New Jersey, pp.498.*

PATERSON, R.J. and KINSMANN, D.J.J. 1981. Hydrologic framework of a sabkha along the Arabian Gulf. *American Association of Petroleum Geologists Bulletin, v.65, p.1457-1475.*

PATERSON, R.J. and KINSMANN, D.J.J. 1982. Formation of diagenetic dolomite in coastal sabkhas along the Arabian (Persian) Gulf. *American Association of Petroleum Geologists Bulletin, v.66, p.28-43.*

PURSER, B.H., BROWN, A. AND AISSAOUI, D.M. 1994. Nature, origins and evolution of porosity in dolomites *In: Purser, B., Tucker, M. and Zenger, D. (eds). Dolomites: A volume in Honour of Dolomieu. International Association of Sedimentologists, Special Publication, v.21, p.283-308*

QING, H. & MOUNTJOY E.W. 1992. Large-scale fluid flow in the Middle Devonian Presqu'ile barrier, Western Canada Sedimentary Basin. *Geology, v.20, p.903-906.*

QING, H. & MOUNTJOY, E.W. 1994. Rare earth element geochemistry of dolomites in the Middle Devonian Presq'ile barrier, Western Canada Sedimentary Basin: implications for fluid-rock ratios during dolomitization. *Sedimentology, v41, p787-804.*

REINHOLD, C. 1998. Multiple episodes of dolomitization and dolomite recrystallization during shallow burial in Upper Jurassic shelf carbonates; eastern Swabian Alb, southern Germany. *Sedimentary Geology. 121; 1-2, Pages 71-95. 1998*

SALLER, A.H. 1984. Petrologic and geochemical constraints on the origin of subsurface dolomite: Enewetak Atoll: an example of dolomitization by normal seawater. *Geology, v.12, p.217-220.*

SASS, E. and KATZ, A. 1982. The origin of plaform dolomites. *American Journal of Science, v.282, p.1184-1213.*

SCHOFIELD, K. and ADAMS A.E. 1986. Burial dolomitization of the Woo Dale Limestones Formation (Lower Carboniferous), Derbyshire, England *Sedimentology, Vol. 33(2), 207-219.*

SEARS, S.O. and LUCIA, F.J. 1980. Dolomitisation of Northern Mitchigan Niagara reefs by brine refluxation and freshwater seawater mixing. *in: Zenger, D.H., Dunham, J.B. and Ethington, R.L. (eds) Concepts and models of dolomitisation, SEPM Spec. Pub. 28, 215-235*

SHINN, E.A. 1983. Tidal flat environment. *In: SCHOLLE, P.A., DEBOUT, D.G. and MOORE, C.H. (eds), Carbonate Depositional Environments. American Association of Petroleum Geologists Memoirs, v.33, p.173-210.*

SHINN, E.A., GINSBURG, R.N. and LLOYD, R.M. 1965. Recent supratidal dolomite from Andros Island, Bahamas. *In: PRAY, L.C. and MURRAY, R.D. (eds), Dolomitisation and Limestone Diagenesis, a Symposium. Society of Economic Paleontologists and Mineralogists Special Publication, v.13, p.112-123.*

SIBLEY, D.F. 1980. Climatic control of dolomitization, Seroe Domi formation (Pliocene), Bonaire, N.A. *In: Zenger, D.H., Dunham, J.B. and Ethington, R.L. (eds). Concepts and models of dolomitization. SEPM Special Publication, v.28, p.247-258.*

SIBLEY, D.F.and GREGG, J.M. 1987. Classification of dolomite rock textures. *Journal of Sedimentary Petrology, v.57(6), p.967-975.*

SIBSON, R.H., MOORE, J.McM, AND RANKIN, A.H. 1975. Seismic pumping - a hydrothermal fluid transport mechanism. *Journal of the Geological Society, London, v.131, p.653-659.*

SIMMS, M. 1984. Dolomitization by groundwater-flow systems in carbonate platforms. *Transactions of the Gulf Coast Assoc. Geol. Soc., v.34, p.411-420.*

SKALL, H. 1975. The paleoenvironment of the Pine Point lead-zinc District. *Economic Geology, v.70, p.22-47.*

SMITH, D.B. 1981. Bryozoan-algal patch reefs in the Upper Permian Magnesian limestones of Yorkshire, Northeast England. in: TOOMEY, D.F. (ed) European Fossil Reef Models. Society of Economic Paleontologists and Mineralogists Special Publication, v.33, p.187-202.

SONNENFELD, P. 1964. Dolomites and dolomitization: a review. Canadian Petroleum Geologists Bulletin, v.12, p.101-152.

SURDAM, R.C., BOESE, S.W. and CROSSEY, L.J. 1984. The chemistry of secondary porosity. in, McDonald, D.A. & Surdam, R.C. (eds.), Clastic Diagenesis. American Association of Petroleum Geologists, Memoir v.37, p.127-150.

TEAL, C.S., MAZZULLO, S.J. and BISCHOFF, W.D. 2000. Dolomitization of Holocene shallow-marine deposits mediated by sulfate reduction and methanogenesis in normal-salinity seawater, northern Belize. *Journal of Sedimentary Research, v.70(3), p.649-663.*

Tucker, M.E. and Wright, V.P. 1990 Carbonate Sedimentology. *Blackwell, 482pp.*

VIAU, C.A. and OLDERSHAW, A.E. 1984. Structural controls on sedimentation and dolomite cementation in the Swan Hill Field, Central Alberta. *in: Carbonates in Subsurface and Outcrop. Canadian Society of Petroleum Geologists Core Conference, 1984, p.103-131.*

VON DER BORCH, C.C. 1976. Stratigraphy and formation of Holocene dolomitic carbonate deposits of the Coorong area, South Australia. *Journal of Sedimentary Petrology., v.v.46, p.952-966.*

VON DER BORCH, C.C. and JONES, J.B. 1976. Spherular modern dolomite from the Coorong area, South Australia. *Sedimentology, v.23, p.587-591.*

WALTER, L.M. 1985. Relative reactivity of skeletal carbonates during dissolution: implications for diagenesis. *In: SCHNEIDERMANN, N. and HARRIS, P.M. (eds), Carbonate Cements. Society of Economic Paleontologists and Mineralogists Special Publication, v. 36, p.3-16.*

WANLESS, H.R. 1979. Limestone response to stress: pressure solution and dolomitisation. *Journal of Sedimentary Petrology., v.49, p.437-462.*

WOOD, G.V. and WOLFE, M.J. 1969. Sabkha cycles in the Arab/Darb Formation off the Trucial Coast of Arabia. *Sedimentology, v.12, p.165-191.*

WRIGHT, D.T. 1997. An organogenic origin for widespread dolomite in the Cambrian Eilean Dubh Formation, Northwestern Scotland. *Journal of Sedimentary Research, v.67(1), p.54-64.*

WRIGHT, D.T. 2000. Benthic microbial communities and dolomite formation in marine and lacustrine environments – a new dolomite model. *in GLENN, C.R., PRÉVÔT-LUCAS, L. and LUCAS, J. (eds) Marine Authigenesis from Global to Microbial. Society of Ecconomic Mineralogists and Palaeotonologists, Special Publication. v.60, p.7-20.*

XUN, Z. and FAIRCHILD, I. 1987. Mixing zone dolomitisation of Devonian carbonates, Guangxi, South China. *In. MARSHALL, J.D. (ed.) Diagenesis of sedimentary Sequences. Geological Society London, special Publication, v.36, p157-170..*

YOO, C.M., GREGG, J.M. and SHELTON, K.L. 2000. Dolomitization and dolomite neomorphism: Trenton and Black River Limestones (Middle Ordovician) Northern Indiana, U.S.A. *Journal of Sedimentary Research, v.70(1)*