Concepts and models of dolomitization: a critical reappraisal

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Abstract: Despite intensive research over more than 200 years, the origin of dolomite, the mineral and the rock, remains subject to considerable controversy. This is partly because some of the chemical and/or hydrological conditions of dolomite formation are poorly understood, and because petrographic and geochemical data commonly permit more than one genetic interpretation. This paper is a summary and critical appraisal of the state of the art in dolomite research, highlighting its major advances and controversies, especially over the last 20–25 years.

The thermodynamic conditions of dolomite formation have been known quite well since the 1970s, and the latest experimental studies essentially confirm earlier results. The kinetics of dolomite formation are still relatively poorly understood, however. The role of sulphate as an inhibitor to dolomite formation has been overrated. Sulphate appears to be an inhibitor only in relatively low-sulphate aqueous solutions, and probably only indirectly. In sulphate-rich solutions it may actually promote dolomite formation.

Mass-balance calculations show that large water/rock ratios are required for extensive dolomitization and the formation of massive dolostones. This constraint necessitates advection, which is why all models for the genesis of massive dolostones are essentially hydrological models. The exceptions are environments where carbonate muds or limestones can be dolomitized via diffusion of magnesium from seawater rather than by advection.

Replacement of shallow-water limestones, the most common form of dolomitization, results in a series of distinctive textures that form in a sequential manner with progressive degrees of dolomitization, i.e. matrix-selective replacement, overdolomitization, formation of vugs and moulds, emplacement of up to 20 vol% calcium sulphate in the case of seawater dolomitization, formation of two dolomite populations, and – in the case of advanced burial – formation of saddle dolomite. In addition, dolomite dissolution, including karstification, is to be expected in cases of influx of formation waters that are dilute, acidic, or both.

Many dolostones, especially at greater depths, have higher porosities than limestones, and this may be the result of several processes, i.e. mole-per-mole replacement, dissolution of unreplaced calcite as part of the dolomitization process, dissolution of dolomite due to acidification of the pore waters, fluid mixing (mischungskorrosion), and thermochemical sulphate reduction. There also are several processes that destroy porosity, most commonly dolomite and calcium sulphate cementation. These processes vary in importance from place to place. For this reason, generalizations about the porosity and permeability development of dolostones are difficult, and these parameters have to be investigated on a case-by-case basis.

A wide range of geochemical methods may be used to characterize dolomites and dolostones, and to decipher their origin. The most widely used methods are the analysis and interpretation of stable isotopes (O, C), Sr isotopes, trace elements, and fluid inclusions. Under favourable circumstances some of these parameters can be used to determine the direction of fluid flow during dolomitization.

The extent of recrystallization in dolomites and dolostones is much disputed, yet extremely important for geochemical interpretations. Dolomites that originally form very close to the surface and from evaporitic brines tend to recrystallize with time and during burial. Those dolomites that originally form at several hundred to a few thousand metres depth commonly show little or no evidence of recrystallization.

Traditionally, dolomitization models in near-surface and shallow diagenetic settings are defined and/or based on water chemistry, but on hydrology in burial diagenetic settings. In this paper, however, the various dolomite models are placed into appropriate diagenetic settings.

Penecontemporaneous dolomites form almost syndepositionally as a normal consequence of the geochemical conditions prevailing in the environment of deposition. There are many such settings, and most commonly they form only a few per cent of microcrystalline dolomite(s). Many, if not most, penecontemporaneous dolomites appear to have formed through the mediation of microbes.

Virtually all volumetrically large, replacive dolostone bodies are post-depositional and formed during some degree of burial. The viability of the many models for dolomitization

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in such settings is variable. Massive dolomitization by freshwater–seawater mixing is a myth. Mixing zones tend to form caves without or, at best, with very small amounts of dolomite. The role of coastal mixing zones with respect to dolomitization may be that of a hydrological pump for seawater dolomitization. Reflux dolomitization, most commonly by mesohaline brines that originated from seawater evaporation, is capable of pervasively dolomitizing entire carbonate platforms. However, the extent of dolomitization varies strongly with the extent and duration of evaporation and flooding, and with the subsurface permeability distribution. Complete dolomitization of carbonate platforms appears possible only under favourable circumstances. Similarly, thermal convection in open half-cells (Kohout convection), most commonly by seawater or slightly modified seawater, can form massive dolostones under favourable circumstances, whereas thermal convection in closed cells cannot. Compaction flow cannot form massive dolostones, unless it is funnelled, which may be more common than generally recognized. Neither topography driven flow nor tectonically induced ('squeegee-type') flow is likely to form massive dolostones, except under unusual circumstances. Hydrothermal dolomitization may occur in a variety of subsurface diagenetic settings, but has been significantly overrated. It commonly forms massive dolostones that are localized around faults, but regional or basin-wide dolomitization is not hydrothermal.

The regionally extensive dolostones of the Bahamas (Cenozoic), western Canada and Ireland (Palaeozoic), and Israel (Mesozoic) probably formed from seawater that was 'pumped' through these sequences by thermal convection, reflux, funnelled compaction, or a combination thereof. For such platform settings flushed with seawater, geochemical data and numerical modelling suggest that most dolomites form(ed) at temperatures around 50–80 °C commensurate with depths of 500 to a maximum of 2000 m. The resulting dolostones can be classified both as seawater dolomites and as burial dolomites. This ambiguity is a consequence of the historical evolution of dolomite research.

More than 200 years ago Déodat de Dolomieu was the first to provide a description of a rock consisting chiefly of the mineral dolomite (Dolomieu 1791). Dolomite, the mineral and the rock, has been found in almost all diagenetic settings, and in rocks that range in age from the Precambrian to the Recent. Yet, despite its widespread occurrence, and after more than 200 years of research, several aspects of the mineral dolomite, especially the origin of massive dolostones, are still much debated, as highlighted by the conference 'The Geometry and Petrogenesis of Dolomite Hydrocarbon Reservoirs', held by the Geological Society in London on 3–4 December 2002. This paper is an outgrowth of the author's presentation and discussions at that conference, with the objective of providing a critical summary of the state of the art of the most important aspects of dolomite, dolostones, and dolomitization. An article with these same objectives was published some 20 years ago under the title 'Chemistry and environments of dolomitization – a reappraisal' (Machel & Mountjoy 1986). This paper was a reappraisal of the state of the art of dolomite research at that time, as represented in the Society of Economic Paleontologists and Mineralogists (SEPM) Special Publication No. 28 (Zenger *et al.* 1980), entitled *Concepts and Models of Dolomitization*. The title used here is a deliberate hybrid of Machel & Mountjoy's (1986) title and that of the SEPM Special Publication, reflecting a reappraisal of dolomite research over the last 20–25 years. The sources underlying the arguments made below are hundreds of articles published mainly over the last 50 years, while some notable sources are much older, as well as studies by the author and his research group, including collaborating researchers.

Scanning the scientific literature published after World War II (WW II), one gets the impression that not much was learnt about dolomite and dolomitization for the first 130–150 years after its discovery. This impression, however, is incorrect. The first comprehensive review paper on dolomite and dolomitization was written by van Tuyl (1914) some 90 years ago. van Tuyl (1914, p. 257) began his long paper with the following sentences: 'Bischof has well said: "No rock has attracted greater attention than dolomite". The problem of the origin of this rock has long occupied the minds of geologists and many theories have been advanced for its formation'. van Tuyl (1914) then documented a large array of studies with knowledge, data, interpretations, theories, and hypotheses that had been published since the discovery of dolomite. van Tuyl's (1914) insights and those of the researchers he cited are positively astounding to the reader even today, considering what is being discussed at present in

the dolomite research community. For example, the first viable experimental studies and a whole series of dolomitization models, some of them remarkably similar to modern ones, date from well over 100 years ago. Most of van Tuyl's (1914) paper rings true even today, in the early part of the 21st century, and only very few aspects are outdated. This writer salutes our scientific forefathers for their diligent work and ingenuity, and encourages everyone to read van Tuyl's (1914) most enlightening contribution. Several aspects of his work and the sources cited therein are included below where appropriate. Most of the numerous sources published in the 1800s could not be obtained, however, and reference is made to them as 'cited in van Tuyl (1914)'.

Between van Tuyl (1914) and the end of World War II not much was added to the knowledge on dolomite and dolomitization, probably because dolomite was of no particular significance to civilization, and possibly because of the geopolitical developments during that period. In the 1920s the first hydrocarbon reservoirs in dolomitized carbonates were discovered, most notably the giant PJWDM oil field in the Permian of west Texas (e.g. Major *et al.* 1988) and the Turner Valley gas condensate field in the Mississippian of Alberta, western Canada (Gray 1970; Stenson 1992). Although these discoveries shifted petroleum exploration in the USA and Canada in new directions, throughout the 1920s–1940s most oil companies were primarily interested in finding oil in the easiest and cheapest way possible, for which one needed only a structure map and a drilling rig. Hence, the fact that some hydrocarbon reservoir rocks were dolomitized received little more than passing attention, and academically carbonate geology was focused on palaeontology and biostratigraphy. In those years, to quote James Lee Wilson, dolomite was considered 'a disease' (Lucia pers. comm. 2003). Reservoir work was focused on dolomite porosity and petrophysics.

All this changed in 1947, when the Leduc No. 1 drillhole in Alberta, western Canada, found oil in a dolomitized Devonian reef that had exceptionally high porosities and permeabilities. This discovery ushered in the modern oil and gas era in Canada, and essentially provided the foundation for Canada's petroleum industry (Gray 1970; Stenson 1992). In rapid succession many more oil pools were discovered in dolostone reservoir rocks, not only in Alberta but also in the United States. Coincidentally, it was found that many dolostone reservoirs had higher porosities and permeabilities, and thus had better reservoir properties, than limestone reservoirs. This finding, together with the advent of relatively modern investigative techniques (certain downhole logging tools, X-ray diffractometry, porosimetry, thin-section petrography, isotope geochemistry), led to a dramatic increase in the intensity of dolomite research in the 1950s. Suddenly dozens of case studies were published each year on every aspect of dolomitization imaginable. An SEPM symposium in 1964, subsequently published as SEPM Special Publication No. 13 (edited by Pray & Murray 1965), acted as a further important catalyst for dolomite research. In this volume, dolomitization was covered with three discoveries of penecontemporaneous dolomites (i.e. Illing *et al.*'s study in the Persian Gulf; Shinn *et al.*'s study on Andros Island; and Deffeyes *et al.*'s study on Bonaire). Major compilations of research papers on concepts and models of dolomitization followed as SEPM Special Publication No. 28 (Zenger *et al.* 1980), then SEPM Special Publication No. 43 (Shukla & Baker 1988), and the International Association of Sedimentologists (IAS) Special Publication No. 21 (Purser *et al.* 1994). These books attained a status similar to that of seminal textbooks of their times because they provided comprehensive state-of-the-art views of dolomite research, albeit in somewhat fragmented form, as many authors contributed to each volume. In addition, a few notable individual review articles were published by Morrow (1982*a*, *b*, 1999), Machel & Mountjoy (1986, 1987), Hardie (1987), Last (1990), Budd (1997), Mazzullo (2000), and Warren (2000), who succinctly summarized dolomite research or aspects thereof.

Judging from the literature it is clear that the last 50 years, and especially the last 20–25 years, have resulted in major advances of our understanding of dolomite and dolomitization. Nevertheless, several aspects of the so-called 'dolomite problem' remain unresolved and controversial, and these are one of the reasons for writing this reappraisal. Collectively, four aspects make-up the 'dolomite problem': (a) dolomites occur in many different sedimentary and/or diagenetic settings; (b) in many cases the available data permit more than one genetic interpretation; (c) dolomite is fairly rare in Holocene environments and sediments, yet very abundant in older rocks; and (d) well-ordered, stoichiometric dolomite has never been successfully grown inorganically in laboratory experiments at near-surface conditions of 20–30 °C and 1 atm pressure. The fourth aspect necessitates that geochemical parameters that are

needed for back-calculating the composition(s) of the dolomitizing fluid(s), such as the equilibrium oxygen isotope fractionation and trace-element partition coefficients, have to be extrapolated from high-temperature experiments. This renders them notoriously inaccurate and often leads to ambiguous genetic interpretations in studies of dolomitization. This paper addresses all of these aspects to one degree or another.

The most controversial aspects of dolomite research are the various models for dolomitization, and whether or not they can explain the origin of massive dolostones. Many researchers applied these models as soon as they had been published, in spite of the fact that many model(s) had not been sufficiently tested or verified. Thus, almost every new model became a bandwagon until it proved to be insufficient in some way. By the time of the bicentennial conference in honour of Déodat de Dolomieu in Ortisei 1991, a 'seawater model' had emerged that was prominently featured in IAS Special Publication No. 21 (Purser *et al.* 1994) that arose from the conference. At the same time, the gamut of dolomite models had been enlarged to include new variants of the compaction model, dolomitization by tectonically expelled fluids, and various forms of dolomitization by thermal convection, along with other more exotic alternatives. Some of these new(er) models, such as hydrothermal dolomitization (Machel & Lonnee 2002), have since attained bandwagon status, at least in certain parts of the world.

This paper summarizes the major advances and current controversies in dolomite research. Following Machel & Mountjoy (1986), it begins with a brief review of the chemical (thermodynamic and kinetic) conditions that favour dolomitization, including mass-balance considerations for the generation of massive dolostones. Classifications for dolomite textures and pore spaces in dolostones are presented, along with a series of photographs of representative textural types and development. These parts provide the basis for a discussion of porosity evolution during, and as a result of, dolomitization, one of the more controversial aspects of dolomitization, yet of great practical importance to the petroleum industry. The following section provides a brief overview of the geochemical methods used in dolomite studies, emphasizing the role of recrystallization, another controversial subject. A major part of this paper deals with the various dolomitization models, starting with a rigorous definition of the term 'model'. The final section briefly covers secular variations in dolomite abundance.

Basic facts and terminology

Ideal, ordered *dolomite* has a formula of $CaMg(CO_3)_2$ and consists of alternating layers of Ca^{2+}–CO_3^{2-}–Mg^{2+}–CO_3^{2-}–Ca^{2+}, etc., perpendicular to the crystallographic *c*-axis. Most natural dolomite has up to a few per cent Ca-surplus (and a corresponding Mg-deficit), as well as less than ideal ordering. *Protodolomite* has about 55–60% Ca, is poorly ordered, i.e. the alternating cation layer structure is poorly developed, and is common as a metastable precursor of well-ordered, nearly stoichiometric dolomite in both laboratory experiments and in nature (Graf & Goldsmith 1956; Gaines 1977). Good arguments have been made to abandon the term protodolomite (e.g. Land 1980) or to restrict it to laboratory products (Gidman 1978), yet the term is useful to describe metastable precursors of dolomite in nature. The term *dolostone*, introduced by Shrock (1948) and semantically equivalent to limestone, refers to a rock that consists largely (>75%) of the mineral dolomite. The term dolostone has been rejected (e.g. Vatan 1958), mainly because the term *dolomite* has historical priority for the rock (Dolomieu 1791 discussed the rock, not the mineral). However, *dolostone* has gained wide acceptance during the last 20 years, probably because of the confusion arising from the word dolomite referring to both a mineral and a rock. The term *dolomites* is used to refer to types of dolomite that vary in texture, composition, genesis, or a combination thereof.

Two types of *dolomite formation* are common: *dolomitization*, the replacement of $CaCO_3$ by $CaMg(CO_3)_2$; and *dolomite cementation* (*precipitation*), the precipitation of dolomite from aqueous solution as a cement in primary or secondary pore spaces. Contrary to common practice, the term dolomitization should not be applied to dolomite cementation. Similarly, the term dolomitization should not be applied to cases where a hot or hydrothermal fluid leads to recrystallization of pre-existing dolomites. Dolomites and dolostones that originate via replacement of $CaCO_3$ are called *replacement dolomites* or *secondary dolomites*, especially in the older literature. A third type, called *primary dolomites*, originates by direct precipitation from aqueous solution to form sedimentary deposits.

Genetically, all natural dolomites can be placed in two major families, *penecontemporaneous* dolomites and *post-depositional*

dolomites (*sensu* Budd 1997). Penecontemporaneous dolomites may also be called *syndepositional* dolomites. They form while carbonate sediment or limestone resides in the original environment of deposition as a result of the geochemical conditions that are 'normal' for that environment. Such dolomites are also called *primary* or *early diagenetic*, although these terms are not strictly synonymous with 'penecontemporaneous'. For example, dolomites that formed syndepositionally may well be secondary and formed by replacement of $CaCO_3$. Also, dolomite may form after hundreds of thousands or even millions of years in limestones that have resided in their original environment of deposition throughout this time or that returned to this environment after some burial or exposure. In the latter case the term 'early diagenetic' is not justified. In any event, true penecontemporaneous dolomites appear to be relatively rare, most are of Holocene age, and are restricted to certain evaporitic lagoonal and/or lacustrine settings. It is possible, however, that such dolomites are more common in the geological record than is presently known, but their presence is hard to prove because of diagenetic overprinting.

Post-depositional dolomites may also be called *post-sedimentary*. They form after carbonate sediment has been deposited and removed from the active zone of sedimentation. This may happen through progradation of the sedimentary surface, burial and subsidence, uplift and emergence, eustatic sea-level fluctuations, or any combination of these. Such dolomites and dolostones are commonly called *late diagenetic*, although this term is not synonymous with post-depositional. Carbonate sediment may be rapidly removed from its site of deposition, i.e. within a few hundreds to thousands of years, and dolomite formed during this time would be early diagenetic compared with the truly 'late diagenetic' phases that formed millions to tens of millions of years later. Almost all examples of massive, regionally extensive dolostones are post-depositional, and they are the main topic of this paper.

One aspect that transcends the above genetic grouping is that of hydrology. Whether syndepositional or post-depositional, the formation of large amounts of dolomite requires advection, i.e. fluid flow, because of chemical mass-balance constraints (discussed below). On the other hand, small amounts of dolomite can be formed without advection. In such cases the Mg needed for dolomite formation is locally derived and redistributed, or it is supplied via (slow) diffusion. Examples include dolomite formed from Mg contained in (high-) Mg calcite, adsorbed to the surfaces of minerals, organic substances or biogenic silica, or contained in older primary or secondary dolomites (e.g. Lyons *et al.* 1984; Baker & Burns 1985). Dolomites formed in these ways are mentioned only briefly or in connection with other, volumetrically much more important, types.

Thermodynamic and kinetic constraints

The chemical conditions of dolomite formation have been under investigation ever since the rock and the mineral were defined. van Tuyl (1914, p. 306) elegantly summarized the first 100 years of experimental and circumstantial evidence, and found that 'experiments have failed to indicate the conditions under which dolomite can be precipitated directly at ordinary temperatures and pressures', a statement that is still (almost) true today. However, even back in the 1800s, several researchers had managed to grow dolomite at elevated temperatures, either directly from solution or as replacements of calcium carbonate. Similar experiments were carried out by others, most notably after World War II.

As a result, the thermodynamic conditions of dolomite formation have been known quite well, at least since the 1970s (see summary in Carpenter 1980). The only notable new experimental studies in this context are those of Usdowski (1994), Land (1998), and Arvidson & MacKenzie (1999). Usdowski (1994) ran his experiments for up to 7 years, and Land (1998) ran his for 32 years, the longest run laboratory experiments to form dolomite to date. Land did not manage to grow dolomite in his particular set-up (dilute solution, 25 °C, 1000-fold supersaturation with respect to dolomite), whereas both Usdowski's and Arvidson & MacKenzie's studies essentially confirmed the results of earlier experimental studies. However, the kinetics, i.e. catalysts and inhibitors of dolomite formation, continue to be a source of controversy.

According to present knowledge, dolomite formation is thought to be favoured chemically, that is thermodynamically and/or kinetically, under the following conditions: low Ca^{2+}/Mg^{2+}-ratios; low Ca^{2+}/CO_3^{2-} ratios (i.e. high carbonate alkalinity); high temperatures; salinities substantially lower or higher than that of seawater; and where fluids suddenly release CO_2 (Carpenter 1980; Morrow 1982*a*; Machel & Mountjoy 1986; Leach *et al.* 1991; Usdowski 1994; Arvidson & MacKenzie 1999) (Figs 1 and 2). These constraints translate into four

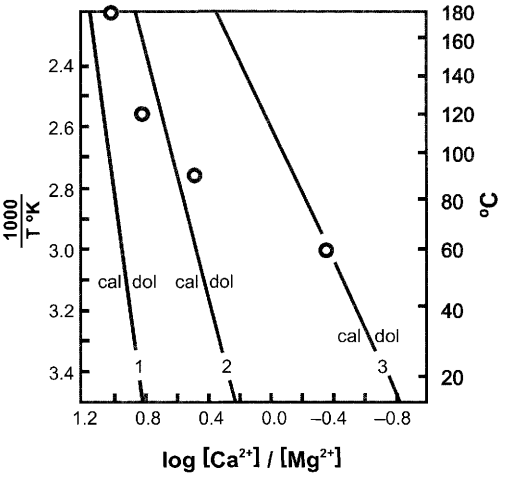

Fig. 1. Bivariate thermodynamic stability diagram for the system calcite–dolomite–water. Square brackets denote activities. Lines are calculated from experimental data: line 1, calcite + ideal, fully ordered dolomite; line 2, calcite + ordered dolomite with slight Ca-surplus; line 3, calcite + fully disordered protodolomite. The four open circles denote the experimental results of Usdowski (1994), whose up to 7 year-long runs represent the lowest-temperature experimental dolomite formation performed to date. Usdowski's (1994) data for 90, 120 and 180 °C plot close to line 2, but his data for 60 °C plot on line 1, which probably reflects the fact that protodolomite rather than dolomite formed at 60 °C. Data from natural aquifers (not shown) cluster close to line 2, which can be considered representative of most natural dolomite. This figure is modified from Carpenter (1980).

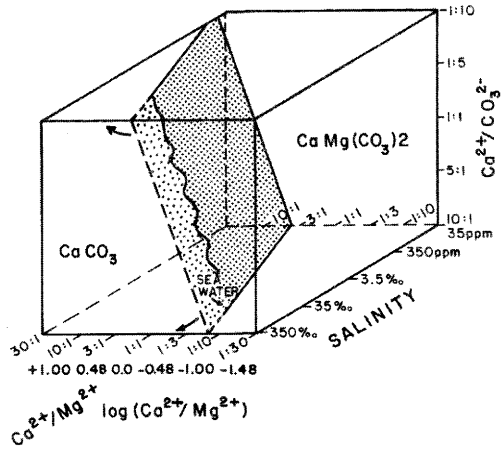

Fig. 2. Trivariate kinetic stability diagram for the system calcite–dolomite–water. The ionic ratios are molar ratios. Seawater plots just in the calcite field. The stippled field boundary is bent towards higher Ca/Mg ratios at salinities greater than 35‰. The figure is reproduced with permission from Machel & Mountjoy (1986).

common conditions to form dolostones in natural settings.

(1) *settings with a sufficient supply of Mg^{2+} and CO_3^{2-}*; this condition favours marine and burial-diagenetic settings with pore fluids of marine parentage because seawater is the only common Mg-rich natural fluid in such settings;
(2) *settings with a long-lasting and efficient delivery system for Mg^{2+} and/or CO_3^{2-}* (and also exporting Ca^{2+} in the case of calcite replacement); this favours settings with an active and long-lasting hydrologic drive;
(3) *carbonate depositional settings* or limestones that can be replaced, i.e. abundant calcium carbonate must be available to be replaced;
(4) *from hydrothermal solutions* that ascend rapidly through fault systems.

Considering that the above chemical constraints allow dolomite formation in almost the entire range of surface and subsurface diagenetic settings, the question arises as to why there are so many undolomitized limestones. The likely conditions for the lack of dolomitization are:

(5) *ion pair formation* (especially hydration), inactivating much of the Mg^{2+} and CO_3^{2-} in solution;
(6) *insufficient flow* because of the lack of a persistent hydraulic head, too small a hydrologic head, or insufficient diffusion, resulting in insufficient magnesium and/or carbonate ion supply;
(7) *the limestones are cemented and not permeable enough*, inhibiting or prohibiting the throughput of Mg-rich waters;
(8) *the diagenetic fluids are incapable of forming dolomite because of kinetic inhibition*, e.g. because the environment is too cold; most kinetic inhibitors of dolomite nucleation and growth are rather potent at temperatures below about 50 °C, and the Ca^{2+}/Mg^{2+} ratio of many relatively cold diagenetic fluids is not low enough for dolomitization;
(9) *the conditions conducive to dolomite formation do not last long enough to overcome the induction period* (discussed below).

The last point leads to the kinetic factors, many of which are relatively poorly understood. Three aspects deserve special mention. First, almost all researchers agree that most kinetic inhibitors that lower the nucleation rate and growth rate of dolomite are especially potent at temperatures below about 50 °C (see summaries in Morrow 1982*a*; Machel & Mountjoy 1986). Hence, dolomite formation is easier at higher temperatures. Secondly, it is also generally acknowledged that dolomite forms via metastable precursors, but the significance of this phenomenon for studies of massive dolomitization is not clear and much debated. Thirdly, the role of sulphate in dolomitization is highly controversial.

Regarding the second point, it has been known for a long time that quartz, metal sulphides and other minerals do not form directly from aqueous solution. Rather, the first phases to form during the overall replacement process are metastable phases with a similar, but not identical, composition and/or ordering to the final replacement product, such as opal-A or mackinawite that transform (often in multiple steps – a process commonly referred to as Ostwald's step rule) to the actual and final replacement products of quartz and pyrite, respectively (e.g. Morse & Casey 1988). It only stands to reason that dolomite could also form via some metastable precursor(s). This was elegantly demonstrated in a series of hydrothermal experiments by Sibley (1990), Nordeng & Sibley (1994) and Sibley *et al.* (1994) (see also Gaines 1974; Katz & Matthews 1977), who showed that dolomite forms after an induction period, during which no detectable products form, via so-called VHMC (very-high-Mg calcite with about 36 mole% Mg), then VHMC plus non-stoichiometric dolomite, then stoichiometric dolomite. The induction period can be very long and is one, and perhaps the best, explanation for the apparent lack of dolomite in recent and geologically relatively young marine carbonate environments (Nordeng & Sibley 2003). The transformations from one metastable phase to another are a form of recrystallization, and they take place very fast, i.e. within hours–days in hydrothermal experiments. By analogy, metastable precursors to dolomite (often referred to as protodolomite) are common in a variety of Holocene sediments but nearly absent in older settings. It appears, therefore, that Nature 'performs' the various steps of recrystallization from the VHMC nucleus to dolomite very fast, i.e. commonly within a few hundreds to a few thousands of years in typical low-temperature diagenetic settings, and obviously even faster in deep-burial and hydrothermal settings. Hence, these transitions are pretty much irrelevant for the investigation of ancient (older Cenozoic, Mesozoic and Palaeozoic) dolomites, except for some exceptional cases where the fluid chemistry has changed dramatically within the short time frame of these transitions. This topic is further discussed in the section on recrystallization below.

The role of sulphate as a potential kinetic inhibitor to dolomitization deserves special mention and is much debated. Following the hydrothermal–experimental study by Baker & Kastner (1981), which suggested that dissolved sulphate inhibits dolomite formation and that lowered sulphate concentrations can enhance the rate of dolomite formation, a number of studies have been published that proposed a positive correlation between (bacterial) sulphate reduction and dolomitization, or they claimed that sulphate reduction is necessary for dolomite formation. However, Morrow & Rickets (1986) and Morrow & Abercrombie (1994) have shown through further experiments and geochemical modelling that the amount of dissolved sulphate has no influence on the rate of dolomitization under relatively low-temperature diagenetic (<80 °C) conditions. On the other hand, they also showed that dissolved sulphate does appear to reduce dolomite formation at relatively high-temperature diagenetic conditions (*c.* 100–200 °C), but only indirectly, because the degree of calcite undersaturation correlates inversely with the sulphate concentration. This leads to higher calcite dissolution rates, and these enhance the rate of dolomite formation when the sulphate concentration is reduced. But even this effect is probably negligible in most natural environments (Morrow & Abercrombie 1994).

Brady *et al.* (1996) went further and suggested, on the basis of field relationships and their own experimental data, that one path for dolomite growth is through the adsorption of Mg-sulphate complexes, which at the very least provides a mechanistic explanation for dolomite formation in sulphate-rich fluids. Thus, where this path is taken, sulphate actually promotes dolomitization. In Brady *et al.*'s (1996, p. 730) words: 'We argue that massive dolostone sequences formed from evaporatively modified seawater due, in part, to the attendant high sulfate levels', and '. . . in a kinetic sense, sulfate does not hinder dolomite growth in evaporitic environments but, rather, accelerates it'. For sulphate-poor solutions, Brady *et al.*'s (1996) results support those of Baker & Kastner (1981).

These considerations suggest that the role of sulphate as an inhibitor for dolomitization has been significantly overrated. On the one hand, there is little doubt that sulphate reduction can significantly enhance or even trigger dolomitization in pelagic environments and in at least some lacustrine settings that are relatively rich in organic matter, as suggested by the formation of dolomite with negative (organogenic) carbon isotope ratios in such settings (e.g. Mazzullo 2000). However, the generalization that low sulphate concentrations and/or bacterial sulphate reduction always enhance or even trigger dolomite formation is unjustified. This notion is supported by three direct or circumstantial lines of evidence: (a) gypsum and anhydrite appear to be common by-products of dolomitization from seawater (discussed below); (b) ancient examples show that dolomitization can happen in or from mesohaline–penesaline seawater, i.e. seawater evaporated between normal salinity and gypsum saturation, and therefore with considerable amounts of dissolved sulphate (e.g. Qing *et al.* 2001; Melim & Scholle 2002); and (c) there are many modern evaporitic environments rich in dissolved sulphate that form dolomite (Friedman 1980; Brady *et al.* 1996).

Mass-balance constraints

Within the chemical constraints outlined in the previous section, the amount of dolomite that can be formed in a given diagenetic setting depends on the stoichiometry of the reaction, the temperature, and the fluid composition (Morrow 1982*a*; Land 1985; Machel & Mountjoy 1986; Machel *et al.* 1996*b*). Dolomitization can be represented by two equations:

$$2CaCO_3\,(s) + Mg^{2+}(aq) \rightarrow CaMg(CO_3)_2\,(s) + Ca^{2+}(aq) \qquad \text{(reaction 1)}$$

(where s = solid and aq = aqueous) or by

$$CaCO_3\,(s) + Mg^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaMg(CO_3)_2\,(s). \qquad \text{(reaction 2)}$$

Reactions 1 and 2 are end members of a range of possible reaction stoichiometries, *i.e.*

$$(2-x)\,CaCO_3\,(s) + Mg^{2+}(aq) + xCO_3^{2-}(aq) \rightarrow CaMg(CO_3)_2\,(s) + (1-x)\,Ca^{2+}(aq) \qquad \text{(reaction 3)}$$

(Lippman 1973; Morrow 1982*a*; Machel & Mountjoy 1986 – these authors discussed several other mass-balance reactions for dolomitization). Reaction 3 can be used to represent dolomitization in general, as it 'contains' reactions 1 and 2. For $x = 0$, reaction 3 becomes reaction 1, and for $x = 1$ reaction 3 becomes reaction 2. Magnesium has to be imported to the reaction site and calcium has to be exported from it in the case of reaction 1, whereas there is no export of calcium in reaction 2. Intermediate cases of reaction stoichiometry are represented by values of x between 0 and 1.

Dolomite cementation is most simplistically represented by:

$$Ca^{2+}(aq) + Mg^{2+}(aq) + 2CO_3^{2-}(aq) \rightarrow CaMg(CO_3)_2\,(s) \qquad \text{(reaction 4)}$$

If dolomitization proceeds via reaction 1, and if the dolomitizing solution is average (normal) seawater, about 650 m^3 of solution are needed to dolomitize 1 m^3 of limestone with 40% initial porosity at 25 °C (Land 1985). However, dolomitization may not take place with 100% efficiency, and some Mg in excess of that required for saturation is carried away by the dolomitizing solution. In such cases, larger water/rock ratios are needed for complete dolomitization. If seawater is diluted to 10% of its original concentration, as is the case in a typical seawater–freshwater mixing zone, 10 times as much water is needed. By contrast, only about 30 m^3 of halite-saturated brine are needed per m^3 of limestone at 100% dolomitization efficiency. The role of increasing temperature in the underlying thermodynamic calculations is to reduce the amount of magnesium necessary for dolomitization because the equilibrium constant (and hence the equilibrium Ca/Mg-ratio) is temperature-dependent (Fig. 1). For example, at 50 °C only about 450 m^3 of seawater are needed for complete dolomitization of 1 m^3 of limestone with 40% initial porosity at 100% efficiency. The amounts of dilute and hypersaline waters change accordingly.

These calculations have two major implications. First, large water/rock ratios are required for complete dolomitization, whereby the more dilute the solution, the larger the water/rock ratio. This necessitates advection for extensive and pervasive dolomitization, and this is why all models for the genesis of massive dolostones are essentially hydrogeological models. The exceptions are natural environments where carbonate muds or limestones are dolomitized via diffusion of magnesium from seawater rather than by advection. Secondly, variable reaction stoichiometries result in variable porosity development during dolomite formation (discussed below).

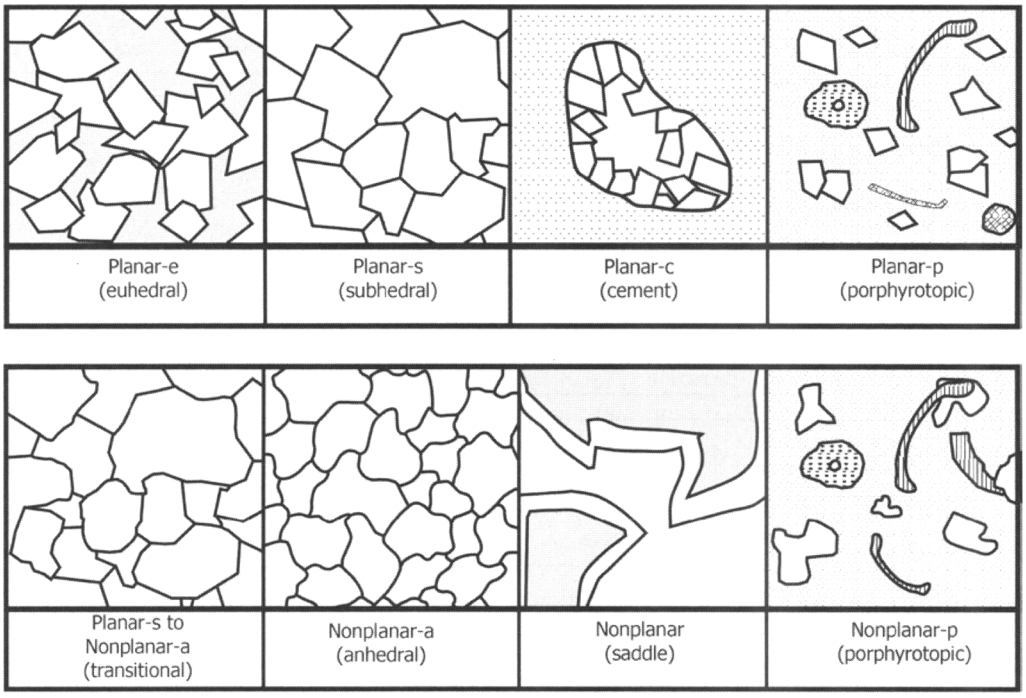

Fig. 3. Dolomite textural classification combined from Gregg & Sibley (1984) and Sibley & Gregg (1997), supplemented by a 'transitional' form. The figure is reproduced with permission from Wright (2001).

Textures

Rock classification

The most widely used classification of dolomite/dolostone textures is that proposed by Sibley & Gregg (1987), based on Gregg & Sibley (1984) (Fig. 3). This classification is popular because it is simple and largely descriptive. However, it carries some genetic implications, and it is restricted to the microscopic scale (in this aspect it differs from the classification(s) for porosity – see below). Crystal size distributions are classified as 'unimodal' or 'polymodal', whereas crystal shapes are classified as 'planar-e' (euhedral), 'planar-s' (subhedral), and 'nonplanar-a' (anhedral). Using this semantic scheme, almost all dolomite texture types can be named, e.g. planar-c (cement), planar-p and nonplanar-p (both porphyrotopic). Saddle dolomite, with its distinctive warped crystal faces, is categorized as nonplanar or nonplanar-c (when it is a cement). Wright (2001) defined one additional texture type, i.e. planar-s to nonplanar-a (transitional), in which planar and nonplanar crystals occur side by side (Fig. 3). A complete textural description includes recognizable allochems or biochems, matrix and void fillings. Particles and cements may be unreplaced, partially replaced or completely replaced. Replacement may be mimetic or non-mimetic, depending mainly on crystal size (Bullen & Sibley 1984; Sibley 2003), and qualifying terms such as 'unimodal, non-mimetic planar-s dolomite' can be added to a rock description.

Many authors use the time-honoured terms euhedral, subhedral and anhedral, as well as the equivalent terms idiomorphic, hypidiomorphic and xenomorphic. While these terms are accurate in principle for characterizing dolomite crystals that display free growth surfaces, they are inappropriate for describing interlocking crystals in thin sections. This is because the identification of crystal–crystal boundaries as growth faces requires use of the universal stage (Sibley 2003).

Pore classification(s)

Pores in dolostones are commonly addressed using the pore classification for limestones proposed by Choquette & Pray (1970). This classification is texturally descriptive, i.e. it discriminates between pore types (such as mouldic, vuggy, shelter, etc.), while it is also

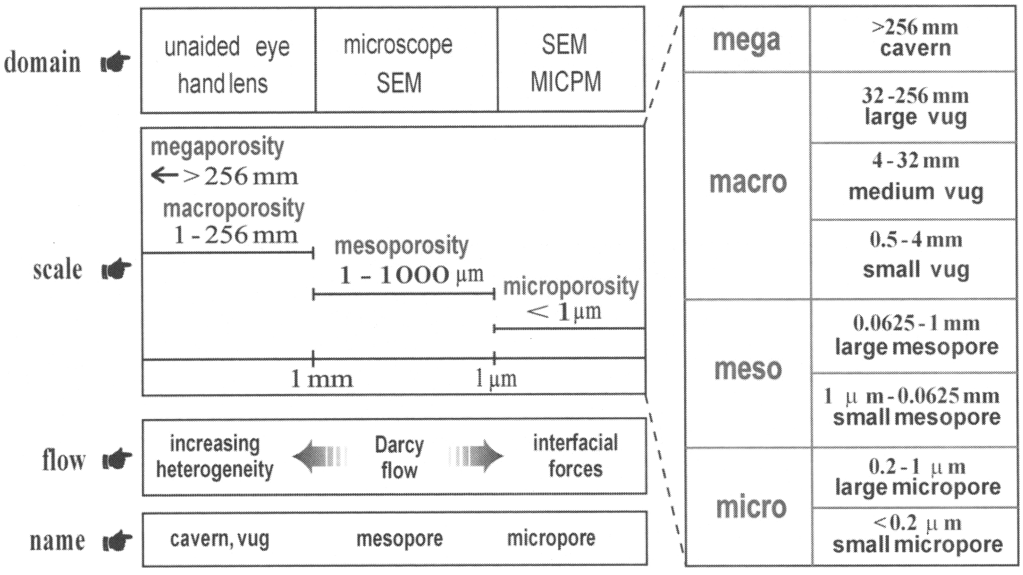

Fig. 4. Pore size classification for carbonates. Measurements under 'scale' refer to pore diameters. The figure is reproduced with permission from Luo & Machel (1995).

genetic (primary v. secondary), yet it is independent of pore size. The petroleum industry, however, is also, and often more so, interested in pore sizes and overall porosity. For this reason, Luo & Machel (1995) established a carbonate pore size classification (Fig. 4) that is applicable to both limestones and dolostones. This classification is based on the textural and petrophysical classifications of Archie (1952), Choquette & Pray (1970), and Pittman (1979, 1992), as well as Luo & Machel's (1995) investigations of dolostone reservoir rocks. The categories contained in this classification range in size/magnitude from the very smallest to the very largest, i.e. from MICPM (mercury injection capillary measurements) and SEM (scanning electron microscopy) to karst caverns, respectively.

At about the same time as the classification scheme by Luo & Machel (1995) appeared in print, Lucia (1995) published his 'geological and petrophysical classification of carbonate interparticle pore space', which resembles Luo & Machel's classification in several aspects. At the time of writing this article, it remains to be seen whether one or the other of these classifications will take hold.

It is important to remember that both Luo & Machel's (1995) and Lucia's (1995) classifications are essentially of pore types, not of porosity, which is the sum of all pore spaces relative to the total rock volume. Both classification schemes contain elements of permeability, which is commonly positively correlated with porosity. These aspects are discussed below.

Textural evolution

The textures and hydrocarbon reservoir characteristics of dolostones are highly variable. On the microscopic scale, unimodal size distribution generally results from a single nucleation event and/or a unimodal primary (predolomite) size distribution of the substrate. Polymodal size distributions indicate multiple nucleation events, differential nucleation on an originally polymodal substrate, or both. Planar crystal boundaries tend to develop up to the so-called 'critical roughening temperature', which appears to be about 50–60 °C for dolomites (Gregg & Sibley 1983, 1984), whereas nonplanar boundaries tend to develop at higher temperatures and/or high degrees of supersaturation. It is not clear, however, whether a critical roughening temperature really exists for dolomites that are replacive (Braithwaite 1991). On a macroscopic scale, there is a distinctive difference in the textures resulting from 'low-temperature' v. 'high-temperature' dolomitization of limestones, i.e. fabric-retentive v. fabric-obliterative. Within this framework, observations from many dolostone occurrences show that dolomitization often proceeds in a certain sequence of steps that correspond to

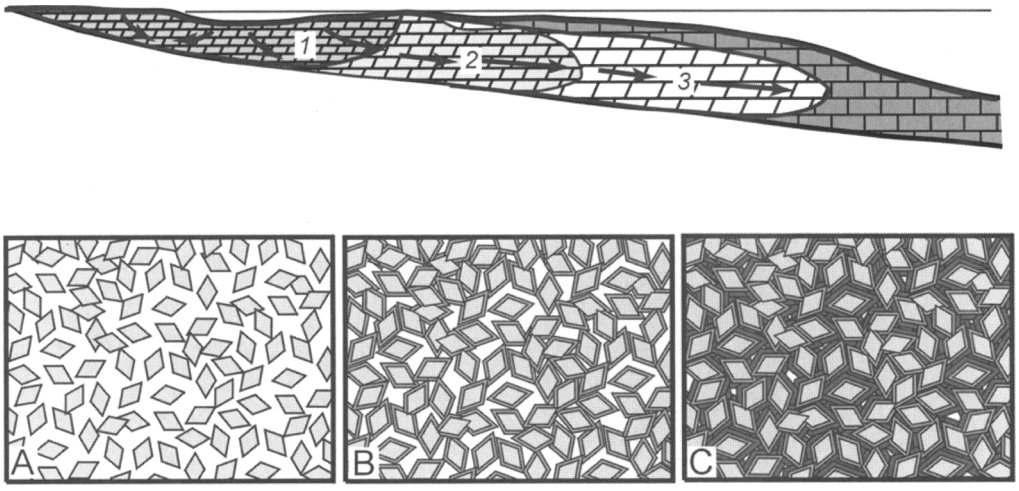

Fig. 5. Schematic model of reflux dolomitization where the dolomitizing brines form on tidal flats and/or in an evaporative lagoon. The textural evolution shown in the bottom row is representative for all situations of matrix-selective dolomitization, not just by evaporative reflux. Numbers denote areas/zones of dolomitization, whereby the locus of dolomitization moves progressively basinward with time. Dolomitization starts in zone 1. Once the dolomitizing fluids have exhausted their Mg, they keep flowing basinward without causing further dolomitization. New increments of the dolomitizing fluids through zone 1 will lead to dolomite cementation, i.e. overgrowths around the earlier formed dolomite crystals, as there is no more calcite to replace, and excess Mg will form new dolomite downflow. Successive time steps in zone 1 are shown in (**A**)–(**C**). Initial replacive dolomitization would form a loose meshwork of dolomite crystals, but porosity would decrease over time via progressive dolomite cementation. This diagram is modified from Saller & Henderson (2001).

specific textural types on the macroscopic scale. Within limits, these steps also reflect particular types of dolomitizing fluids, especially seawater and its derivatives, or meteoric water incursion.

Matrix-selective dolomitization. Most commonly, dolomitization begins as a selective replacement of the matrix, probably as the result of three interacting and reinforcing factors: (a) the matrix contains or consists of thermodynamically metastable carbonates (aragonite and/or high-Mg-calcite), which have higher solubilities than low-Mg-calcite; (b) the matrix has much smaller grain sizes and, thus, a higher surface area per grain than the larger biochems, allochems or cement crystals formed prior to dolomitization; and (c) the matrix has a higher permeability than the larger, more massive particles or cements. The nuclei that are commonly scattered in the matrix become more abundant and grow to form microscopic crystals over time. Soon they form a loose meshwork of crystals that ultimately coalesce to an interconnected mosaic (Fig. 5, bottom row; the textural evolution shown is applicable to replacement dolomitization in general, although this figure was designed to represent replacement dolomitization by evaporative reflux). If the fluid composition does not change significantly over the course of the dolomitization process, the crystals will be unzoned on the scale of thin-section microscopy. The zoning shown in Figure 5B is included to illustrate successive overgrowths on the originally smaller nuclei, and does not mark a change in composition. If dolomitization begins or proceeds below the critical roughening temperature, these crystals tend to be planar-e and/or planar-s.

In the early stages of such matrix-selective dolomitization, large and relatively much less soluble (more stable) biochems and allochems remain unreplaced. This type of texture is shown in Figure 6A. In this particular example, a Devonian reef rock from western Canada, the outer walls and even the most delicate intraskeletal platelets of fasciculate corals are preserved as calcite, despite the fact that these corals are completely uncemented. More commonly, the internal pores of biochems are partially or completely cemented prior to dolomitization, rendering them almost impermeable to the dolomitizing fluids. The corals shown in Figure 6A survived initial dolomitization because of their mineralogical stability

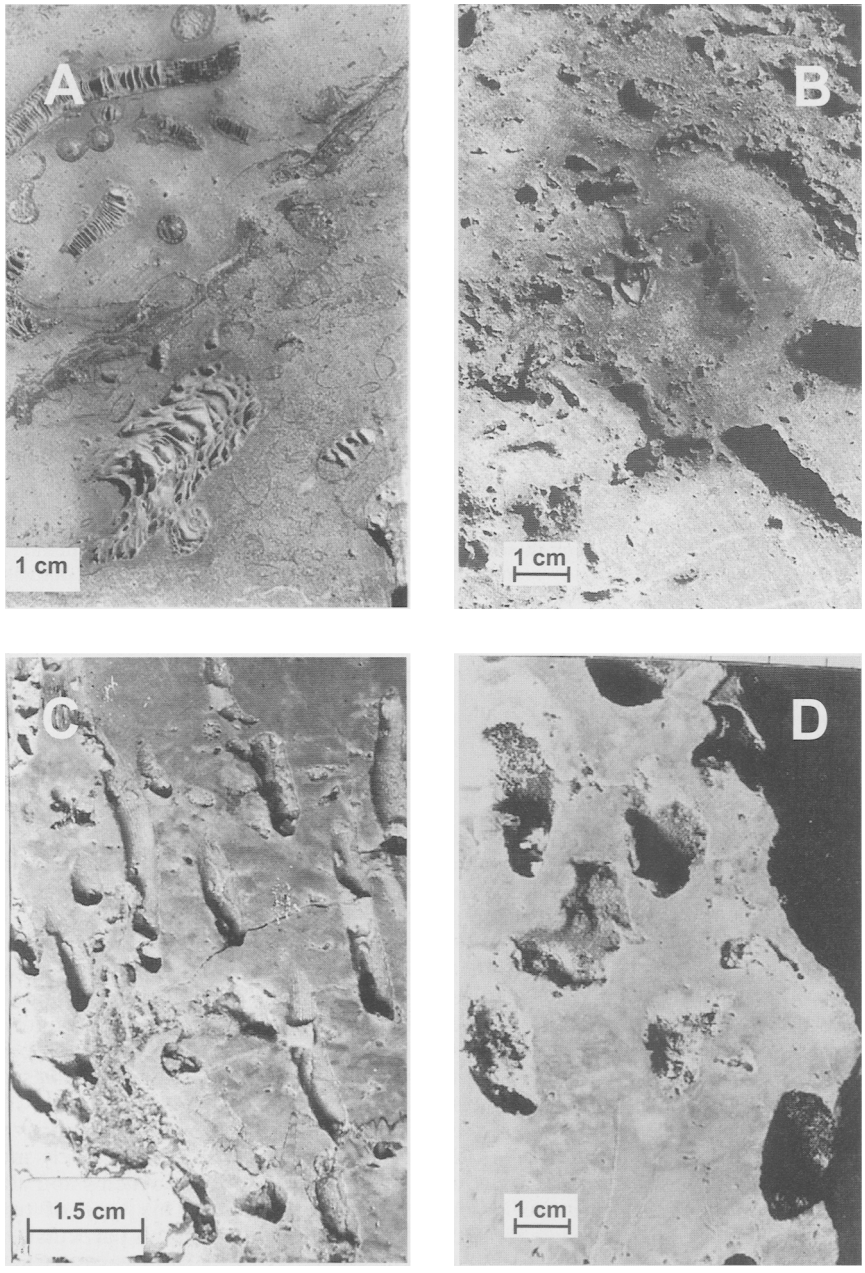

Fig. 6. Successive steps during matrix-selective dolomitization with subsequent dissolution of unreplaced calcite. All samples are from the Upper Devonian Nisku Formation, Alberta, Canada. (**A**) Uncemented *Smithiphyllum* and *Phacelophyllum* with calcite preservation of the delicate chamber walls (trabeculae) in partially dolomitized matrix. (**B**) Vuggy dolostone that resulted from (macro-) dissolution of unreplaced calcite matrix and fossils similar to the sample shown in (A). Connection of pores is intercrystalline-pervasive. (**C**) Coral-mouldic porosity in tight matrix dolomite. The moulds originated from dissolution of corals such as the slender *Smithiphyllum* shown in (A). Connection of macropores is mainly via hairline fractures (centre). (**D**) Coral-mouldic porosity in tight matrix dolomite. The moulds originated from dissolution of corals such as the large *Phacelophyllum* shown in (A). Connection of macropores is mainly via fractures (top right margin of sample).

(low-Mg calcite), not because of low permeability.

In this context the resistance to dissolution of metastable calcium carbonates is governed by an interplay of three factors: permeability and an interplay of microstructure and thermodynamic solubility (Walter 1985). Hence, one should expect certain biochems or allochems to be more susceptible to dissolution and dolomitization than others.

Dolomite cementation ('overdolomitization'). The replacement of lime mud or limestone by dolomite may generate up to 13% interparticle or intercrystal porosity as a function of reaction stoichiometry (discussed below). If so, this newly formed porosity may not survive the continued influx of the dolomitizing solution, which, being supersaturated with respect to dolomite, will tend to form dolomite cement as overgrowths on the earlier formed dolomite crystals, as shown in Figure 5 for reflux dolomitization. Lucia (2002, 2004) calls this process 'overdolomitization'. As pointed out by Saller & Henderson (2001) and Lucia (2002, 2004), this process could severely reduce the porosity and permeability in dolostones, at least in situations of evaporative reflux where the refluxing brines tend to have very high degrees of supersaturation, and where fluxes tend to be high.

Vugs and moulds. Vugs and moulds, the two most common forms of secondary macroporosity, develop without or during dolomitization. The best-known example of the first possibility is meteoric dissolution of biochems or allochems consisting of relatively unstable calcium carbonate, such as aragonite or high-Mg calcite fossils, or grains with a very high surface area (e.g. Tucker & Wright 1990). If a limestone with vugs or moulds is dolomitized, these secondary pores tend to remain open during the dolomitization process.

The advanced stages of dolomitization are characterized by two possibilities: dolomitization of unreplaced biochems and allochems; or their dissolution. The first alternative commonly results in mimetic replacement to some variable degree, depending on dolomite crystal size. Vugs and moulds result from dissolution during advanced stages of dolomitization that appears to be an integral part of the replacement process. This is indicated by numerous cases of limestones that did not contain secondary macroporosity before penetration by dolomitizing fluids, yet where vugs and moulds appeared once the percentage of dolomite replacement exceeded about 70–80 vol%. Examples are shown in Figure 6B–D. Where the matrix was not entirely dolomitized, dissolution removed both the remnants of unreplaced matrix and larger unreplaced particles, generating highly permeable dolostones with vuggy porosity (Fig. 6B). Where matrix dolomitization had gone to completion, only the larger allochems or biochems are removed, as they are the only undolomitized particles left, leaving moulds in a fairly tight matrix. This is shown in Figure 6C & D, with moulds of elongate and more equant corals, such as those in Figure 6A, connected only via fractures in a relatively tight matrix. By comparison, the rock shown in Figure 6B is a much better reservoir rock than those in Figure 6C & D, mainly because the larger voids are connected through pervasively distributed intercrystal pores. The development of mouldic porosity can be spatially highly restricted. This was recognized long ago in various Palaeozoic sequences of the United Stated (e.g. Landes 1946 and references therein), then also in much younger carbonates, including the sub-recent (less than 2200 years old) reflux dolomites from Bonaire, where shells and pellets are dissolved in dolomite crusts but not in the adjacent limestone layers (Deffeyes *et al.* 1965).

Vuggy dolostones are commonly interpreted to result from dissolution that took place in a completely matrix-dolomitized rock, whereby dissolution started in the unreplaced larger allochems and biochems and then proceeded beyond the margins of the moulds into the already dolomitized matrix. This interpretation, however, not only requires that the solution had stopped 'making' dolomite, but also two unlikely circumstances, namely that the solution had attained undersaturation with respect to dolomite, and that the principle of Occam's Razor was violated. The thermodynamically and kinetically much more likely, and thus more plausible, explanation of vuggy dolostones is that the matrix was incompletely replaced before the vugs formed.

The cause of the development of vuggy and mouldic porosity is probably an interplay of fluid supply, composition, and reaction kinetics. One possibility is that the dolomitizing flow system continues to supply fluid, yet the Mg available for dolomitization (in excess of saturation) is used up while undersaturation with respect to calcium carbonate is maintained or acquired, as suggested by geochemical modelling (Sun 1992; Morrow 2001). Another possibility is that the fluid, while approaching dolomite–calcite–water three-phase equilibrium through continued Mg-loss and/or Ca-gain, passes a kinetic threshold below which

dolomite formation is severely limited or inhibited while calcite dissolution remains relatively rapid. Thermodynamic and kinetic experiments and modelling are needed to evaluate these alternatives.

Calcium sulphate. The next step in textural evolution during dolomitization is the emplacement of calcium sulphate, either as gypsum or as anhydrite. This step is typical for, and largely restricted to, cases where the dolomitizing solution is seawater or a derivative of seawater (evaporated or slightly changed by water–rock interaction). This reflects the fact that seawater and its derivatives are relatively rich in dissolved sulphate and, as Butler (1970) and others have pointed out, calcium sulphate is a common by-product of dolomitization by such fluids. Curiously, most geochemical modelling of dolomitization has ignored the formation of calcium sulphate during seawater dolomitization, with the notable exceptions of Wilson *et al.* (2001) and Whitaker *et al.* (2002, 2004). The textural development and attendant geochemical (isotopic and trace-element) characteristics of dolomitization with concomitant calcium sulphate formation are extensively discussed in Machel (1985, 1986) yet largely overlooked.

Reefs and platform carbonates of the Upper Devonian Nisku Formation in the West Pembina area of western Canada, presently at depths of about 2600–4600 m, were dolomitized by chemically slightly modified seawater (Anderson 1985; Machel 1985; Machel & Anderson 1989). Anhydrite is absent in undolomitized and in little to moderately (up to about 70 vol%) dolomitized parts of the Nisku Formation in the up-dip part of the reef trend. Down-dip, however, where the Nisku is largely to completely dolomitized, anhydrite is abundant and comprises up to about 20 vol% over any 20–40 m-core interval.

Three questions arise. (1) Did the anhydrite replace calcite or dolomite? (2) In the case of calcite replacement, did anhydrite form before or after the dolomite? Lastly, (3) did the anhydrite form as anhydrite or originally as gypsum? All of these questions can be answered using petrography.

In hand specimen, the most conspicuous features are that most of the anhydrite (more than 90 vol%) appears both as a cement in mouldic pores and also as a partial replacement of the matrix dolomite (Fig. 7). It is clear that these textures did not originate from calcium sulphate replacing calcite because of the combined occurrence of the following features: (a) the moulds originated from the removal of calcite (Fig. 6C & D); (b) the dissimilarity in the appearance of vuggy pores and the replacive anhydrite (compare Figs 6B and 7C: the anhydrite forms much more massive areas/volumes than the calcite that had survived dolomitization and that is now represented by the vugs); (c) the common occurrence of 'islands' of dolomite floating in anhydrite, both on the macroscopic (Fig. 7C) and on the microscopic scale (Fig. 7B); (d) marginal, partial replacement of individual dolomite crystals; and (e) the complete absence of calcite remnants (small, 'undigested' calcite islands or crystals are common when anhydrite replaces calcite).

The microscopic textures further reveal whether the original calcium sulphate mineral was gypsum or anhydrite. Specifically: (a) the textures shown in Figure 7 are absent from primary anhydrites, yet (b) similar textures occur in salt dome cap rocks that have undergone repeated gypsum–anhydrite transformations (Goldman 1952); (c) the presence of large porphyroblastic/porphyrotopic anhydrite crystals floating in a relatively fine-crystalline, partially felted, anhydrite matrix that appears to marginally corrode some of the large crystals (Fig. 7D & E); (d) large porphyroblasts impinge upon one another, generating stress twins and crystal breakage (Fig. 7E). These features indicate that the calcium sulphate was originally emplaced as gypsum that dewatered to anhydrite during further burial, thereby generating the 'corroblastic' or 'corrotopic' textures shown in Figure 7D & E. Apparently the porphyroblasts grew floating in a dewatering gypsum mush until they ran out of room, at which point the remainder of the gypsum mush converted to the finer-crystalline, partially felted anhydrite matrix. Machel (1985, 1986) called this type of anhydrite 'corroblastic' or 'corrotopic' because, in thin section, the most striking features are the corroded porphyroblasts/porphyrotopes.

These observations suggest that anhydritization took place during progressive burial in an interval that overlaps with the gypsum–anhydrite transformation depth. This depth depends on temperature, pressure, and the composition of the fluid (Cruft & Chao 1970), and is normally of the order of 600–800 m, but somewhat greater in overpressured regions. This depth range coincides with the later stages of matrix dolomitization in the Nisku Formation, the total range of which is interpreted to be about 300–1000 m (Machel & Anderson 1989). There also are minor amounts (commonly less than 10 vol%) of anhydrite cement and replacive anhydrite with 'pile-of brick' textures (Carozzi 1960) that appear to be

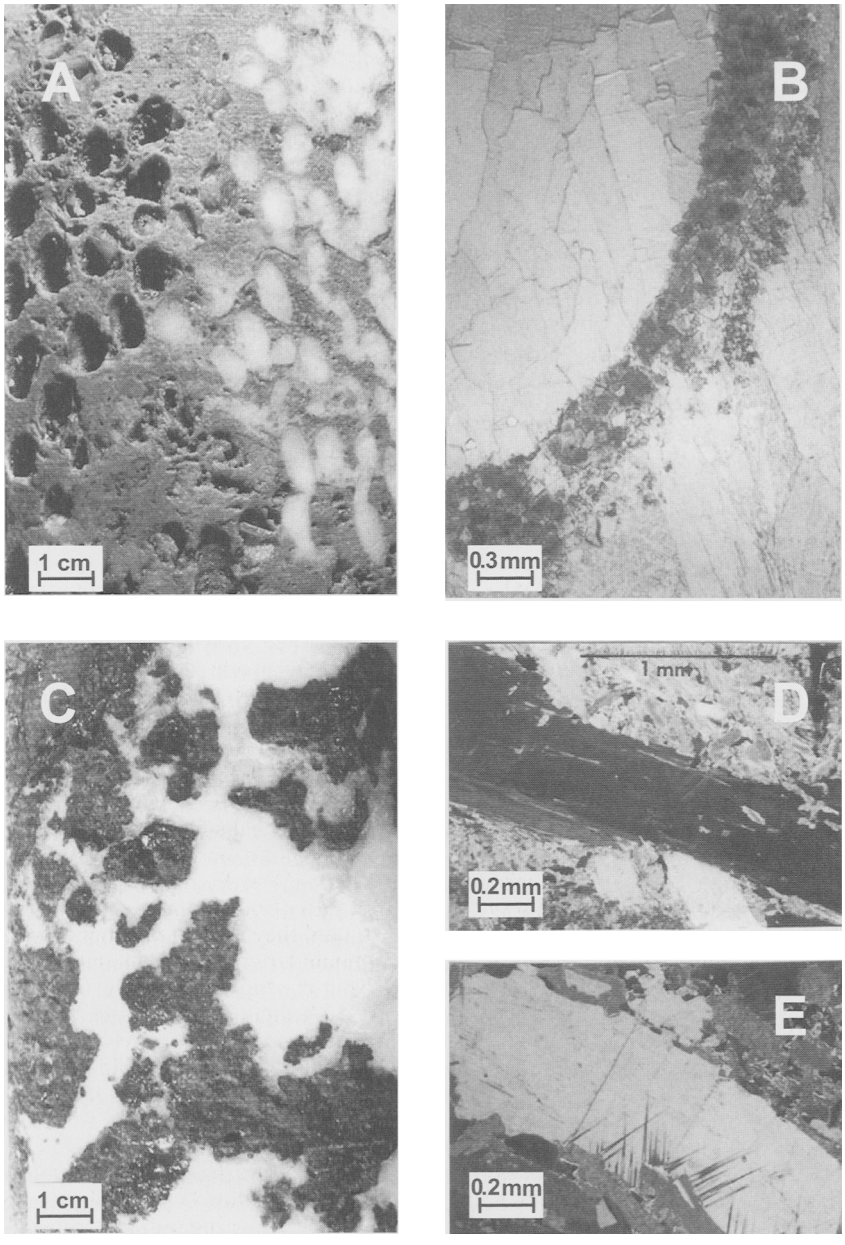

Fig. 7. Calcium sulphate formed as a by-product of dolomitization from (chemically slightly modified) seawater. All samples are from the Upper Devonian Nisku Formation, Alberta, Canada, from depths of 3300–4300 m. (**A**) White anhydrite partially as a replacement (top right) and partially as a cement in coral-mouldic porosity (centre and bottom right). (**B**) Thin-section photomicrograph of top right of sample shown in (A). The interior of the coral contains sparry anhydrite cement, while outside of the coral the anhydrite is replacive/corrotopic. (**C**) White anhydrite that is replacive after dolomite, as it contains 'islands' of undigested dolostone. (**D**) and (**E**) Thin-section photomicrographs, crossed polars, of anhydrite shown in (**A**)–(**C**). Note corroblastic/corrotopic fabrics, i.e. the anhydrite consists of large porphyroblastic/porphyrotopic crystals that float in a medium- to fine-crystalline 'felted' anhydrite matrix. Some of the large crystals appear corroded (top of D), giving the name to this type of anhydrite (Machel 1985, 1986). The large crystal in (E) has strain twins that originate from the point near the bottom where another large crystal impinges.

'primary', i.e. they formed without a gypsum precursor. In combination, these observations indicate that anhydritization started at depths of about 600–800 m (perhaps up to 1000 m if the strata were somewhat overpressured) during advanced phases of dolomitization. During progressive burial, the gypsum transformed to corroblastic/corrotopic anhydrite, and some anhydrite formed directly as anhydrite during the deepest, most advanced, phases of anhydritization.

The emplacement of gypsum–anhydrite during the latter stages of dolomitization from seawater or chemically altered seawater is probably a general phenomenon. It is widespread in the Devonian of western Canada (Mountjoy *et al.* 1999). Conversely, neither gypsum nor anhydrite emplacement should be expected from relatively sulphate-poor dolomitizing solutions, such as in dilute mixing zones, hydrothermal brines, etc.

Two dolomite populations. A common phenomenon in massive dolostones is the occurrence of two crystal populations with different sizes and shapes, and with differing pore types and degrees of pore interconnection. A typical example is shown in Figure 8 in various magnifications. Two aspects of these textures are especially noteworthy. First, crystals of the smaller sized population are commonly 'cloudy' with or without clear rims (overgrowths), whereby the rims appear to be similar to the larger sized population. Secondly, the domains with the coarser crystal size population have a much higher intercrystal porosity and permeability than those with the finer crystal size. In such rocks most petroleum is stored in and flows through the coarser domains, which have a much higher permeability.

These types of textures are genetically ambiguous, whereby the crystals with cloudy centres and clear rims are most easily understood. Initially dolomitization most probably forms short-lived, metastable phases, and large(r) rhombs overgrow the initial phases. This has been shown in hydrothermal experiments, in which the very irregular interiors of larger crystals (equivalent to the cloudy interiors of natural dolomites) apparently underwent intracrystalline recrystallization during or after formation of the stable overgrowths (e.g. Sibley 1990).

The two size populations may result from one dolomitization event or from dolomite recrystallization. In the first alternative, the two dolomite types may reflect textural differences in the precursor limestone(s). One example would be a lime mud or a limestone that consisted of irregularly shaped domains of two populations of matrix, such as lime mud and lime silt or sand. Another example would be a more or less homogeneous lime sediment or limestone that had undergone heterogenous lithification before dolomitization, such that some patches were better cemented or recrystallized than others. In both cases dolomitization could result in the textures shown in Figure 8. The geochemical compositions of both textural types of dolomite would be identical or nearly so, possibly with very small differences inherited from the precursor substrate(s), if the geochemical system is not entirely water-dominated. An example of this type of situation is the Devonian Nisku Formation in central Alberta, Canada, where two populations of matrix dolomite are geochemically indistinguishable within the margin of analytical error (Machel & Anderson 1989).

The second alternative, recrystallization, would be expected where dolomites formed very near the surface and/or in evaporitic environments. Such dolomites commonly form as metastable 'protodolomites' that are prone to recrystallization during burial (discussed below). It is conceivable that recrystallization proceeds in a spatially heterogeneous manner, or at different times within a given volume of rock, or both, governed by heterogeneities in permeability, mineralogy, and corresponding reaction kinetics. As a result, some rock domains may recrystallize to a coarser crystal mosaic than others, possibly including the development of zonation in one domain but not in another. In such cases, there may be a marked difference in the geochemical compositions of the two dolomite populations. An example of this type of situation is the reflux dolomites in the Upper Devonian Grosmont Formation in eastern Alberta, Canada (Huebscher 1996; Machel & Huebscher 2000).

Dolomite dissolution. Textures that resemble those shown in Figure 8 in hand specimen may also result from dolomite dissolution. Great care must be taken to differentiate this alternative from the two discussed in the previous section.

Figure 9 shows samples from the karst-modified part of the Upper Devonian Grosmont Formation in eastern Alberta, Canada. An undolomitized sample (Fig. 9A) would become a dolostone with mouldic porosity (Figure 9B) if matrix-selective dolomitization was accompanied or followed by the dissolution of biochems that had survived replacement. Closer

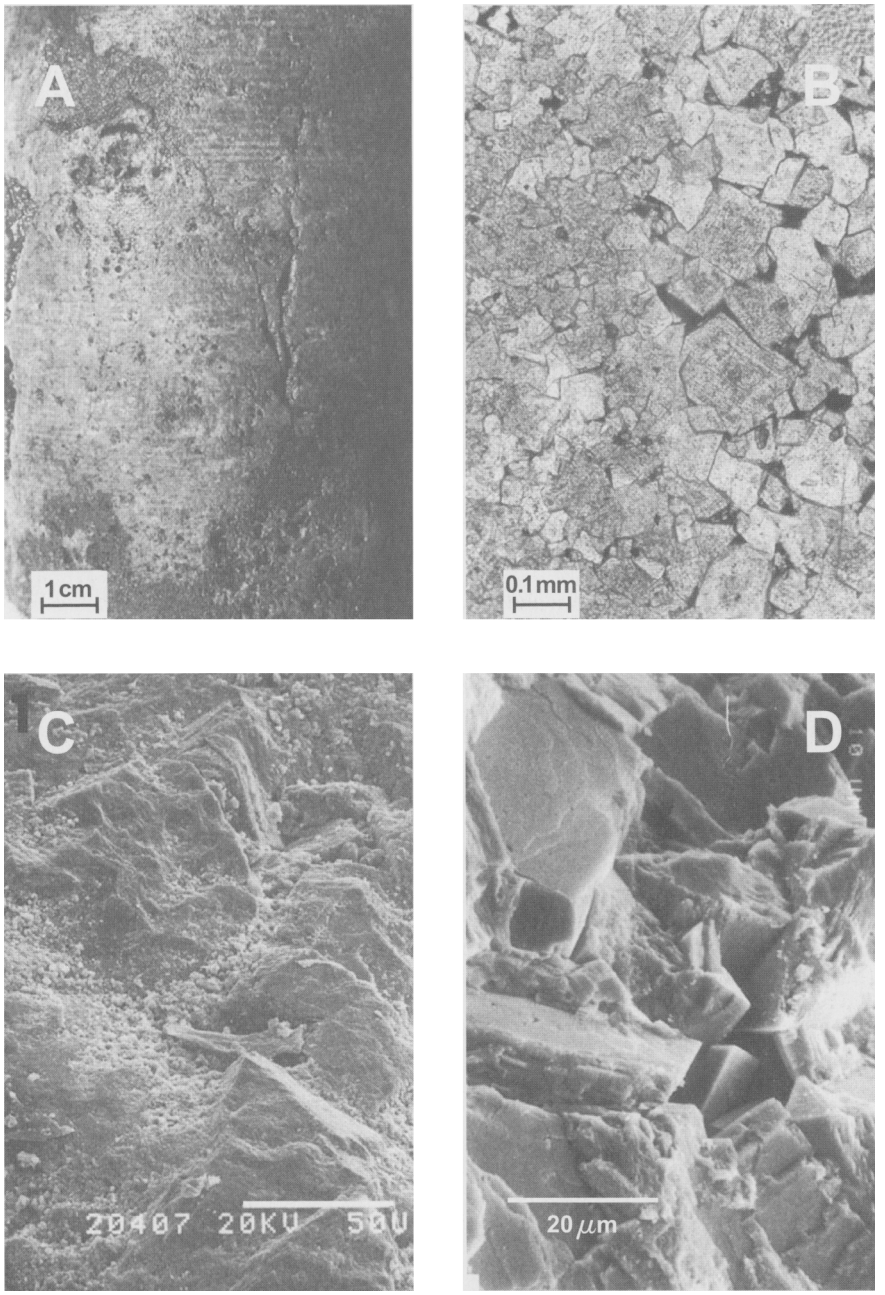

Fig. 8. Dolostones consisting of domains of relatively tight, light- to medium-grey dolomite intergrown with domains of highly porous, brownish dolomite. The porous domains originated either from replacement of coarser matrix, or from recrystallization of the tight dolomite type. All samples are from the Upper Devonian Nisku Formation, Alberta, Canada. (**A**) Hand specimen. (**B**) Thin-section photomicrograph of sample shown in (A), from the boundary region between the two dolomite types. (**C**) SEM of tight dolomite domain (left in B). Most crystals are planar-s. The pore throats are rather tight yet lined with small 'roundish' calcite crystals that look like rubble in morphological depressions. Permeability is through these parts of the rock, i.e. along crystal boundaries. (**D**) SEM of porous dolomite domain (right in B). The crystals are also planar-s but much larger than those in (C), and there is significant intercrystalline porosity and permeability.

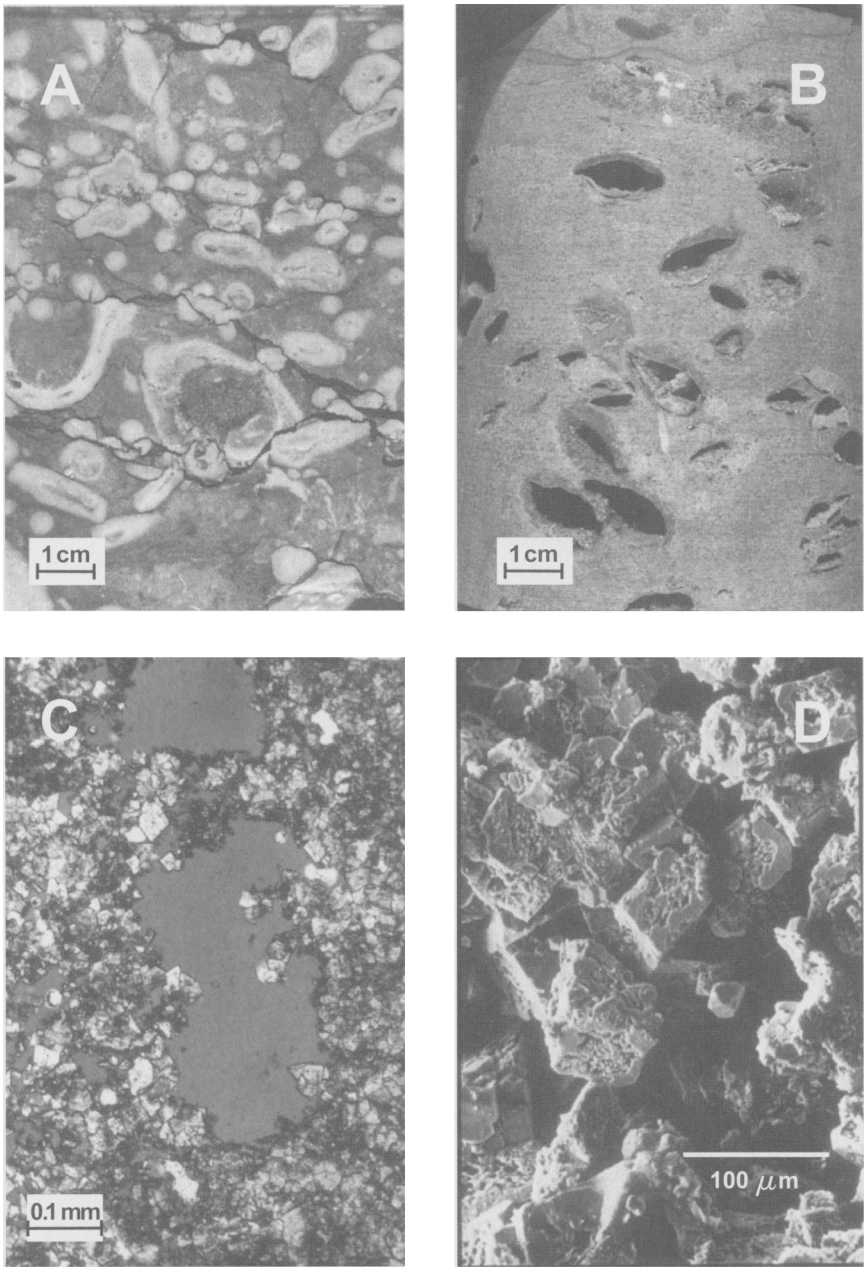

Fig. 9. Development of matrix-selective dolomitization, subsequent dissolution of unreplaced biochems (mainly brachiopods), marginal recrystallization around moulds, and subsequent partial dissolution of dolomite. All samples are from the Upper Devonian Grosmont Formation, Alberta, Canada. (**A**) Hand specimen of (rare) limestone with partial matrix dolomitization. (**B**) Hand specimen of rock type shown in (A) after complete matrix dolomitization, development of mouldic porosity from dissolution of biochems (mainly brachiopods), as well as enhanced porosity around moulds (dark fringes). The domains with enhanced porosity originated from a combination of dolomite dissolution and recrystallization. (**C**) Thin-section photomicrograph of sample shown in (B), illustrating oversized dissolution pores from dark, porous fringes around moulds. (**D**) SEM photomicrograph of sample shown in (B), illustrating intra-crystal dissolution porosity from dark, porous fringes around moulds.

inspection shows that the matrix immediately surrounding the moulds is more coarsely crystalline, as well as more porous and more permeable, than the bulk of the rock. Similar textural differences occur in larger patches in other core intervals, resembling those shown in Figure 8A. However, thin section and SEM images of the Grosmont samples reveal the presence of oversized pores (Fig. 9C) and abundant dissolution pits in the dolomite crystals (Fig. 9D), which indicate that these textures originated from dolomite dissolution. In the Grosmont Formation dissolution was facilitated by meteoric water (Machel & Huebscher 2000), but other mechanisms are possible, as discussed below.

Saddle dolomite. Saddle dolomite, also called baroque dolomite, pearl spar and other names, is a distinctive type of dolomite. Its crystallographic, geochemical and paragenetic characteristics suggest a special type of genesis with respect to the crystal growth mechanism and diagenetic setting(s) (Radke & Mathis 1980; Machel 1987; Searl 1989; Kostecka 1995; Spötl & Pitman 1998).

Saddle dolomite is almost invariably coarse crystalline and milky-white or pink in hand specimens, with a pearly lustre and a distinctively distorted crystal structure that is macroscopically expressed as warped crystal faces and cleavage planes, and microscopically as sweeping extinction. The crystal faces, although well developed, are often faceted like a pavement. Fluid-inclusion homogenization temperatures commonly range between about 80 and 150 °C, in some places up to about 300 °C. There are no confirmed cases of saddle dolomite formation below 60–80 °C; hence, this temperature may be taken as a minimum for the formation of this phase (Spötl & Pitman 1998).

The association of saddle dolomite is also distinctive. It commonly occurs as a gangue mineral in Mississippi Valley-type (MVT) metal sulphide deposits, including features characteristic of thermochemical sulphate reduction (solid bitumen, elemental sulphur, depleted carbon isotope ratios, etc.: Machel *et al.* 1995; Machel 2001). Saddle dolomite is, however, also common as cement in dolostones without any association to MVT-sulphides or hydrocarbons.

Figure 10 illustrates typical occurrences and textural associations of saddle dolomite. As shown in Figure 10A, matrix-selective dolomitization generated grey medium-crystalline dolomite, and later calcite dissolution created elongate moulds after fasciculate corals (compare to Fig. 6C). These moulds were probably filled during stylolitization of the matrix dolomite with milky-white saddle dolomite cement derived from matrix dolomite dissolved along the stylolite(s). Similar moulds are empty or open about 50 cm above and below this core sample, indicating that the material for saddle dolomite was derived locally rather than by advection, a relatively common process in deeply buried dolostones. In Figure 10B, most of the saddle dolomite is replacive (nonplanar-a, using the classification shown in Fig. 3), but some of it is cement and intergrown with galena. Prior to saddle dolomite formation the host rock was medium-grey matrix dolomite, some of which is still visible as dark bands. In some locations, such bands alternate with bands of white saddle dolomite, a texture commonly referred to as 'zebra dolomite'. The origin of zebra dolomite is much debated and probably involves more than one mechanism, including repeated fracturing or some type of geochemical self-organization (e.g. Krug *et al.* 1996). Figure 10C & D illustrate the common association of solid bitumen with saddle dolomite. In these samples, the saddle dolomite is the latest paragenetic phase, and the crystals grew into large voids that were already partially coated with oil. The crystals nucleated on small dolomite crystals of the wall rock that protruded through the oil coating, which may or may not have been solidified at the time of dolomite formation.

The peculiar crystal structure and features associated with saddle dolomite require special conditions during crystal growth. The crystallographic and geochemical characteristics indicate that the crystals most probably grow very fast from highly supersaturated solutions, together with or under conditions where surface-related activation energy barriers are much reduced (Searl 1989). The former can be expected in hydrothermal solutions that cool or depressurize and de-gas rapidly. The reason for the occurrence of the latter condition is not obvious. Considering, however, that saddle dolomite usually forms at temperatures in excess of about 60–80 °C, it seems logical to assume that elevated temperatures are a key factor in reducing the surface energy barriers. On a macroscopic scale, studies have shown that saddle dolomite can be formed as a cement or as a replacement in at least three ways: from advection (commonly, but not necessarily, by hydrothermal fluids), from local redistribution of older dolomite during stylolitization, and as a by-product of thermochemical sulphate reduction in a closed or semi-closed system (Radke & Mathis 1980; Machel 1987; Machel & Lonnee 2002).

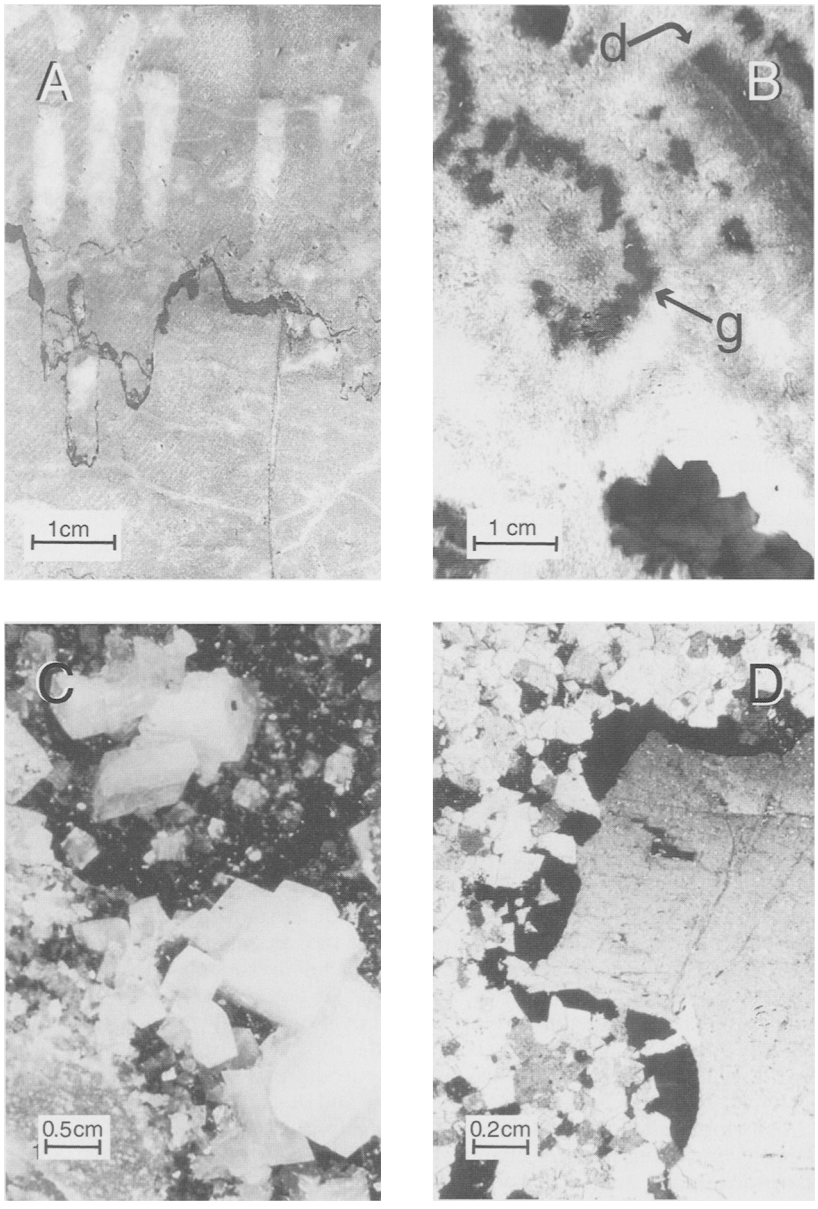

Fig. 10. Saddle dolomite. All samples are from western Canada. Sample (A) is from the Upper Devonian Nisku Formation; (B) is Middle Devonian Presqu'ile dolomite from the MVT mine site at Pine Point; (C) and (D) are from the Upper Devonian Leduc Formation. (**A**) Hand specimen of stylolitized dolostone with milky-white saddle dolomite cement in coral moulds (compare with Fig. 6C). (**B**) Hand specimen of milky-white, coarse-crystalline saddle dolomite intergrown with bands of galena (g). Typical MVT-paragenesis. Most of the saddle dolomite replaced grey matrix dolomite, which is preserved in some thin bands (d). Saddle dolomite forms subhedral cement fringes around some large vugs (lower right). (**C**) Core specimen of milky-white saddle dolomite cement in vug that is coated with solid bitumen ('dead oil'). Host rock is grey matrix dolomite. Note than the saddle dolomite postdates the emplacement of the bitumen. (**D**) Thin-section photomicrograph, transmitted light with crossed polarizers, of sample shown in (C). Most bitumen displays round convex surfaces toward the centre of the pore, mimicking formerly liquid oil droplets that clung to the margins of this pore. This bitumen may have formed as a byproduct of thermal cracking or from thermochemical sulphate reduction. Saddle dolomite appears as large crystals in the centre and lower right, with undulouse extinction.

'Low-temperature' v. 'high-temperature' dolomitization. Outcrop evidence shows that there may be a distinct difference in the textures resulting from 'low-temperature' v. 'high-temperature' dolomitization of limestones. Empirical evidence suggests that the range of 50–80 °C marks the approximate boundary between these two temperature realms, but this aspect remains to be investigated.

In low-temperature settings dolomitization is commonly matrix-selective and at least partially fabric-retentive, as discussed earlier, whereas in high-temperature settings it tends to be fabric-destructive. Figure 11 shows examples from outcrops of Carboniferous carbonates in Cantabria, Spain, where high-temperature solutions dolomitized shallow-marine limestones that constitute the wall rocks around the dolomitized domains. Based on uncorrected fluid inclusion homogenization temperatures, these dolomites formed at a minimum of 130–140 °C, i.e. they are high-temperature dolomites. Furthermore, they are hydrothermal because they formed at temperatures significantly higher than the wall rocks that, based on Conodont Alteration Index (CAI) values, experienced maximum burial temperatures of about 70–95 °C (Gasparrini 2003). Hence, the temperature differential between the wall rock and the intruding hydrothermal solutions was 35–70 °C. The limestone–dolostone boundaries are sharp, and sedimentary, as well as diagenetic, features of the limestone are largely or completely obliterated in the dolomitized portions of the outcrops. Similar textures are common in Devonian reef carbonates of Germany (Machel 1990; Grobe & Machel 1996, 1997; Grobe 1999), and in Cambrian carbonates of the Rocky Mountains, Canada (Moore 1994; Yao & Demicco 1995; Spencer & Hutcheon 1999) where high-temperature, hydrothermal solutions dolomitized limestones.

Figure 12 is a schematic comparison of low-temperature and high-temperature dolomitization. In low-temperature settings dolomitization proceeds essentially as documented in the previous sections and in Figures 6–9 (bottom part of Fig. 12). In high-temperature settings it tends to proceed via a sharp, straight–irregular front behind which sedimentary and diagenetic textures are obliterated (top part of Fig. 12). However, there are counter-examples. Dolomitization of fossils in hydrothermal bombs produced fabric-retentive dolomite (Bullen & Sibley 1984), whereas low-temperature dolomitization in Eniwetok atoll is fabric-destructive, at least in part (Saller 1984). In some locations, such as western Canada, hydrothermal fabric-obliterative dolomites grade laterally into fabric-retentive dolomites, suggesting that both types of replacement were generated by a single fluid pulse, and that the textural gradient reflects a decrease in temperature, temperature differential, and supersaturation away from the faults from which the fluids emanated (Spencer & Hutcheon 1999). It seems plausible that fabric-obliterative replacement may be favoured by an overall high temperature (wall rock plus intruding dolomitizing solution); by a high temperature differential between the wall rock and an intruding dolomitizing solution (which would be hydrothermal); by high supersaturation of the intruding solution with respect to dolomite; or by a combination of these factors. A delicate interaction may be at play.

Porosity and permeability

It has long been claimed that most dolostones are more porous and more permeable than limestones (e.g. Blatt *et al.* 1972), a circumstance of obvious importance for the petroleum industry. A related aspect is that dolostones commonly form aquifers and preferential migration pathways for hydrocarbons, or both. A striking example is the dolomitized margin of the Devonian Cooking Lake platform in Alberta, Canada, that has acted as a water and hydrocarbon migration pathway over a distance of several hundred kilometres (e.g. Amthor *et al.* 1993, 1994).

The claim that most dolostones are more porous and permeable than limestones is contentious. van Tuyl (1914, p. 259) stated that 'Some dolomites are very compact, but most of them are vesicular and porous', a view held for many years. Schmoker & Halley (1982) and Halley & Schmoker (1983), however, demonstrated with porosity–depth profiles of Cenozoic carbonates in southern Florida that many dolostones that have not been buried too deeply (less than about 1 km) have porosities equal to or less than those of adjacent limestones. Budd (2001) showed that the same is true for permeability in these particular rocks, where many dolostones have permeabilities equal to or less than those of adjacent limestones. On a larger scale, Schmoker *et al.* (1985) compared thousands of limestones and dolostones from across the USA and found that dolostone reservoirs commonly have lower matrix porosities and permeabilities, yet higher fracture porosities and permeabilities, than limestones. However, Amthor *et al.* (1994) in a study of 31 wells from Devonian reservoirs in Alberta that span a depth range of several thousand metres, found

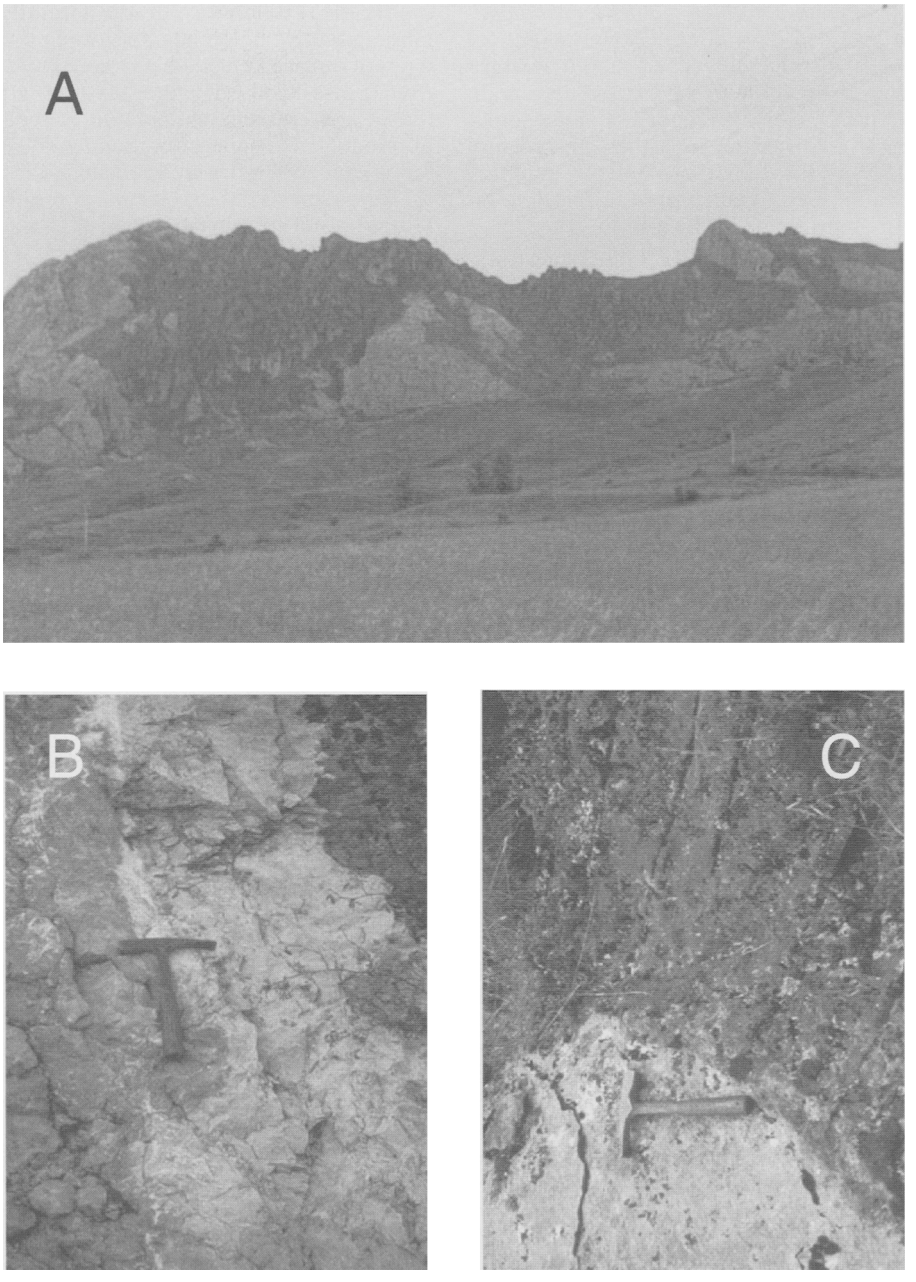

Fig. 11. Outcrop photographs of Upper Carboniferous carbonates from the SW Cantabrian zone, Spain: hydrothermal and high-temperature dolomitization of limestones. Photographs courtesy of M. Gasparrini. (**A**) Cliff face showing sharp, irregular contacts and irregular distribution of limestone (light) v. dolomite (dark). In this location the dolomite appears dark because of the lichen cover (the lichen grows only on the dolostone). The dolomitizing fluids ascended via faults. (**B**) Close-up of limestone–dolostone contact such as shown in (A) from a location nearby. The dolostone appears dark where covered with lichen (upper right corner) yet light beige where cleaned of lichen (centre). The limestone (left) has a medium-grey colour. Note the sharp yet irregular contact between the limestone and dolostone. Sedimentary and diagenetic textures visible in the limestone are obliterated in the dolostone. The hammer is for scale. (**C**) Rock face similar to that shown in (B), rotated by 90° (top to the left). Note that the limestone (dark, top) is well bedded, whereas the bedding is obliterated in the dolostone (light, bottom; no lichen cover). The hammer is for scale.

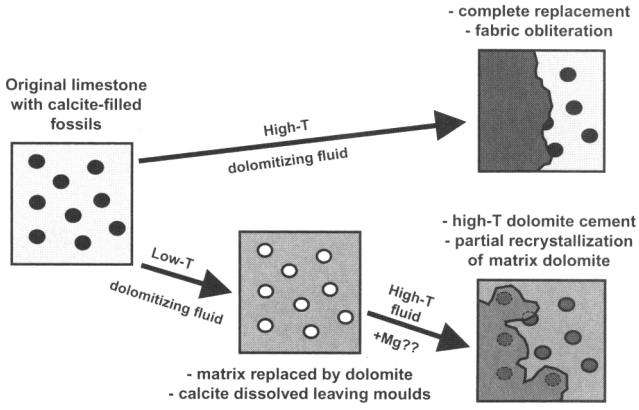

Fig. 12. Schematic illustration of limestone replacement by low-temperature and high-temperature dolomitizing solutions. See text for further explanation.

that there is a distinct dependence on depth. If considered irrespective of depth, limestones and dolomitic limestones are more porous than dolostones, whereas at burial depths of greater than 2000 m dolostones are significantly more porous and permeable than limestones. There are also notable examples of very young, near-surface dolomites that are tight and apparently devoid of porosity generated during the replacement process, as in the Plio-Pleistocene carbonates of Bonaire (Lucia & Major 1994).

Porosity

The theory that dolostones have higher porosities than limestones originated with the classic work by Elie de Beaumont in 1836 (cited by van Tuyl 1914), who proposed that 'molecular replacement' of limestone by dolomite would result in a volume loss of 12.1% (this is now called 'mole-per-mole' replacement, and the percentage commonly cited is 13%: discussed below). This view, however, is far too simplistic. Several other processes are involved, summarized diagrammatically in Figure 13. Some of these processes, such as excess calcite dissolution over dolomite, were recognized fairly early (Landes 1946; Murray 1960), and one relatively recent article provided an overview of several of the processes involved with reference to the ages and types of dolomite reservoirs (Sun 1995). Figure 13 is designed to represent the porosity and permeability evolution in both limestones and dolostones. The only aspect specific to dolostones is the effect of variable reaction stoichiometry during replacement, as represented by reactions 1–4 (earlier). Reaction stoichiometry can be added to all parts of the circle in Figure 13 because it can reduce, leave unchanged, or enhance porosity and/or permeability. The porosity and permeability distribution and evolution in dolomites and dolostones should be discussed in this context. Some of the processes are illustrated in Figures 6–10.

Six processes appear to be responsible for this phenomenon: (a) mole-per-mole replacement; (b) dissolution of unreplaced calcite (the solution is undersaturated for calcite after all Mg in excess of dolomite saturation is exhausted); (c) dissolution of dolomite (without externally controlled acidification); (d) acidification of pore waters (via decarboxylation, clay mineral diagenesis, etc.); (e) fluid mixing (mischungskorrosion); and (f) thermochemical sulphate reduction, which may generate porosity under certain circumstances (Machel 2001). The porosity v. depth compilations of Schmoker & Halley (1982), Halley & Schmoker (1983), and Amthor *et al.* (1994) did not separate these possibilities or recognize the lack of porosity destruction (porosity preservation) with depth. In fact, most workers have made no attempt to discriminate between these alternatives. The wide scatter and lack of systematic relationships between the porosity of limestones and dolostones observed in Florida and Alberta probably reflects locally and regionally heterogeneous interplays between the various processes that generate, preserve, or destroy porosity (Fig. 13). Clearly, it appears unwise to make generalizations about the porosity development of dolostones, which should be evaluated individually regarding their porosity development.

Perhaps the best known and/or most widely

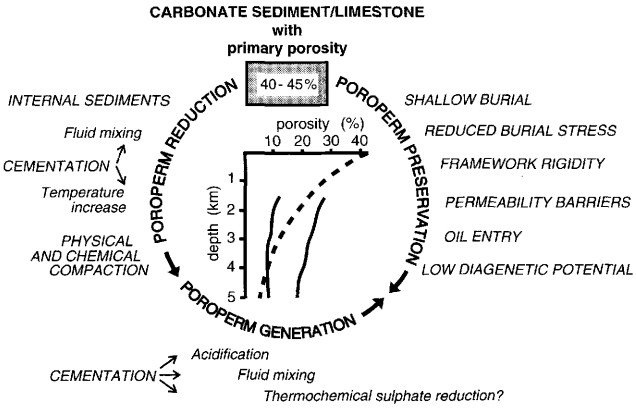

Fig. 13. Major processes of porosity and permeability ('poroperm') generation, preservation and reduction in carbonates. The inset contains averaged porosity–depth data from Mesozoic and Cenozoic limestones and dolostones in south Florida (stippled trend, from Schmoker & Halley 1982) and of the Jurassic Smackover oolite carbonate reservoirs in the southern United States (solid trends, which envelope the measured maximum and minimum values below depths of about 1.5 km, from Scholle & Halley 1985; Heydari 1997). The Florida trend can be considered typical for most carbonates elsewhere. The large variations in the Smackover carbonates at any given depth reflect highly variable degrees of porosity generation, preservation and reduction due to competing diagenetic processes. The figure is reproduced with permission from Machel (1999).

recognized mode of porosity gain during dolomitization is the replacement process *sensu stricto*. Comparison of the molar volumes of calcite and dolomite reveals that about 13% of porosity is generated in the so-called 'mole-per-mole' replacement of calcite by dolomite according to reaction 1 (section on 'Mass-balance Constraints': 2 moles of calcite are replaced by 1 mole of dolomite). If, for example, a limestone has 40% initial porosity, mole-per-mole replacement will generate a dolostone with about 45% porosity. More generally, porosity gains or losses can be represented by the values of x in reaction 3 ('Mass-balance Constraints'). Volume-per-volume replacement is represented by the special cases of $x = 0.11$ and $x = 0.25$ (for aragonite and calcite, respectively), when there is no volume loss or gain (Morrow 1982*a*). It is not clear how Nature 'chooses' one reaction stoichiometry over another. Geochemical modelling suggests that an interplay of the degree of evaporation and flow rate determines the relative saturation states of dolomite to calcite and aragonite through space and time (Sun 1992; Morrow 2001). This also controls the rates of calcite/aragonite dissolution relative to dolomite formation, and where and when macrodissolution of calcium carbonate (formation of moulds and vugs) happens along the flow path of the dolomitizing solution.

Lucia (2002, 2004) claimed that dolomitization does not normally result in an increase in porosity, arguing against the notion that the commonly observed higher porosity of dolostones compared to limestones is the result of the dolomitizing process. Rather, he suggests that most dolostones have lower porosities than limestones due to 'overdolomitization', i.e. dolomite cementation following matrix replacement and reducing pore sizes (Fig. 5), as well as permeability. However, Lucia's argument, although correct, is an incomplete explanation of those dolostones that have lower porosities than corresponding limestones. Where dolomitization is only partial, mole-per-mole replacement, if it takes place, will generate porosity. Where dolomitization is complete, mole-per-mole replacement, if it takes place, will generate porosity only if the supply of the dolomitizing solution ends roughly at the time of dolomitization approaching completion. If, however, there is a continued supply of dolomitizing solution, then 'overdolomitization' may indeed obliterate much or most of the porosity previously generated. It remains to be seen just how common 'overdolomitization' really is.

Dissolution of unreplaced calcite has the potential of generating much more than the theoretical maximum of 13% porosity in the mole-per-mole replacement process. This potential appears to be realized quite frequently (Landes 1946; Amthor *et al.* 1994). In addition, the fact that dolostones are more porous than

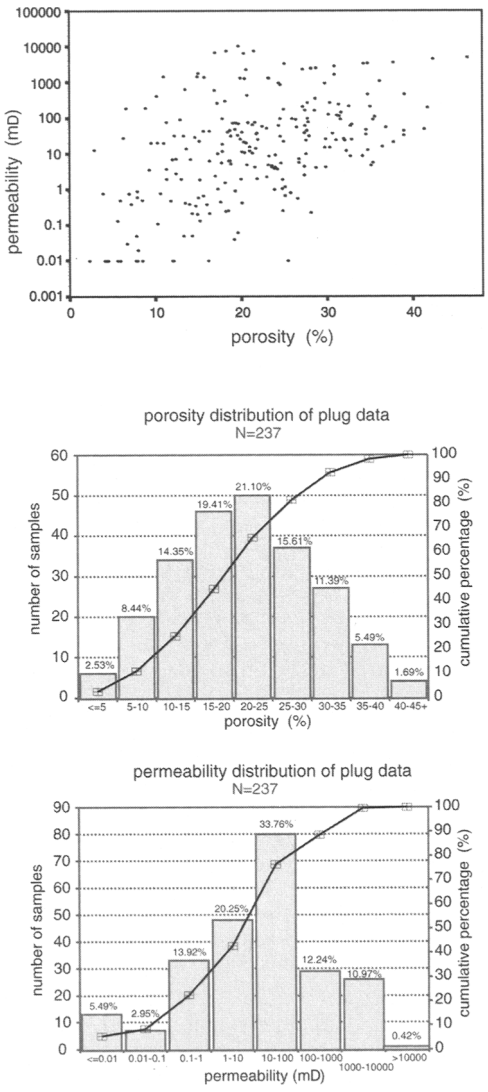

Fig. 14. Cross-plot of porosity and permeability data from 237 core plugs from 24 wells in the Upper Devonian Grosmont Formation, Alberta, Canada, with histograms of porosity and permeability. Despite considerable scatter, these data show a general positive correlation between porosity and permeability, and also attest to the excellent reservoir quality of the Grosmont Formation with modes around 20–25% and 10–100 mD, respectively (where $1D = 0.9868 \times 10^{-12}$ m^2). The figure is reproduced with permission from Luo *et al.* (1994).

limestones at depths greater than 2000 m in some basins, such as in Alberta, is caused at least in part by the greater extent of stylolitization of the limestones, which have a higher pressure-solubility than dolostones at any given depth (Amthor *et al.* 1994).

The textural developments discussed previously illustrate some common possibilities of porosity development during, or as a result of, dolomitization; that is, porosity gain through 'excess' calcite dissolution (Fig. 6) and through dolomite dissolution (Fig. 9). On the other hand, porosity loss may occur through gypsum and/or anhydrite emplacement (Fig. 7), as well as cementation with saddle dolomite (Fig. 10), or with base-metal sulphides. The completely dolomitized Cambrian Bonneterre Formation in the USA is a case in point. Thin-section petrography, gas porosimetry and point counting show that the porosity of these rocks was reduced from about 19% prior to mineralization to less than 4% in several steps by successive cement generations of dolomites, quartz and sulphides, whereas some porosity was re-established during sulphide mineralization with concurrent dolomite dissolution (Gregg *et al.* 1993).

In this context, a few generalizations can be made regarding textural development. In cases of mole-per-mole replacement, the fabrics of the original limestone must be at least partially obliterated in order to account for the volume change during the replacement process. On the other hand, limestones dolomitized in a volume-per-volume replacement should not contain secondary intercrystal pores or dolomite cements, and the primary textures may be partially or largely, even mimetically (if the crystal size is very small), preserved. Partial or complete obliteration of primary textures can occur even in a volume-per-volume replacement, however, if there is a marked change in crystal size (usually an increase, due to Ostwald ripening), with or without porosity redistribution.

Permeability

Dolomitization almost invariably involves the reorganization of permeability pathways. Commonly, permeability increases along with porosity, and vice versa. This is documented through studies of examples such as the Upper Devonian Grosmont Formation in eastern Alberta, which hosts a giant heavy-oil reservoir (Luo *et al.* 1994; Luo & Machel 1995; Machel & Huebscher 2000). A comparison of porosity and permeability data from 237 core plugs reveals an overall positive correlation, despite considerable scatter (Fig. 14). This correlation is also expressed in the displacement pressures from mercury injection capillary measurements that

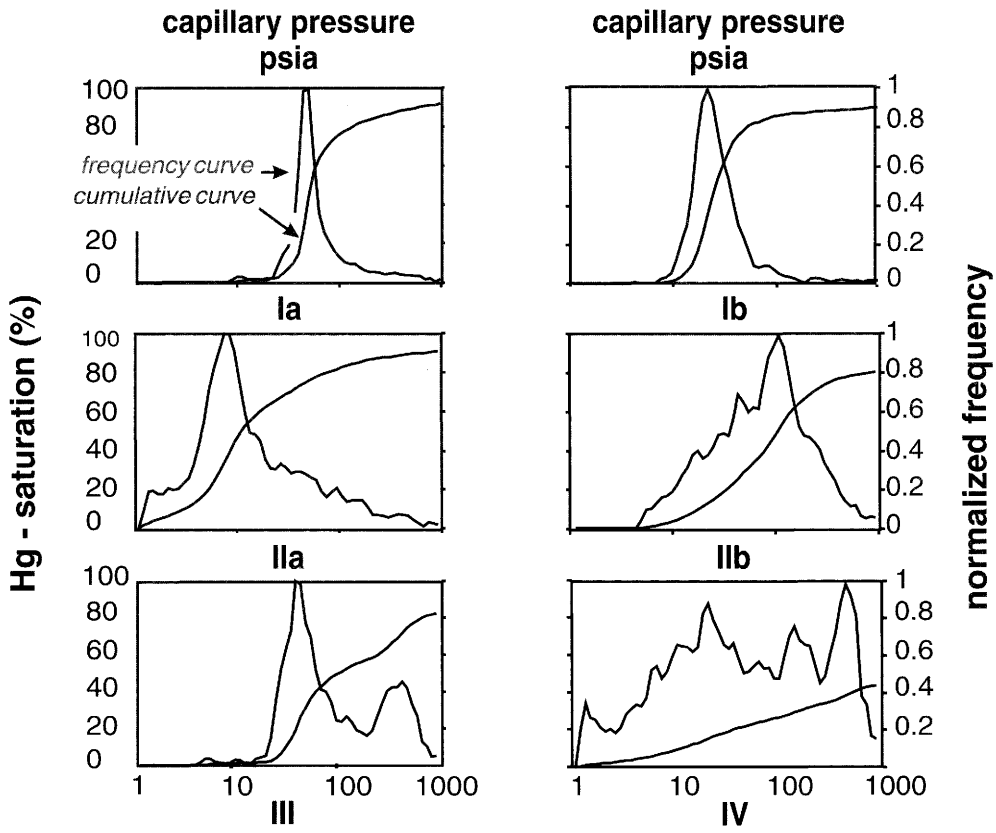

Fig. 15. Mercury injection capillary pressure measurement curve types that represent six groups of samples out of a total of 38 samples from the Upper Devonian Grosmont Formation of Alberta, Canada, which is a heavy oil reservoir. (**Ia**) Symmetrical frequency curve, representing porosity enhanced by pervasive dissolution after dolomitization. (**Ib**) Symmetrical curve, representing intercrystalline porosity generated during dolomitization. (**IIa**) Finely-skewed curve. (**IIb**) Coarsely skewed curve. (**III**) Bimodal curve. (**IV**) Non-sorting curve. The various frequence curves (IIa)–(IV) reflect a complex interplay of porosity–permeability generating processes (see Fig. 13). The figure is modified from Luo & Machel (1995).

permit the identification of four major and two minor dolomite reservoir rock types (Fig. 15). Types Ia, IIb and III have relatively high displacement pressures that correspond to the lowest porosities and permeabilities (Luo *et al.* 1994; Luo & Machel 1995). Using a similar approach (thin-section and SEM petrography, combined with helium porosimetry and mercury injection capillary measurements) Woody *et al.* (1996) documented positive and statistically significant correlations between porosity and permeability for planar dolomites in the Cambrian–Ordovician Bonneterre Formation of Missouri, USA, host to one of the world's largest MVT-sulphide deposits. Woody *et al.* (1996) further found that the planar-e dolomites have the highest porosities and permeabilities, the latter caused by well-connected pore systems with low pore to throat size ratios (as indicated by mercury injection curves); in planar-s dolomite the permeabilities do not increase as rapidly with increasing porosity, corresponding to relatively large pore to throat size ratios; and nonplanar dolomites have a statistically insignificant porosity–permeability relationship, whereby the pore systems have a high tortuosity and large pore to throat size ratios (see also Gregg 2004).

Other authors have contended that there is no systematic correlation between porosity and permeability in dolostones, or that these two petrophysical parameters are enhanced in dolostones relative to limestones. Halley & Schmoker (1983), in the absence of reliable or sufficient permeability data, attempted to assess the permeability of carbonate rocks from

porosity data. They found that carbonate aquifers and carbonate aquicludes cannot be distinguished on the basis of porosity. Lucia (2002, 2004) claimed that '. . . there is no relationship between porosity and permeability in dolostones . . . and dolomite crystal size and the precursor fabric are key elements in predicting permeability', and 'Dolomitization of grain-dominated limestones usually does not change porosity–permeability relationships. Instead, the precursor fabric controls pore-size distribution'. While this may be so in some, perhaps many, cases, the Grosmont and the Bonneterre examples clearly show that there is a relationship between porosity and permeability in at least some major and economically important dolostone sequences. The cause(s) for this relationship are not just the dolomitization process itself but an interplay of various diagenetic processes. If these processes can be quantified, the diagenetic evolution of a dolomitized rock unit could be used as a predictor for the petrophysical properties of the resulting dolostone reservoir unit (Woody *et al.* 1996).

Dolomite geochemistry

A wide range of geochemical methods may be used to characterize dolomites and dolostones, and to decipher their origins. The most extensively applied are the analysis and interpretation of stable isotopes (O, C), Sr-isotopes, trace elements, and fluid inclusions, along with less common methods such as palaeomagnetics and others (e.g. Land 1980; Tucker & Wright 1990; Allen & Wiggins 1993; see also various case studies in Purser *et al.* 1994). This paper cannot discuss all of these possibilities, most of which are adequately covered in the references cited. The focus here is on two aspects of particular interest, the determination of the type of the dolomitizing fluid(s) (marine, evaporitic, subsurface brine, etc.), and the identification of the direction of fluid flow during dolomitization. The latter can commonly be determined by mapping a gradient in dolomite abundance, from complete dolomitization near the upflow direction to decreasing abundance downflow. However, this approach necessarily fails where dolomitization is 'complete' or where exposure and/or core material are insufficient. In such cases the geochemical compositions of dolomites can be used, within limits, to determine the flow direction.

Stable isotopes and fluid inclusions

Oxygen and carbon isotope ratios ($\delta^{18}O$ and $\delta^{13}C$) are the most widely applied and probably the best understood geochemical parameters in dolomite research. In brief, $\delta^{18}O$ values of carbonates can be used, within limits, to determine the $\delta^{18}O$ value and/or temperature of the fluid present during crystallization, providing a possible distinction between meteoric, marine and/or evaporitic waters.

Fluid-inclusion homogenization temperatures are arguably the best means of determining the temperature of formation of dolomites (or any other minerals), in addition to the highly desirable information on fluid compositions that can be gained from freezing experiments (e.g. McLimans 1987). Unfortunately, the vast majority of fluid inclusions in dolomites are too small for standard heating–freezing runs, and thus phase transitions within the inclusions are not observable. This is especially true of matrix-selective, replacive dolomites. On the other hand, sparry saddle dolomite cements found in late-diagenetic dissolution vugs, but also as a replacement, commonly yield excellent fluid-inclusion data.

Where possible, fluid-inclusion homogenization temperatures are used in conjunction with $\delta^{18}O$ values to further characterize the conditions of dolomite formation. This type of analysis can reveal the direction(s) and temperature gradient(s) of the dolomitizing fluid flow on a local (a few kilometres: Wilson *et al.* 1990) or on a regional scale (over several hundred kilometres: Qing & Mountjoy 1992, 1994). These latter two studies are special, in that mapping and contouring of the oxygen isotope and/or fluid-inclusion homogenization temperatures display clear, spatially resolved gradients. Unfortunately, such gradients do not appear to be particularly common.

The $\delta^{13}C$ values of the carbonates can be used to identify whether meteoric water (carrying soil CO_2) was involved, whether thermogenic or biogenic CH_4 was oxidized, whether CO_2 from microbial processes or organic matter maturation was available, or whether thermochemical sulphate reduction (TSR) contributed carbon to the system (e.g. Hudson 1977; Machel *et al.* 1995). There also is a secular carbon isotope trend that may be used for dating marine dolostones, but only under very favourable circumstances (Veizer *et al.* 1999).

Sr-isotopes

Radiogenic isotopes are less commonly used in studies of carbonate diagenesis, mainly because their analysis is much more expensive. Yet, strontium isotopic compositions (usually quoted as $^{87}Sr/^{86}Sr$ ratios) are an excellent parameter to deduce compositional changes and especially

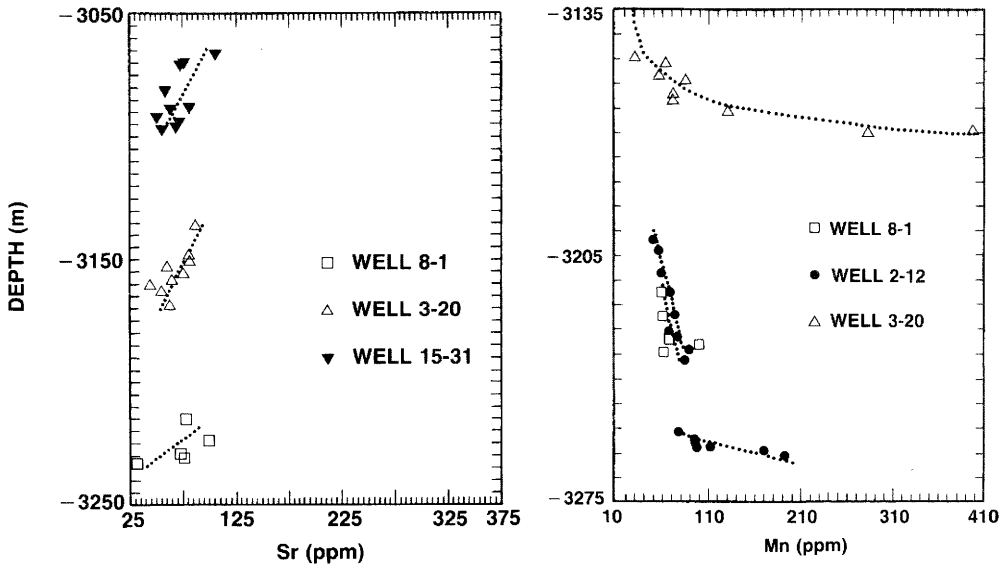

Fig. 16. Sr v. depth and Mn v. depth cross-plots of matrix dolomites from four Upper Devonian Nisku drill cores in two traverses down the structural dip of the Nisku reef trend. Well 15–31 is structurally the shallowest and 2–12 is structurally the deepest. The rocks cored in these wells were nearly at the same depth during dolomitization (very minor structural dip at that time). Sr increases upwards in each well, whereas Mn decreases upwards in each of these wells that penetrate two facies types. These trends demonstrate that dolomitization was post-depositional and that the dolomitizing fluid flow was upwards. Figures are reproduced with permission from Machel (1988).

flow directions of the fluids from which diagenetic carbonates have formed. This is because Sr isotopes, unlike the more commonly used stable isotopes of oxygen and carbon, are not fractionated by pressure, temperature and microbial processes (e.g. Faure & Powell 1972), and $^{87}Sr/^{86}Sr$ ratios display a distinctive secular trend (Smalley *et al.* 1994; Veizer *et al.* 1999).

Examples of how $^{87}Sr/^{86}Sr$ ratios can be used to decipher palaeofluid flow direction (and origin) are provided by Machel & Cavell (1999) and Buschkuehle & Machel (2002). In these studies, the spatial distribution of the $^{87}Sr/^{86}Sr$ ratios in sparry calcite cements, and to a minor degree in sparry dolomite cements, suggests a general W–E flow pattern through an Upper Devonian carbonate complex, with $^{87}Sr/^{86}Sr$ ratios decreasing eastward as a result of dilution and increasing water–rock interaction.

Trace elements

The direction of fluid flow can also be determined using trace elements. This is especially attractive because trace-element analysis is the cheapest of all the common geochemical methods. To this end, Machel (1988) developed a mathematical model applying a variant of the Heterogeneous Distribution Law. Mechanistically, dolomitization is assumed to take place in a manner analogous to the textural evolution shown in Figure 5, and the resulting trace-element compositions are obtained by drilling out powders that sample batches of several tens to hundreds of crystals, rather than individual crystals. The model predicts that systematic trace-element trends indicating fluid flow direction(s) can result during dolomitization. Unfortunately, any transition is possible between: (a) a large up-flow and down-flow trace-element difference stretched over a large flow distance, and (b) a small up-flow and down-flow trace-element difference over a negligible flow distance, depending on the interplay of all involved parameters. In the case of dolomite cementation, trace elements with distribution coefficients smaller than 1 increase, and those with a distribution coefficient larger than 1 decrease, in the down-flow direction. Trace-element trends have been documented in several Phanerozoic dolostone sequences (Machel 1988), and one example is shown in Figure 16. Such trends may be more common than previously recognized. Their absence in

other dolostone sequences may be real in a percentage of cases, because dolomitization does not necessarily yield trace-element trends.

Recrystallization

For all practical applications, such as the determination of fluid composition and flow direction, the absence, presence and/or degree of recrystallization is important. The degree of recrystallization in dolomites and dolostones is much in dispute (Mazzullo 1992; Machel 1997). Some authors claim that all dolomites and dolostones are recrystallized, and that recrystallization commonly proceeds by multiple steps (Land 1992). Implicit in Land's contention is that all dolostones form near the surface from seawater (see also Land 1985) and that such seawater dolomites are thermodynamically unstable during burial. Others claim that 'early' near-surface and shallow subsurface dolomites commonly (but not always) recrystallize during burial, but that burial dolomites often do not recrystallize because they have little if any thermodynamic drive to do so (e.g. Machel *et al.* 1994). A resolution of this problem is of utmost importance for genetic interpretations of dolomites and dolostones. This has led to broadening of the definition of the term recrystallization, and to the introduction of the concept of 'significant recrystallization' (Machel 1997), which is of great use in genetic interpretations of dolomites and dolostones.

As pointed out earlier, it is well known from hydrothermal experiments that dolomite forms in stages via so-called VHMC (very-high-Mg calcite with about 36 mole% Mg), then VHMC plus non-stoichiometric dolomite, then stoichiometric dolomite. These recrystallization steps commonly appear to take place very fast, i.e. within a few hundreds to at most a few thousands of years in low-temperature diagenetic settings, but are even faster in high-temperature settings. Hence, these transitions are pretty much irrelevant for the investigation of ancient (older Cenozoic, Mesozoic and Palaeozoic) dolomites, except for some exceptional cases where the fluid chemistry has changed dramatically within this time frame. One example would be hypersaline protodolomites that may recrystallize in meteoric or brackish water relatively soon after their formation. Furthermore, additional recrystallization may (and often does) happen after many thousands to millions of years, especially during deep burial, and it is these later recrystallization(s) that are of concern.

If changes in texture, structure, composition and/or palaeomagnetic properties through recrystallization are so small that the total range of properties after recrystallization is the same as when the dolomite first formed, a dolomite/dolostone is said to be 'insignificantly recrystallized' (Fig. 17, top), and its properties are still representative of the fluid and environment of dolomitization. On the other hand, if these changes result in ranges of properties that are larger than the original ones, a dolomite/dolostone is said to be 'significantly recrystallized' (Fig. 17, bottom), and its properties are no longer representative of the fluid and environment of dolomitization. In this case, the measured properties are reset and characterize the last event of recrystallization. Not all measurable properties are necessarily reset during recrystallization. For a dolomite to be recognized as 'significantly recrystallized' only one of the measurable properties has to be modified to a range larger than that in the original crystals. In this case, the inherited properties may still represent the event of dolomitization, whereas the reset properties represent recrystallization.

At present it is not clear how common significant recrystallization is in dolomites and dolostones. There are unequivocal examples of the lack of recrystallization and of insignificant recrystallization (e.g. Tan & Hudson 1971; Packard 1992), and there also are convincing cases of significant recrystallization, especially in geologically young dolomites of evaporative origin, but also in some ancient examples (e.g. Gregg *et al.* 1992, 2001; Montañez & Reid 1992*a*; Malone *et al.* 1994; Durocher & Al-Aasm 1997). The progressive and stepwise recrystallization proposed by Land (1992) has been found in only a few geologically young dolomites, most notably in the hemipelagic Miocene Monterey Formation, California (Malone *et al.* 1994). In many, if not most, other cases the evidence is ambiguous.

The Carboniferous dolostones of the Dunvegan gas field in Alberta, Canada, provide a striking, albeit unusual, example of a lack of significant recrystallization. The Dunvegan gas field is a trend about 24 km long, 5 km wide and 35 m thick that was buried for about 300 Ma to depths of up to 4000 m. Yet, the Dunvegan dolomites are texturally and geochemically (stable isotopes, stoichiometry, ordering) virtually identical to the Recent dolomites of the Abu Dhabi sabkha (Packard 1992). This is highly unusual because sabkha dolomites tend to recrystallize fairly easily and early in the burial history, due to the fact that they usually form as metastable protodolomites. A case in

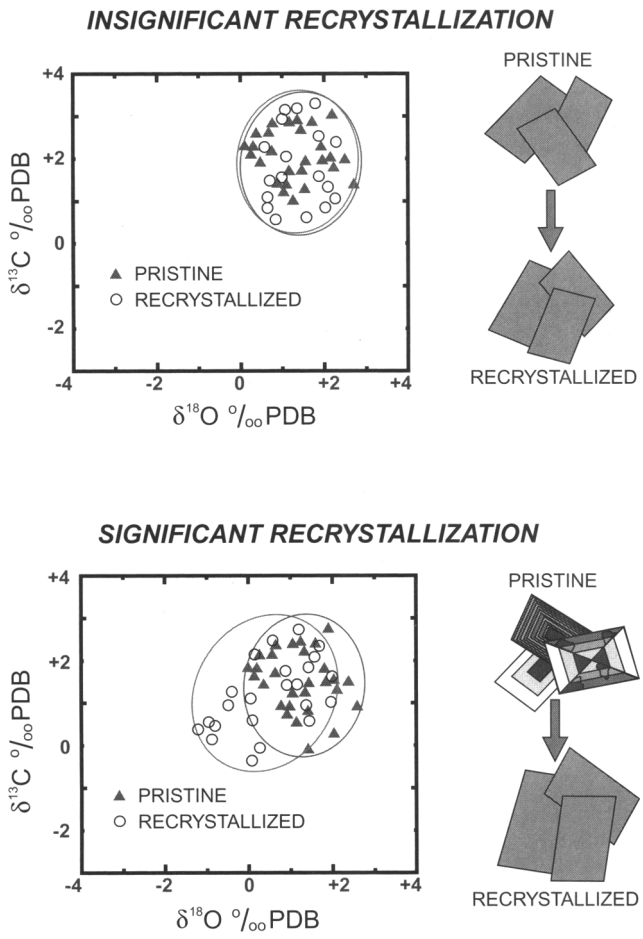

Fig. 17. Schematic illustration of insignificant and significant recrystallization. For the properties shown, $\delta^{13}C$ and $\delta^{18}O$ values, crystal sizes and luminescence, the ranges in the pristine and recrystallized samples are identical for insignificant recrystallization but different, despite some overlap, for significant recrystallization, where at least some isotope values of the recrystallized samples fall outside the range of the pristine samples. The crystals have also increased in size and lost their zonation. The figure is reproduced with permission from Machel (1997).

point is the genetically similar dolomites of the Ordovician Knox Group in the Appalachians, USA, that are significantly dolomitized (Montañez & Read 1992*a*).

There also are examples where, up to now, it has not been possible to determine the extent of recrystallization, or where the evidence shows a lack of significant recrystallization, as in most of the massive dolostones of the Devonian of western Canada. A particularly instructive example is the famous Rimbey–Meadowbrook reef trend that extends through the subsurface of Alberta for several hundred kilometres, forming a structural homocline with burial depths near 200 m at its NNE end and about 6 km near its SSW end. The reefs are located on top of the Cooking Lake platform, and both the platform margin and the overlying reefs have been replaced by matrix-replacive, commonly fine- to medium-crystalline dolomites. Multiple lines of evidence (facies, structure, petrography, and geochemistry) taken together suggest that the reef trend and the underlying platform margin were dolomitized by chemically modified seawater at depths of about 500–1500 m (Amthor *et al.* 1993; Machel *et al.* 1994; Mountjoy *et al.* 1999). Considering that the Rimbey–Meadowbrook reef trend is so long

and now varies widely in depth from one end to the other, this trend is an ideal place to test the hypothesis of Land's (1992) 'quantum theory of dolomite stabilization'. If there is any place where a stepwise progression in recrystallization with increasing temperature and pressure (depth) and time is developed, this is it. However, there is no evidence of systematic significant recrystallization in this reef trend. Plots of textural and geochemical data form clusters (with a few outliers), and there are no stepwise offsets down-dip (Amthor *et al.* 1993; Machel *et al.* 1994; Horrigan 1996; Drivet & Mountjoy 1997; Mountjoy *et al.* 1999). Only the early, peritidal–supratidal dolostones of the Grosmont formation at the shallow end of the trend (Huebscher 1996; Machel & Huebscher 2000), and the most deeply buried dolostones close to the Rocky Mountain deformed belt presently at depths in excess of about 4500 m and formerly buried by up to 2000 m more, are significantly recrystallized (Machel *et al.* 1996*b*; Drivet & Mountjoy 1997).

Taken together the data suggest the following generalizations. Most dolomites that originally form very close to the surface and/or from evaporitic brines tend to recrystallize with time and burial because they form as metastable protodolomite phases and become thermodynamically highly unstable as a result of increasing temperature and pressure, and changing fluid composition. A perhaps typical example is the Monterey Formation, yet there are exceptions, the Dunvegan gas field being particularly striking. By contrast, dolomites that form at several hundred to a few thousand metres depth are either not or hardly prone to recrystallization because they tend to form as rather stable (nearly stoichiometric, well-ordered) phases, the stability of which does not change much during further burial and with increasing time. A conspicuous example in this regard is the replacive matrix dolomites of the Rimbey–Meadowbrook reef trend, except for its most deeply buried part.

Environments and models of dolomitization

One of the most striking developments in dolomite research after World War II was the rapid evolution of a series of models of dolomitization that started in the 1950s and is continuing to this day. These models were designed to explain the origin of the various types of dolomite, and especially of massive dolostones. Interestingly, many of them, some long forgotten, had first appeared in the 100 years after the discovery of dolomite. van Tuyl (1914), in a section entitled 'Historical Review' discussed in great detail eight models, then called 'theories of the origin of dolomite', which he presented in three groups:

I. Primary deposition theories:
   - IA: The chemical theory
   - IB: The organic theory
   - IC: The clastic theory.

II. Alteration theories:
   - IIA: The marine alteration theory
   - IIB: The groundwater alteration theory
   - IIC: The pneumatolytic alteration theory.

III. Leaching theories:
   - IIIA: The marine leaching theory
   - IIIB: The surface leaching theory.

Some of these theories/models are outdated in the light of present knowledge, but several form the basis of current models of dolomitization, as will be pointed out below.

Traditionally, dolomitization models have been defined or based on water chemistry in near-surface and shallow diagenetic settings, but on hydrology in burial diagenetic settings (e.g. Morrow 1982*b*). This poses an obvious dilemma where a near-surface diagenetic fluid moves into the deeper subsurface, or where a deep(er) subsurface fluid ascends into shallow diagenetic settings. Research over the last 15–20 years has revealed several such 'crossovers' or 'overlaps' between models that have resulted in ambiguities in semantics and classification. This problem became bothersome about 15 years ago and surfaced at two major international conferences held in the early 1990s, i.e. the 1991 Dolomieu conference in Ortisei, Italy, and the 1992 National Conference of Earth Science in Banff, Canada. As the most striking example, there was an intense debate at the Banff conference regarding the meaning of the term 'burial dolomite', which meant 3000+ m for some, yet encompassed a much wider range from a few hundred to a few thousand metres of burial for others. If nothing else, this debate highlighted the need to establish clear definitions of burial diagenetic settings, and these were eventually published by Machel (1999) (Fig. 18). Additional research has led to considerable refinements of some established models and to a small number of new ones. For all these reasons, the various models currently in use are discussed in new categories or groups and are placed into an unambiguous, clearly defined context of diagenetic settings (Fig. 18).

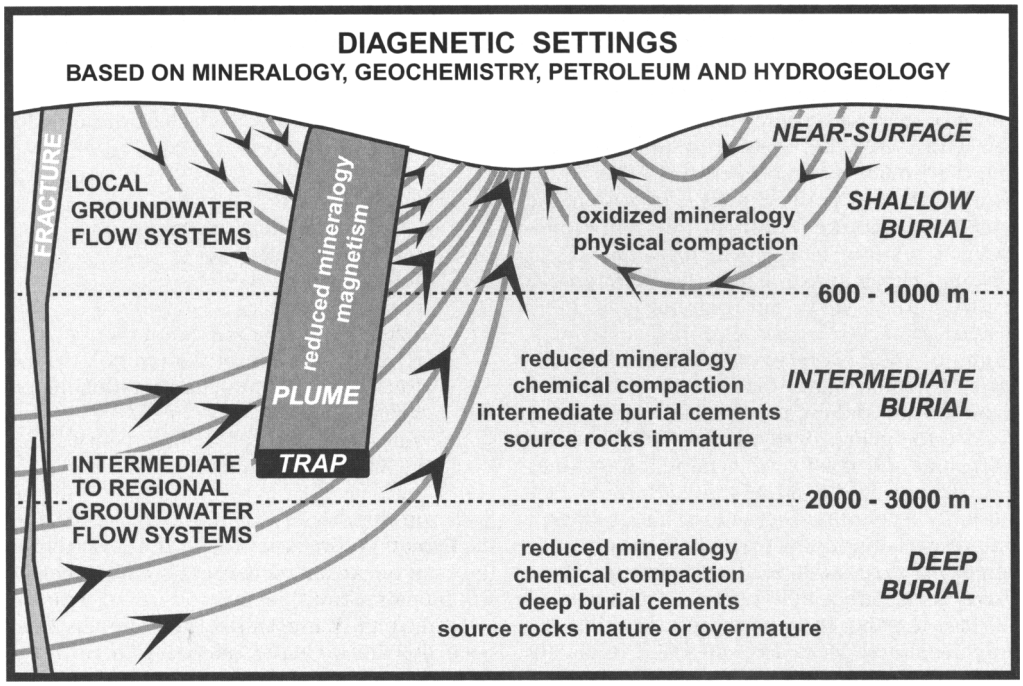

Fig. 18. Classification of diagenetic settings on the basis of mineralogy, petroleum, hydrogeochemistry, and hydrogeology. For illustrative simplicity, the geological section is assumed to be isotropic and homogeneous, with idealized groundwater flow lines. The hydrocarbon-contaminated plume is slightly deflected by the local and regional groundwater flow systems. The depth limits separating the burial diagenetic settings are approximate and based on geological phenomena that are easily recognizable. Near-surface settings may be meteoric, brackish, marine, or hypersaline. The figure is reproduced with permission from Machel (1999).

However, there is certainly more than one viable way to group dolomitization models.

A further problem in dolomite research is a commonly unwitting and certainly needless obfuscation: the widespread practice of calling any interpretation a 'model'. A model is not the same as an interpretation. Rather, a model is a complex concept that is based on a set of criteria, one of which is an interpretation. Unfortunately, this is often ignored, so it appears necessary to define what a model is, what it consists of, and what it can or cannot do. In a general sense, a model is:

> a working hypothesis or precise simulation, by means of description, statistical data, or analogy, of a phenomenon or process that cannot be observed directly or that is difficult to observe directly. Models can be derived by various methods, e.g. by computer, from stereoscopic photographs, or from scaled experiments (AGI 1999).

Walker (1992), using stratigraphic models as an example, elegantly summarized the general criteria for a model, which must act as:

(1) a norm for purposes of comparison;
(2) a framework and guide for future observations;
(3) a predictor in new geological situations;
(4) an integral basis for interpretation of the environment or system that it represents.

Several so-called models do not fulfill these criteria but are merely interpretations. In addition, dolomite models must fulfill three specific criteria, i.e.

(5) *thermodynamic*: there must be supersaturation for dolomite, with variable saturation states for calcite and aragonite; replacement dolomite (dolomitization *sensu stricto*) requires undersaturation with respect to calcium carbonate; otherwise there will be dolomite cementation;

(6) *kinetic*: the rate of dolomite formation must be equal to or greater than the rate of calcium carbonate dissolution, otherwise there will be significant dissolution porosity up to the scale of megascopic karst;
(7) *hydrologic*: there must be long-lasting pore-water flow, preferentially with high Mg-content (an exception is Mg-supply via diffusion).

Several models have been published that fail one or more of these criteria specific for dolomitization. Some examples are discussed below.

The following sections critically evaluate the major dolomitization models, with emphasis on those dealing with the origin of the massive dolostones that commonly form hydrocarbon reservoir rocks and/or regional aquifers. Some of the less important models that deal with small amounts of dolomite formation, and are insignificant regarding the formation of reservoir rocks, are mentioned only briefly. These include the relatively well-researched and academically interesting lacustrine Coorong dolomite(s) (von der Borch 1976; Muir *et al.* 1980; Rosen *et al.* 1989), the microbial/organogenic dolomites, and most other penecontemporaneous dolomites. For more information on these types of dolomite see the summary articles by Last (1990), Budd (1997), and Mazzullo (2000).

This section contains a series of illustrations of flow mechanism and domains, and the resulting dolomite/dolostone bodies (Figs 19–23). Whitaker *et al.* (2003, 2004) recently emphasized that it may be misleading to conceptualize individual flow mechanisms in isolation, and that fluid flow in a geologic situation may be the product of a number of different drives acting simultaneously or consecutively. As a result, the dolomite bodies resulting from a single hydrologic drive, such as those shown in Figure 19, may also be misleading. This is correct in principle and should be kept in mind at all times. However, illustrations of amalgamated flow regimes and the resulting dolomitization would be confusing, and most probably there are dolostone bodies that originated from one predominant flow mechanism. Hence, the examples shown in the following figures are schematic illustrations of individual flow regimes and resulting dolomitization, as they would be expected from field data and circumstantial evidence, including the most relevant numerical models. The reader is referred to Whitaker *et al.* (2004) for a detailed evaluation of the various analytical and numerical models used to predict the patterns of groundwater flow, the rate and distribution of dolomitization resulting from groundwater flow, and the limitations of these types of models.

Penecontemporaneous dolomites and the microbial/organogenic model

Penecontemporaneous (synsedimentary) dolomites form very shortly after deposition, i.e. within a few years to tens of years, as a normal by-product of the geochemical conditions at the site of deposition. There are two preferred settings for penecontemporaneous dolomite formation, shallow marine to supratidal and hemipelagic to pelagic. In terms of diagenetic environments, these are near-surface settings (Fig. 18).

In shallow-marine to supratidal environments, penecontemporaneous dolomites commonly form in quantities of <5 vol%, mostly as Ca-rich and poorly ordered, microcrystalline to fine-crystalline cements, or directly from aqueous solution (see summary in Budd 1997). These occurrences include lithified supratidal crusts (e.g. Andros Island; Sugarloaf Key; Ambergris Cay); thin layers in salinas (e.g. Bonaire; West Caicos Island) and evaporative lagoons/lakes (e.g. the Coorong); fine-crystalline cements and replacements in peritidal sediments (e.g. Florida Bay; Andros Island). The dolomite-forming fluid is normal seawater and/or evaporated seawater, in some cases with admixtures of evaporated groundwater. There also are two examples of penecontemporaneous dolomite formation in association with volcanic activity: dolomite as a fine-crystalline supratidal weathering product of basic rocks (Capo *et al.* 2000), and hydrothermal dolomite forming at submarine vents (Pichler & Humphrey 2001). These cases have in common that the amount of dolomite formed is very small, and that it is well ordered and nearly stoichiometric.

One especially important type of penecontemporaneous dolomite forms lenses and layers of up to 100 vol% in sabkhas. Genetically, these dolomites belong to the family discussed in this section. However, they are considered separately below because of their historical significance, and because they have a genetic affinity to reflux dolomitization where sabkhas grade into evaporative lagoons.

Penecontemporaneous dolomites in hemipelagic to pelagic settings commonly form in very small quantities as microcrystalline protodolomite, generally less than 1 wt% (Lumsden 1988). However, under favourable circumstances the amount of dolomite locally

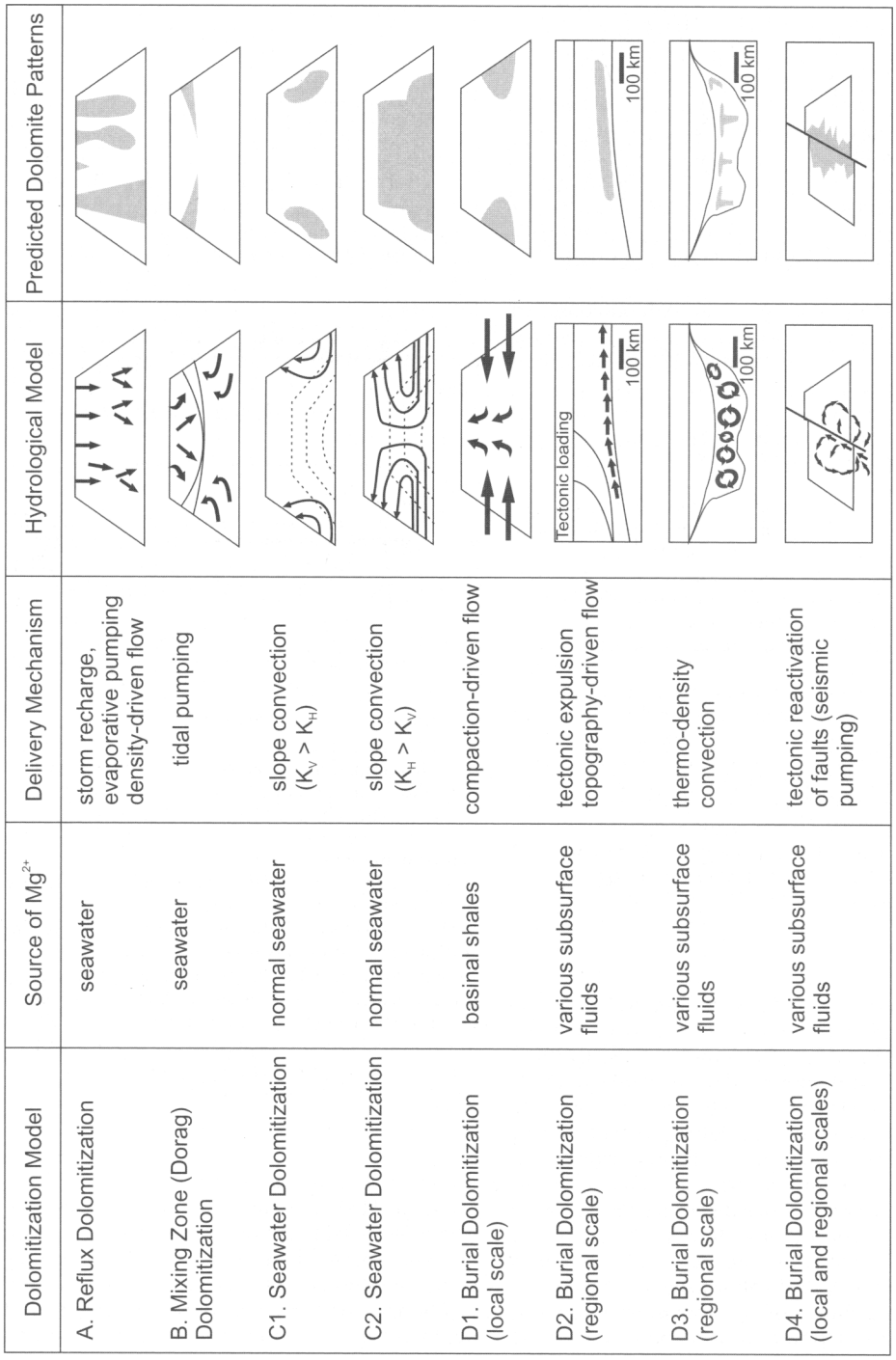

Fig. 19. Selected models of dolomitization, illustrated as groundwater flow systems and predicted dolomitization patterns. Examples are of incomplete dolomitization of carbonate platforms or reefs, i.e. they represent early phases of dolomitization. Arrows denote flow directions; dashed lines show isotherms. Predicted dolomitization patterns are shaded. Models A–D1 and D4 are kilometre-scale; models D2 and D3 are basin-scale. The figure is modified from Amthor *et al.* (1993).

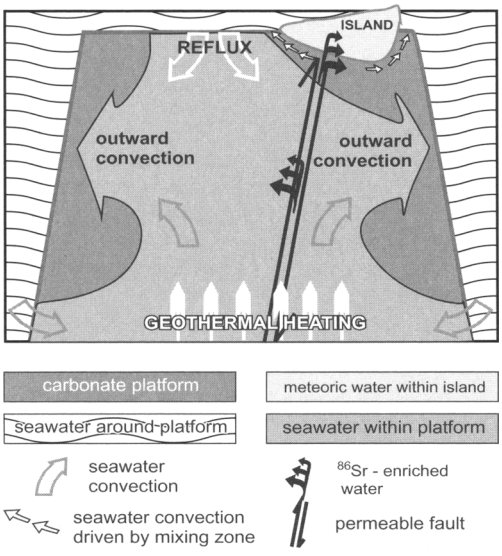

Fig. 20. Postulated seawater circulation systems capable of dolomitization in carbonate platforms and beneath islands. The diagram is not to scale, yet typically represents several hundred metres vertically and up to a few hundred kilometres laterally. There are at least four competing and/or interacting types of circulation: (1) thermal convection driven by heat from below; (2) density driven reflux caused by slight surface evaporation; (3) seawater convection driven by freshwater–seawater mixing around meteoric water lenses of islands; and (4) permeable faults/fractures in the crust, schematically shown as one deep-reaching fault, facilitate rapid ascent of fluids from the platform interior, possibly hydrothermal. The figure is reproduced with permission from Machel (2000), modified from similar diagrams in Vahrenkamp *et al.* (1991), Vahrenkamp & Swart (1994) and Whitaker *et al.* (1994).

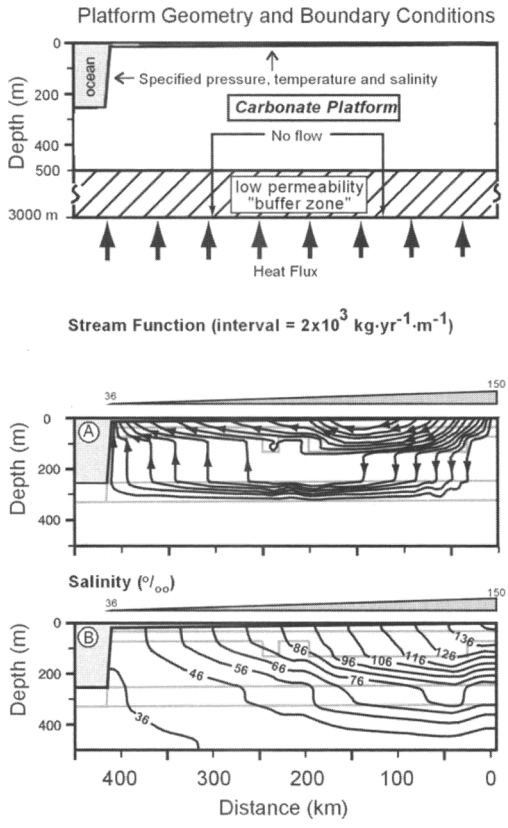

Fig. 21. Simulation boundary conditions (top) and modelling results (A and B) of reflux in a carbonate platform. The salinity at the top of the flooded platform ranges from marine (36 g l^{-1}) near the platform margin to mesohaline–hypersaline (150 g l^{-1}) near the shoreline. The platform contains a weak aquitard near its centre and has a strong aquitard as its base ('buffer zone'; note the change in vertical scale within this zone). (**A**) Fluid flux as stream function; (**B**) salinity distribution (g l^{-1}), after 500 000 years. The weak aquitard shows as a zone with little horizontal flow but is breached vertically. Most of the flow is within the upper and lower, highly permeable, parts of the platform. The diagram is modified from Jones *et al.* (2003).

reaches up to 100%. For example, Miocene hemipelagic carbonate sediments from the margin of the Great Bahama Bank are partially to completely dolomitized over a depth range of about 50–500 m subsea. In this setting, dolomite forms as a primary void-filling cement and by replacing micritic sediments, red calcareous algae and echinoderm grains (Swart & Melim 2000). Dolomites in these settings are prone to recrystallization because they tend to form as metastable protodolomites (e.g. Baker & Burns 1985; Malone *et al.* 1994; Mazzullo 2000).

Both settings of penecontemporaneous dolomite formation appear to be linked to the 'microbial' or 'organogenic' model of dolomitization (Vasconcelos & McKenzie 1997; Burns *et al.* 2000; Mazzullo 2000) that has its roots in the 'Organic theory' based on studies by Forchhammer (1850), Damour (1851), Ludwig & Theobold (1982), and Doelter & Hoernes (1875) that are reported by van Tuyl (1914). According to this model, dolomite may be formed syndepositionally or early post-depositionally and at depths of a few centimetres to a few hundred metres under the influence of, or promoted by, bacterial sulphate reduction and/or methanogenesis. The latter is commonly indicated by

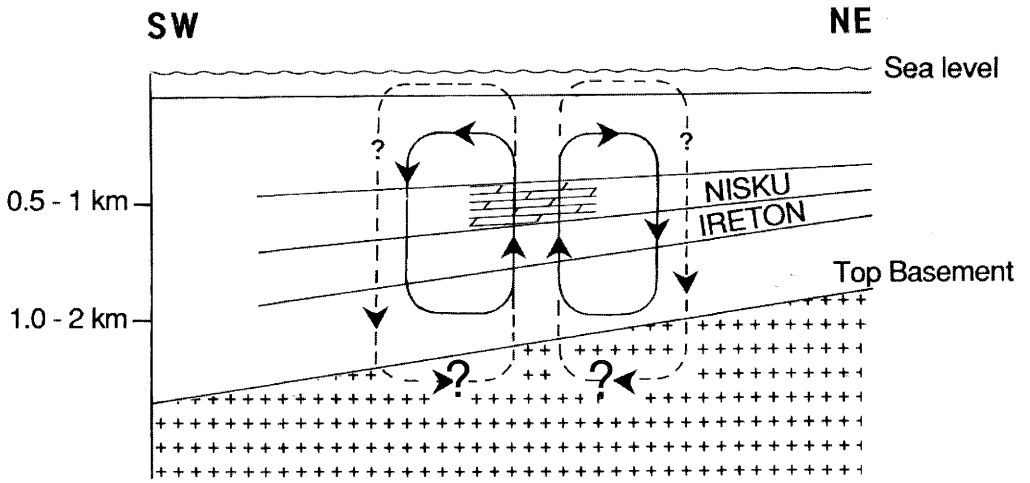

Fig. 22. Thermal convection half-cells that are open to seawater recharge only at the top. Note that thermal convection is assumed to take place only to a depth maximum of 2 km where the strata are still relatively permeable, and where the dolomitized part of the sequence (Nisku) is at shallower depths of ± 1 km, consistent with the recent modelling by Wilson *et al.* (2001). The figure is reproduced with permission from Machel & Anderson (1989); this paper speculated that the convection cells may have penetrated the uppermost parts of the basement, where it was permeable.

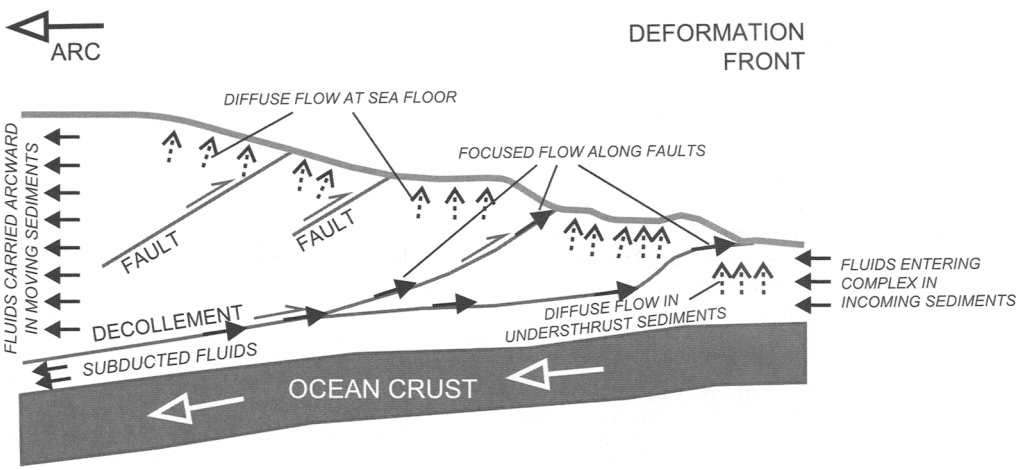

Fig. 23. Schematic cross-section of an accretionary prism/wedge and potential fluid pathways. Flow within the décollement and other faults may be spatially focused in dilated networks, temporally transient, or both. The figure is reproduced with permission from Machel (2000).

depleted $\delta^{13}C$ values. The exact role of microbial activity in reducing the notorious kinetic barriers to dolomitization is unknown, although it seems likely that a reduction of Mg- and Ca-hydration barriers or an increase in alkalinity, or a change in pH, is involved. Most microbial/organogenic dolomites are cements, but some are replacive, typically fine-crystalline–microcrystalline (less than 10 μm), calcic and poorly ordered protodolomites. The chief modes of Mg-supply are diffusion from the overlying seawater or release from Mg-calcites and clay minerals, and these place severe limits on the amounts of dolomite that can be formed.

Microbial/organogenic dolomites may act as nuclei for later, more pervasive, dolomitization during burial.

Hyposaline environments and the mixing zone model

Hyposaline environments are those with salinities below that of normal seawater (35–36 g l^{-1}). These environments include coastal and inland freshwater–seawater mixing zones, marshes, rivers, lakes, and caves. Post-depositional dolomite has been found to form in all of these environments, but only in small amounts and commonly as cements. Virtually all hyposaline environments are near-surface to shallow-burial diagenetic settings at depths of less than about 600–1000 m (Figs 16, 17A, and 18).

One hyposaline environment, the coastal freshwater–seawater mixing zone (often simply called the mixing zone) has given rise to one of the oldest and most popular models, the 'mixing zone model' for dolomitization. Dolomitization by brackish water in a freshwater–seawater mixing zones was first proposed by Hanshaw *et al.* (1971) on the basis of their study of a Tertiary carbonate aquifer in Florida. This concept was expanded to the status of a model by Badiozamani (1973), who coined the term 'Dorag model' and advocated that dolomite should form in massive amounts in those parts of mixing zones where the waters have much less than 50% seawater salinity down to about 5%. His rationale was a thermodynamic calculation of saturation states for dolomite and calcite, whereby the mixing waters were found to be supersaturated for dolomite yet undersaturated for calcite in the said salinity range. At the same time, Land (1973) proposed a mixing model on the basis of his study of dolomites in the Pleistocene Hope Gate Formation, Jamaica, advocating dolomitization by 'high P_{CO_2} meteoric waters and small amounts of seawater . . .' (Land 1973, p. 86).

For several years many authors invoked the mixing model to explain pervasive dolomitization of entire carbonate platforms of several hundreds to thousands of square kilometres in extent (e.g. Choquette & Steinen 1980; Dunham & Olson 1980; Xun & Fairchild 1987). In addition, modelling by Humphrey & Quinn (1989) suggested that coastal mixing zones may form thick sections of dolomite in platform-margin settings, and that such dolostones may be common in the geological record. Their model, however, was based on several incorrect assumptions (see discussion by Machel & Mountjoy 1990).

The mixing model has been highly overrated with regard to its potential to form massive dolostones. Not a single location in the world has been shown to be extensively dolomitized in a freshwater–seawater mixing zone, in recent or in ancient carbonates, and many lines of evidence indicate that massive dolomitization in mixing zones is so unlikely as to be virtually impossible (Hardie 1987; Smart *et al.* 1988; Machel & Mountjoy 1990; Melim *et al.* 2003). Although the waters in many mixing zones are thermodynamically supersaturated with respect to dolomite in at least a part of the mixing range (commonly between about 10 and 50% seawater), these waters also tend to be supersaturated with respect to calcite and/or aragonite in the same salinity range. Thus, the 'salinity window' of dolomitization is much smaller or does not exist, and model criterion (5) (above) is not fulfilled. Moreover, where the waters are supersaturated with respect to dolomite and undersaturated with respect to calcium carbonate, the dissolution rate of calcium carbonate is many times higher than the nucleation and growth rate of dolomite, hence model criterion (6) (above) is also not fulfilled.

The dominant diagenetic process in most typical freshwater–seawater mixing zones is extensive dissolution of calcium carbonate, often up to the dimensions of caves. This has been shown in many studies, especially from Florida and Yucatan (Back *et al.* 1986; Smith *et al.* 2002; Smart & Whitaker 2003; Whitaker *et al.* 2004), and was previously indicated by geochemical modelling (Sanford & Konikow 1989). Also, most coastal mixing zones are only a few hundreds of metres wide and the waters pass relatively quickly through the rocks in response to eustatic sea-level fluctuations and subsidence. This prevents a long-lasting supply of Mg, and model criterion (7) is not fulfilled. Even where mixing zones are capable of forming dolomite, the dolomitized rock volume tends to be relatively small and restricted to the platform margin(s) (Figs 19B and 20). If dolomite forms at all, it is commonly in comparatively minuscule amounts (a few vol%) that form in the more saline parts, i.e. more than 70% seawater, as thin cement fringes, replacements, or both.

Most mixing zone dolomites are petrologically and geochemically distinct. The crystals tend to be relatively clear, planar-e or planar-s, stoichiometric, well-ordered rhombs, although some mixing zone dolomite is non-stoichiometric and poorly ordered. Crystal sizes commonly range from 1 to 100 μm, but reach several

millimetres in some cases. Most mixing-zone dolomite occurs as cement in microscopic interstices and macroscopic voids, moulds, vugs and caverns, and subordinately as a replacement. Alternating generations or growth zones of calcite and dolomite are common in coastal mixing zones with rapid cyclical changes of salinity (Ward & Halley 1985).

The main role of coastal mixing zones in dolomitization might be that of hydrologic pumps for seawater dolomitization, rather than that of a geochemical environment favourable for dolomitization (Machel & Mountjoy 1990). Seawater is driven through the sediments both by the hydrologic action of freshwater–seawater mixing at the seaward margin of a coastal mixing zone, and by tidal pumping. Hence, over time, substantial amounts of seawater may pass through the sediments. Dolomitization would be facilitated by seawater in which the kinetic barriers to dolomitization have been sufficiently lowered, and extensive dissolution is absent. However, the mixing model, as originally proposed with waters of about 10–30% seawater, would form caves with very small amounts of dolomite.

Hypersaline environments and the reflux and sabkha models

Hypersaline environments have salinities greater than that of normal seawater and are widespread at latitudes of less than about 30°, although some occur at higher latitudes. Hypersaline environments thus defined include the so-called mesohaline (also called penehaline: Adams & Rhodes 1960) environments, which are mildly hypersaline, i.e. between normal seawater salinity (35–36 g l^{-1}) and that of gypsum saturation (about 120 g l^{-1}). In all these environments dolomite is formed from water in which the salinity is controlled by surface evaporation, that is, in near-surface and shallow-burial diagenetic settings (Fig. 18). However, the latest numerical modelling suggests that reflux dolomites may also form at intermediate burial depths, as discussed below.

Whereas most dolomites formed from evaporated seawater are post-depositional and form via reflux, a few are penecontemporaneous and form in sabkhas. The latter are discussed in this section because of the geochemical affinity of the two settings, and because sabkhas often grade into evaporative lagoons.

Reflux model. The (evaporative) reflux model, illustrated in various forms in Figures 5, 19B, 20 and 21, was originally proposed by Adams & Rhodes (1960) for seawater evaporated beyond gypsum saturation in lagoonal and shallow-marine settings on a carbonate platform behind a barrier, such as a reef. Surface-water circulation on such a platform is severely restricted because of the barrier, leading to evaporation and a landward salinity gradient. The evaporated seawater flows downward into and seaward through the platform sediments because of its increased density (i.e. active reflux), thereby dolomitizing the penetrated sediments.

This model was first applied to stratiform dolostones that extend over several hundred square kilometres in the Permian Basin of west Texas and New Mexico (Adams & Rhodes 1960). A few years later, this type of reflux was found 'in action' in the Pekelmeer, a lagoon on the island of Bonaire (Deffeyes *et al.* 1965), albeit on a much smaller scale of only a few square kilometres. The reflux model has since become one of the most popular and enduring models of dolomitization, often invoked to explain pervasive dolomitization of entire carbonate platforms and, on an even larger scale, of entire sedimentary basins (Shields & Brady 1995; Potma *et al.* 2001).

Early numerical modelling by Simms (1984) and Kaufman (1994) showed that mesohaline reflux is possible in principle, and is capable of forming dolomite. The latest numerical modelling has reinforced the viability and enlarged the scope of the model, while also placing limits on the possible extent of reflux dolomitization and the amounts of dolomite formed. Jones & Rostron (2000) and Jones *et al.* (2002, 2003, 2004) modelled evaporative reflux with concomitant dolomitization in a carbonate platform of several hundred kilometres width and about 3 km thickness. In the model the platform is flooded by seawater that increases in salinity from normal at the platform edge to 150 g l^{-1} at the coastline, similar to the conditions in the original reflux model of Adams & Rhodes (1960). Figure 21 illustrates these boundary conditions, along with representative distributions of stream lines and salinity contours within the platform. The distributions shown are established after 500 000 years and are representative of future time steps. Under the chosen conditions, the platform is penetrated by mesohaline 'active reflux' at depths that were not anticipated in the original reflux model, down to several hundred metres. Jones *et al.* (2002) also recognized a hitherto unknown type of flow that they termed 'latent reflux'. In their model, latent reflux is predicted to occur following the

cessation of brine generation at the platform top after flooding of the platform with seawater of normal salinity, such as after a significant rise in sea-level. Latent reflux is driven by the greater density of the earlier generated subsurface brines of reflux origin that continue to sink and disperse laterally. At the same time, seawater is entrained (sucked in from above) through the platform top. Latent reflux, like active reflux during brine generation, has the potential to form dolomite, albeit in much smaller amounts. This is because the brine and the entrained seawater together move more slowly and contain less Mg than a pure brine reflux system.

One might think that active plus latent reflux would dolomitize any carbonate platform rapidly and completely. Using realistic assumptions for repeated eustatic sea-level fluctuations that flooded the Devonian Grosmont platform episodically over a period of 1.6 Ma, near the maximum time available for reflux, Jones *et al.* (2003) found that the combined action of active and latent reflux could only form discrete layers of dolostone that alternate with undolomitized limestone. A platform can only be dolomitized completely if it has very high permeabilities and does not contain effective aquitards (such as shale or evaporite layers), and if reflux is permitted to persist for a relatively long time (Jones *et al.* 2003, 2004). At present it is not clear just how commonly such conditions are or have been realized in Nature. Also, it is to be expected that gypsum and/or anhydrite layers would form close to or at the sediment–water interface if the brines were evaporated past 120 g l^{-1} salinity. Such layers of calcium sulphate would tend to be effective aquitards and would thus supress deeply penetrating reflux and 'sucking in' of seawater during times of latent reflux, leading to near-surface brine and seawater runoff that would effectively inhibit dolomitization at greater depths (Machel *et al.* 1996*b*). Alternatively, evaporite aquitards could act to focus reflux at carbonate–evaporite interfaces, as proposed by Adams & Rhodes (1960) and observed on a small scale in the MacLeod Evaporite Basin (Logan 1987).

There are several examples of localities that were probably dolomitized by evaporative reflux, including the type location of the reflux model, the Permian carbonates of west Texas and New Mexico (Adams & Rhodes 1960). In these locations reflux was responsible for dolomitization of lagoonal carbonate sediments. These dolomites are fine to medium crystalline and matrix-selective, commonly with good–excellent fabric preservation, as illustrated in Figures 5 and 9. In addition, they may be intergrown with abundant gypsum and anhydrite in layers and nodules that appear to be cogenetic. This shows that the brines must have been evaporated past gypsum saturation, at least episodically. Recent case studies have shown that reflux can also form dolomite that is free of calcium sulphates, if the brines are mesohaline/penehaline. One example is the peritidal Jurassic carbonates of Gibraltar (Qing *et al.* 2001), formed in a situation corresponding to the model illustrated in Figure 21. Melim & Scholle (2002) investigated another example of apparent mesohaline reflux dolomitization, albeit much less extensive and restricted to fractures in the Capitan Reef, which forms a barrier at the platform margin of the Permian reflux model type location. Such dolomitization can be expected where the lagoonal, platform-interior sediments have been dolomitized almost completely near the surface, and where the dolomitizing fluids have either lost all their calcium sulphate, forming layers or nodules (as suggested above), or never reached gypsum saturation in the first place (Jones *et al.* 2003).

Whether active or latent, all refluxing brines exit at or near the platform margin (Machel *et al.* 1996*b*, 2002; Jones & Rostron 2000; Jones *et al.* 2002, 2003, 2004), and this confines reflux dolomitization to the platform. This recognition is important because some authors have invoked evaporative reflux beyond the platform margin and/or on a basin-wide scale (Shields & Brady 1995; Potma *et al.* 2001). This notion is clearly incorrect because it is physically and hydrologically impossible. The brines simply do not have enough energy to flow through the sediments and rocks beyond the platform margin (Machel *et al.* 1996*b*, 2002; Jones & Rostron 2000; Jones *et al.* 2002, 2003, 2004).

Sabkha model. The sabkha model is hydrologically and hydrochemically related to the reflux model yet differs in several important aspects. Sabkhas are intertidal–supratidal deflation surfaces that are episodically flooded. The sabkha of the Trucial Coast of Abu Dhabi is the type location of the sabkha dolomitization model. It is probably the best researched recent hypersaline intertidal–supratidal flat (Butler 1970; McKenzie *et al.* 1980; Patterson & Kinsman 1982; Müller *et al.* 1990; Baltzer *et al.* 1994), and is also representative of prolific reflux dolomite formation, as most sabkhas elsewhere produce much less dolomite.

In the Abu Dhabi sabkha, the Mg for dolomitization is supplied synsedimentarily (penecontemporaneously) by seawater that is propelled periodically onto the lower supratidal zone and

along remnant tidal channels by strong onshore winds. The seawater has normal to slightly elevated salinity (up to about 38 g l^{-1}) but becomes significantly evaporated beyond gypsum saturation on and within the supratidal flats, through which it refluxes via its increased density, similar to flow in the reflux model. Sabkhas undergo hydrological and hydrochemical cycles as a result of their episodic flooding. A full cycle consists of three phases (McKenzie *et al.* 1980): storm-driven flooding of the near-coastal supratidal flats (and tidal channels); capillary evaporation; and evaporative pumping. The hydrogeological characteristics of the Abu Dhabi sabkha have been confirmed in the study by Müller *et al.* (1990), which prompted these authors to rename the sabkha model the 'flood recharge–evaporative pumping model'. The last part of the cycle, evaporative pumping, briefly gained the status of an independent model (Hsü & Siegenthaler 1969; Hsü & Schneider 1973), but most researchers soon abandoned this independent status.

Sabkha dolomite appears to form via evaporative pumping in a narrow (1–1.5 km) fringe next to the strandline, and in flooded tidal channels that extend farther landward. The distribution of dolomite is uneven. In the Abu Dhabi sabkha, the best dolomitized parts contain from 5 to about 65 wt% protodolomite. Dolomite forms as a cement and aragonite is replaced, but lithification does not occur, or only partially. Dolomitization is restricted to the upper 1–2 m of the sediments and appears to be most intense where the pore waters become chemically reducing, leading to enhanced carbonate alkalinity via sulphate reduction and/or microbial methanogenesis. In this respect, sabkha dolomitization is related to the organogenic/microbial model of dolomitization (see above). Not surprisingly, therefore, sabkha dolomites are texturally and geochemically similar to organogenic dolomites in some respects; they tend to form as protodolomite and may have reduced carbon isotope ratios. However, the oxygen isotope ratios of sabkha dolomites tend to be enriched because of evaporation. Another difference is their association with gypsum and anhydrite, common in sabkhas but missing in hemipelagic and pelagic settings. Sabkha sulphates are formed as by-products of dolomitization in texturally distinctive varieties (nodules, chicken-wire). As a result of repeated eustatic and/or relative sea-level changes, sabkhas commonly form distinctive shallowing-upward cycles that consist of undolomitized shallow-marine or lagoonal sediments at the base, overlain by dolomitized intertidal algal mats that grade up into dolomitized supratidal sediments that contain sulphates (Butler 1970; McKenzie *et al.* 1980).

In most respects, the Abu Dhabi sabkha appears to be a good recent analogue for dolomitization in many ancient intertidal–supratidal flats, such as landward of the famous Permian Capitan Reef complex in Texas and New Mexico. Rather than forming reservoir rocks, these dolostones – including the associated evaporites – generally form tight seals for underlying hydrocarbon reservoirs (e.g. Major *et al.* 1988; Harris & Walker 1990; Machel & Longacre 2000). More generally, sabkhas and similar intertidal–supratidal depositional systems in more humid climates typically form small quantities of fine crystalline protodolomite in thin beds, crusts or nodules, either within the upper 1–2 m of sediment or at the sediment surface. Repeated transgressions and regressions may stack such sequences upon one another to cumulative thicknesses of several tens of metres.

Two ancient examples shed further light on the dynamics and potency of sabkha dolomitization. One is the aforementioned Permian carbonates of Texas and New Mexico. Mutti & Simo (1994) found that the efficiency of sabkha dolomitization was variable during transgression and regression, and suggested that dolomitization during transgressive cycles affected only the intertidal and supratidal facies, whereas during regression it affected supra-, inter- and subtidal facies. These authors also speculated that tidal pumping may have aided in supplying Mg. The other example is the Ordovician Knox Group in the Appalachians, USA, one of the best-documented cases of sabkha dolomitization in ancient carbonates. The Knox carbonates consists of multiple metre-scale dolomitized cycles that formed as a result of fourth- and fifth-order eustatic sea-level changes (Montañez & Reid 1992*a*, *b*; Montañez 1997). These authors found that the transgressive cycles were not dolomitized, whereas the facies within regressive cycles were almost completely replaced by tight fine-crystalline sabkha dolomite. Thus, the timing of dolomitization relative to sea-level fluctuations appears to differ from that in the Permian carbonates of Texas and New Mexico.

Seawater dolomitization

Post-depositional formation of massive dolostones can also be attributed to the 'seawater dolomitization model' or 'seawater dolomitization' (Purser *et al.* 1994). These terms have been

in common use for only about 10 years. Strictly speaking, they do not constitute or identify an independent dolomitization model. Rather, 'seawater dolomitization' refers to a group of models whose common denominator is seawater as the principle dolomitizing fluid, and that differ in hydrology and/or depth and timing of dolomitization. All dolomites in this group are post-depositional, and the diagenetic settings range in depth from shallow to intermediate burial (Fig. 18). Penecontemporaneous dolomites that formed in and from seawater are not part of this group of models but belong to the microbial/organogenic model discussed above.

Dolomitization by seawater appears to be a relatively recent addition to the array of dolomitization models. In modern times, Land (1985) was the first to advocate the notion that post-depositional dolomitization by seawater should be common in the geological record. In the 1980s this idea was unusual and other models were very much in vogue, as it was common and uncontested knowledge that the vast majority of modern marine environments are devoid of dolomite, suggesting that dolomite does not normally form from seawater because of kinetic inhibition. Thus, dolomitization from seawater was disregarded as a viable process by most authors, except for the formation of traces of penecontemporaneous, microcrystalline (proto-) dolomites that were known to form in some hemipelagic settings. However, Land (1985) recognized that seawater is by far the most common natural Mg-rich fluid, and that there had to be mechanisms to pump seawater through carbonates at considerable depths long after deposition, whereby the kinetic barriers to dolomitization are somehow reduced. This advance opened new avenues in dolomite research, now grouped as 'seawater dolomitization model(s)'.

The main credit for these 'models' of dolomitization must go to Dana (1843, again cited by van Tuyl 1914), who was the first to advocate alteration of calcite to dolomite by seawater for the dolomitic reef rock of the coral islands of the Pacific. In 1852, in discussing the origin of a dolomitic coral limestone from the Island of Metia, Dana stated (van Tuyl 1914, p. 275): 'We cannot account for the supply of magnesia except by referring to the magnesium salts of the ocean. It is an instance of dolomitization during consolidation of the rock beneath seawater'. In 1872 Dana extended his 'marine alteration theory' to evaporated seawater in lagoons, and in his *Manual of Geology* (1895) wrote: 'If this is the true theory of dolomite-making, then great shallow areas or basins of salt-pan character must have existed in past time over various parts of the continental area and have been the result of oscillation of the water level... The frequent alternation of calcite and dolomite strata would indicate alternations between the clear water and salt-pan conditions' (cited in van Tuyl 1914, p. 275). From today's point of view, Dana's insights are positively remarkable, as he was clearly almost 100 years ahead of his time. In the early 1900s the 'marine alteration theory' and its variants proposed by a number of other authors was the most popular of the then-existing models for the formation of dolomite (van Tuyl 1914). Skeats (1903, cited in van Tuyl 1914, p. 282) even provided a list of conditions favourable for the formation of dolomite masses that is almost identical to the list in use today, both in case studies and in numerical modelling:

(1) shallow water, between 0 and 150 feet in depth, and corresponding to a pressure of 1–5 atm;
(2) the presence of carbon dioxide in abundance, causing the partial solution of the limestones and the possibility of chemical interchange with the magnesium salts in seawater;
(3) porosity of the limestones, allowing percolation of seawater through the mass of the rocks;
(4) sufficiently slow subsidence of elevation to render the change from calcite to dolomite complete.

Curiously, dolomitization by seawater or evaporated seawater then went out of fashion, only to be rediscovered and embellished long after World War II in the models involving seawater that we recognize today.

The Cenozoic dolostones of the Bahamas platform, often used as an analogue for older dolomitized carbonate platforms elsewhere, can be considered the type location for seawater dolomitization. Petrographic and geochemical data indicate that seawater and/or chemically slightly modified seawater was the principle agent of dolomitization at shallow–intermediate depths and commensurate temperatures. The compositional modifications were caused by slight evaporation and/or water–rock interaction (Dawans & Swart 1988; Vahrenkamp *et al.* 1991; Vahrenkamp & Swart 1994). The hydrology of seawater during dolomitization is still very much contested. Various flow systems (summarized in Fig. 20) have been invoked to drive the large amounts of seawater needed for

pervasive dolomitization through the Bahamas platform: thermal convection (Sanford *et al.* 1998); a combination of thermal seawater convection and reflux of slightly evaporated seawater derived from above (Whitaker *et al.* 1994); or seawater driven by an overlying freshwater–seawater mixing zone during partial platform exposure (Vahrenkamp & Swart 1994), possibly layer-by-layer in several episodes (Vahrenkamp *et al.* 1991). Thermal convection is discussed below under 'burial models', as it necessarily occurs under considerable (at least intermediate: Fig. 18) burial, unless the heat source is a local hot spot, such as an igneous intrusion.

The Bahamas dolostones represent a hybrid with respect to the traditional, conventional classifications of models. Petrographic and geochemical data indicate seawater as the principal dolomitizing agent, yet thermal convection, as a hydrologic system and drive for dolomitization, is better classified under the burial (subsurface) models discussed below. Analogously, the regionally extensive Devonian dolostones in Alberta, western Canada, are also a hybrid. These dolostones probably formed at depths of 300–1500 m at temperatures of about 50–80 °C from chemically slightly modified seawater, and have been classified as burial dolostones (Amthor *et al.* 1993; Machel *et al.* 1994; Mountjoy & Amthor 1994; Mountjoy *et al.* 1999). The regionally extensive dolostones of the Carboniferous of Ireland that are petrographically and geochemically very similar to the Devonian dolostones of Alberta, and whose genesis has been interpreted in an analogous manner (Gregg *et al.* 2001), are another Palaeozoic example. In both cases, the hydrology that facilitated dolomitization is unclear, with thermal convection, reflux, compaction, tectonic expulsion, or a combination thereof as theoretically viable alternatives. Mesozoic examples of this type of dolomitization are the regionally extensive dolostones of the Cretaceous Soreq Formation in Israel investigated by Sass & Katz (1982). All of these Palaeozoic and Mesozoic dolostones can be (re-) classified along with the Cenozoic Bahamas dolostones as 'seawater dolomites'. This classification dilemma arises from the historical evolution of our understanding of these dolostones. This conflict does not invalidate the earlier 'burial' interpretations, which were and are correct.

van Tuyl (1914, p. 334) summarized the various examples of 'alteration theories': 'It is not possible to say in all cases whether the dolomitization took place while the limestone was still beneath the sea, through the agency of seawater, or after its emergence through the agency of ground water'. He was right.

Intermediate–deep burial (subsurface) environments and models

Burial (subsurface) environments are those removed from active sedimentation by burial, and in which the pore-fluid chemistry is no longer entirely governed by surface processes, i.e. where water–rock interaction has modified the original pore waters to a significant degree, or where the fluid chemistry is dominated by subsurface diagenetic processes. Such environments are found in intermediate–deep burial settings (Fig. 18) and are characterized by chemically reducing conditions. These are reflected in the mineralogy of redox-sensitive compounds, such as ferroan carbonates rather than nonferroan carbonates, iron sulphides rather than iron oxides, and hydrocarbons in fluid inclusions, stylolites, etc. (Machel 1999).

The textures, porosities and permeabilities of dolostones formed in intermediate- and deep-burial settings vary. Except for dolomite dissolution textures (Fig. 9), which appear to form largely in near-surface and shallow-burial settings permeated by meteoric water, matrix-selective dolomitization and related textures (Figs 6–8) are as common as in shallower diagenetic settings. Hence, these textures alone are not indicators of depth of burial. Three specific characteristics may be used:

(1) dolomites cross-cut by stylolites suggest burial of at least 600 m; stylolites in dolostones appear to require at least 600 m of burial, as implied by the studies of Lind (1993) and Fabricius (2000);
(2) development of nonplanar crystal textures and coarse planar textures at temperatures in excess of about 60 °C;
(3) the presence of saddle dolomite suggests temperatures of formation in excess of about 80 °C.

All burial (subsurface) models for dolomitization are essentially hydrological models. They differ mainly in the nature of the drives and direction(s) of fluid flow (e.g. Morrow 1982*b*, 1999). Four main types of fluid flow take place in subsurface diagenetic settings: (1) compaction flow; (2) thermal convection; (3) topography driven flow; and (4) tectonically driven flow. Combinations of these flow regimes and fluids are possible under certain circumstances. In addition, hydrothermal or

hydrofrigid fluids may be injected into any burial setting where fractures open up (Fig. 18).

Compaction model. The oldest burial model of dolomitization is the compaction model (Illing 1959; Jodry 1969). According to this model (Fig. 19D, showing only one variant of subsurface compaction flow), seawater or its subsurface derivative(s) buried along with the sediments are pumped through the rocks at several tens to several hundreds of metres as a result of compaction dewatering.

The compaction model in its original form was never especially popular because it rapidly became clear that burial compaction could generate only rather limited amounts of dolostone due to the limited amounts of compaction water (Morrow 1982*b*; Land 1985; mass-balance calculations for specific cases: Machel & Anderson 1989; Amthor *et al.* 1993). However, despite the mass-balance constraint, the compaction model remains a viable alternative for burial/subsurface dolomitization where focusing (funnelling) of the compaction waters through relatively small volumes of limestones is possible. This may happen on a local as well as on a regional–basinal scale. Jodry (1969) was the first to recognize the necessity of focusing and advocated this process for the dolomitization of Silurian reefs in Michigan that are encased in aquitards. Similarly, Machel & Anderson (1989) advocated focused compaction flow as one of two viable alternatives for dolomitization of Upper Devonian reefs in Alberta. On a regional–basinal scale, compaction flow in typical asymmetrical basins is mainly 'up and out' laterally through aquifers, and is cumulative along the flow path (e.g. Garven & Freeze 1984). Very high amounts of Mg can be supplied for dolomitization on this scale, especially where only a part of a geological unit is permeable, such as a carbonate platform margin into which the waters are focused (represented in Fig. 19D2). This may have happened in the several hundred kilometres long Cooking Lake platform margin with the overlying Rimbey–Meadowbrook reef trend in Alberta, Canada. The available data are consistent with focusing of compaction-driven seawater and/or longer-range expulsion of formation fluids from far down-dip where the foreland basin of the Antler Orogen was located (Amthor *et al.* 1993, 1994; Machel *et al.* 1994; Mountjoy & Amthor 1994; Mountjoy *et al.* 1999). This process may be much more common than generally recognized.

Thermal convection models. Thermal convection is driven by spatial variations in temperature that result in changes in pore-water density and thus effective hydraulic head. Variations in temperature may be due to elevated heat flux in the vicinity of igneous intrusions (Wilson *et al.* 1990), the lateral contrast between warm platform waters and cold ocean waters (Kohout *et al.* 1977), or lithology controlled variations in thermal conductivity, for example where carbonates are overlain by thick evaporites (Combarnous and Bories 1975; Wood and Hewett 1982; Phillips 1991; Jones *et al.* 2004). Thermal convection is classified as 'open', 'closed', or 'mixed' (Raffensberger & Vlassopoulos 1999).

Open convection cells (also called half-cells) may form in carbonate platforms that are open to seawater recharge and discharge laterally and at the top (Figs 19C1 & C2 and 20). This type of convection was first recognized in carbonate platforms by Kohout *et al.* (1977), and thus was named Kohout convection. It has been numerically modelled by Simms (1984), Kaufman (1994), Sanford *et al.* (1998), Wilson *et al.* (2001), and Whitaker *et al.* (2002, 2003, 2004). The most recent studies modelled dolomitization and/or calcium sulphate formation resulting from this type of thermal convection in reactive-transport simulations, and also considered platforms that are open to seawater recharge on one side only (platform geometry similar to that shown in Fig. 21). These studies found that the magnitude and distribution of permeability are the most important parameters governing flow and dolomitization, and that Kohout convection is active to a depth of about 2–3 km, provided that the sequence does not contain effective aquitards, such as (overpressured) shales or evaporites. One result of this modelling is especially noteworthy. Dolomitization is most favoured at the depth where the ambient temperature is around 50–60 °C, i.e. 0.5–2 km, depending on the geothermal gradient. Above this thermal regime the formation of dolomite is severely limited because of the low ambient temperatures, whereas at greater depths it is equally limited by very low permeabilities. In other words, below 2–3 km depth compaction has reduced porosity and permeability to levels that are too low to sustain viable convection cells. The models by Whitaker *et al.* (2002, 2003, 2004) also indicate that even at a moderate width of only 40 km, complete dolomitization in a 2 km-thick sequence takes about 30–60 Ma, much longer than most carbonate platforms remain laterally open to seawater recharge. Hence, most carbonate platforms, even if subjected to thermal convection by seawater, would at best get only partially dolomitized

during the time that they are open to seawater recharge.

Furthermore, numerical modelling by Jones *et al.* (2002, 2003, 2004) has shown that thermal convection is overpowered rather easily by reflux, where the latter is established due to surface evaporation (see Fig. 21 and the discussion above). Thus, whether or not open-cell thermal convection is established or leads to dolomitization depends mainly on the permeability distribution within the platform (especially the presence of effective aquitards), but also on the presence or absence of reflux, and the amounts of dolomite formed are constrained by the time the platform is open to seawater circulation.

Kohout convection, as defined above, is enhanced by basin to platform relief (Sanford *et al.* 1998), as shown in Figures 19 and 21, but is also predicted to occur in ramp situations with relatively shallow basins, like the Persian Gulf (Jones 2000). Open convection may occur in the absence of such topographic relief, i.e. far in the interior of an epeiric-scale platform. In this situation, the carbonate strata are open to recharge (and discharge) only at the platform top. Given significant variations in groundwater temperatures and sufficient permeability, it is conceivable that thermal convection could take place in such a situation, at least during shallow–intermediate burial (about 500–1500 m) while the strata are still highly permeable (Fig. 22). Based on circumstantial evidence, this type of open convection was advocated as an alternative for dolomitization of the Nisku reefs near the centre of the Alberta Basin (Machel & Anderson 1989). However, the conditions necessary for this type of open thermal convection await confirmation by appropriate modelling.

In this context, it is worth recalling that the four cases of regional platform and reef dolomitization noted previously (Bahamas, western Canada, Ireland, Israel) have similar petrographical and geochemical characteristics that point to seawater dolomitization of the bulk of the rocks at depths of about 500 m to at most 1–2 km, and temperatures of about 50–80 °C. These depths and temperatures happen to coincide with the depth and temperature range within which Kohout convection is most conducive to dolomitization (see above). The most sophisticated, recent modelling results thus confirm what has been inferred from petrographic–geochemical case studies of massive dolomitization for more than 15 years, i.e. a favourable environment exists for extensive dolomitization by seawater at temperatures of 50–60 (80) °C and commensurate depths of 0.5 to a maximum of 2 km. Hence, it appears likely that these carbonate platforms and reefs were indeed dolomitized by open thermal convection of seawater in one of the scenarios discussed above.

Significantly higher temperatures would favour higher convective fluxes, provided the rocks are permeable enough (Combarnous & Bories 1975; Wood & Hewett 1982; Phillips 1991). Thermal convection half-cells would thus be especially vigorous when a platform is underlain or penetrated by an igneous intrusion, which should result in especially fast and pervasive dolomitization. This appears to have happened in the Triassic Latemar reef in the Italian Alps (Wilson *et al.* 1990). The Latemar reef is dolomitized in a mushroom-shaped body in which oxygen isotope ratios and fluid-inclusion temperatures can be contoured to an underlying igneous intrusion, and in which replacive dolomitization appears to have occurred rapidly from seawater heated to about 200 °C.

Thermal convection can also occur in closed cells, referred to as 'free convection' by some authors (Fig. 19D3). In principle, this can happen in any sedimentary basin over tens to hundreds of metres thickness, provided that the temperature gradient is high enough relative to the permeability of the strata. As a rule of thumb, however, such convection cells will only be established and be capable of dolomitizing a carbonate sequence of interest if this sequence is of substantial thickness (several hundred metres), highly permeable and not interbedded with aquitards (Combarnous & Bories 1975; Wood & Hewett 1982; Bjørlykke *et al.* 1988; Phillips 1991). Such conditions are very rare in typical sedimentary basins, most of which contain effective aquitards. Furthermore, even if closed convection cells are established the amounts of dolomite that can be formed are severely limited, to an even greater extent than in compaction flow, by the pre-convection Mg-content, as no new Mg is supplied to the system. It appears, therefore, that extensive, pervasive dolomitization by closed-cell thermal convection is highly unlikely (Jones *et al.* 2003, 2004). Nevertheless, thermal convection of this type has been suggested, at least in principle, for pervasive dolomitization in carbonate platforms and regional carbonate aquifers (e.g. Morrow 1999).

Mixed convection is a variant of thermal convection and occurs when flow driven by an external hydraulic gradient interacts with thermal convection cells (Raffensberger &

Vlassopoulos 1999). Under such conditions Mg can be supplied to otherwise closed convection cells, thus increasing the potential for dolomitization (see Whitaker *et al.* 2004).

Topography driven model. Topography driven flow takes place in all uplifted sedimentary basins that are exposed to meteoric recharge on scales from a few tens of kilometres to that of whole basins (Tóth 1988; Garven 1995). Porewater flow geometrically resembles the pattern shown in Figure 18 (allowing for the assumption, made here for illustrative simplicity, that the subsurface is hydrologically isotropic and homogeneous). With time, topography can drive enormous quantities of meteoric water through a basin, commonly concentrating it by water–rock interaction (especially salt dissolution), and preferentially focusing it through aquifers. However, volumetrically significant dolomitization can take place only where meteoric water dissolves enough Mg en route before encountering limestones. This does not appear to be common. At present there are no proven cases of extensive dolomitization via topography driven flow, with the possible exceptions of Cambrian carbonates in Missouri (Gregg 1985) and Cambrian–Ordovicain carbonates in the southern Canadian Rocky Mountains (Yao & Demicco 1995). It appears that these strata may have been affected by vigorous topography driven flow, but insufficient evidence is available to demonstrate that the flow system(s) contained enough Mg for regional dolomitization.

Tectonic (squeegee) model. Another type of flow that has been suggested to result in pervasive dolomitization is tectonically driven squeegee-type flow (Oliver 1986). In this type of flow system, metamorphic fluids are expelled from crustal sections affected by tectonic loading so that basinal fluids are driven towards the basin margin (Fig. 19D2). Such fluids could be injected into compactional and/or topography driven flow, with attendant fluid mixing. Tectonically driven flow was invoked by several authors to explain extensive dolomitization. These include Dorobek (1989) for the Siluro-Devonian Helderberg Group, USA, and Drivet & Mountjoy (1997) for Devonian reefs in western Canada. Similarly, Montañez (1994) invoked extensive burial dolomitization via tectonic loading in Ordovician carbonates in several thrust sheets of the southern Appalachians. However, it is unlikely that tectonically-induced flow, or the related fluid mixing, form massive replacive dolostones. Modelling studies have shown that squeegee-type flow systems have low fluxes that are short lived (e.g. Deming *et al.* 1990), which has been affirmed by diagenetic studies (Machel & Cavell 1999; Machel *et al.* 2000; Buschkuehle & Machel 2002). This effectively precludes extensive dolomitization via squeegee flow. On the other hand, if the squeegee fluids are hot and flow relatively fast, and if they encounter highly porous pre-existing dolostones, the latter may significantly recrystallize, such that the textures and geochemistry reflect the hot recrystallization event rather than the original dolomitization event. This appears to have happened in the Ordovician carbonates discussed by Montañez (1994), where squeegee fluids, originally undersaturated with respect to dolomite, invaded the Knox dolostones that were partially dissolved and then recrystallized.

The same argument must apply to a new variant of the squeegee model proposed by Machel (2000) for accretionary prisms (Fig. 23). It has been shown that there is substantial porewater flow in such geological settings, as indicated in Figure 23, and that some isotopically distinct dolomite can be formed in this way (Machel 2000). However, the amount of dolomite that can be produced is limited by the same mass-balance constraints calculated for the compaction model (see above).

High-temperature and hydrothermal dolomitization. Convection cells invariably have rising limbs that penetrate the overlying and cooler strata, linking thermal convection to hydrothermal dolomitization. However, as in dolomitization by seawater, hydrothermal dolomitization is not a model in its own right because hydrothermal conditions may occur in a variety of situations in all types of diagenetic settings from near surface to deep burial, especially where fractures transgress more than one burial-diagenetic zone (Fig. 18, left).

The possibility of hydrothermal dolomitization dates back to the earliest days of dolomite research. In 1779, 12 years before the mineral dolomite was properly defined, Arduino (cited in van Tuyl 1914, p. 288) mentioned a magnesian limestone that he believed to have been formed by alteration of ordinary limestones by volcanic activity. Then Heim (1894) and several others (cited in van Tuyl 1914, pp. 289–290) advocated dolomitization by volcanic vapours or water-bearing magnesia, and these types of dolomitization were summarized under a 'pneumatolytic alteration theory' (van Tuyl 1914). In all cases thus classified at the time, volcanics were near the sites of dolomitization.

It is not clear when the term 'hydrothermal' was first used in the context of dolomitization, but it is frequently misused, giving rise to the relatively new bandwagon of 'hydrothermal dolomitization' on the scale of entire sedimentary basins. Most commonly, dolomites are called hydrothermal on the basis of two observations: (a) the dolomite is saddle dolomite (e.g. Davies 1997, 2002); or (b) the dolomite, whatever its texture, is associated with base metal mineralization (e.g. Auajjar & Boulègue 2002). Both observations are insufficient for a viable identification of hydrothermal activity.

Using White's (1957) time-honoured definition of hydrothermal, including Stearns *et al.*'s (1935) requirement for a 'significant' temperature difference of at least 5–10 °C, a mineral can be described as '*hydrothermal*' only if it is demonstrated to have formed at a temperature that was 5–10 °C higher than the temperature of the surrounding strata, regardless of fluid source or drive. If a mineral was formed at or near the same temperature as the surrounding rocks (within 5–10 °C), it can be described as 'geo*thermal*', whatever the geothermal gradient. The qualifier 'geothermal' may be omitted, unless special emphasis needs to be placed on the geothermal nature of a particular mineralization event. Minerals formed at temperatures significantly lower than ambient (by >5–10 °C) can be described as '*hydrofrigid*', even if they formed at a rather high temperature (Machel & Lonnee 2002).

There are well-documented examples of hydrothermal dolomite on a local as well as on a regional scale. Most are rather small and restricted to the vicinity of faults and fractures and/or localized heat sources (Fig. 19D4). One striking case of this type is the Pb–Zn-mineralized Navan dolomite plume in Ireland (Braithwaite & Rizzi 1997), another is the dolomitized plume of the Latemar build-up in the Italian Alps (Wilson *et al.* 1990). There are also examples of larger scale, even regionally extensive, hydrothermal dolomitization (e.g. Spencer-Cervato & Mullis 1992; Qing & Mountjoy 1992, 1994; Duggan *et al.* 2001) (Fig. 24).

Unfortunately, examples of misinterpretations of hydrothermal dolomitization abound. Dolomite is commonly syngenetic with base-metal minerals in hydrothermal systems, but this is no justification for assuming that all dolomite(s) formed in association with base-metal mineralization are hydrothermal. A study by Auajjar & Boulègue (2002) of dolomites in Liassic rocks of Morocco illustrates this issue. Three paragenetically different dolomites were interpreted as hydrothermal, but only their dolomite type 2 is associated and probably syngenetic with Pb–Zn sulphides. The other two 'hydrothermal dolomites' are not associated with sulphides, and unfortunately no palaeotemperature data have been provided for these dolomites or for their host rocks. On a larger scale, Davies (1997, p. 59) asserted that an 'HTD (hydrothermal dolomite) overprint in Devonian carbonates in Alberta ... often attributed to burial "matrix" processes may be the product of hydrothermal fluid migration'. There is no credible evidence for most of these dolomites being hydrothermal in origin and/or having a hydrothermal 'overprint', except for isolated cases, such as in the Wabamun Group and the Keg River Formation, which are, respectively, in the upper and lower of the four stratigraphic levels of the Devonian (Machel & Lonnee 2002).

Furthermore, hydrothermal dolomitization must be separated from hydrothermal alteration of pre-existing dolomites. Hot and/or hydrothermal fluids often ascend via faults in geologically short time spans and with relatively low fluxes (compared to the overall rock volume outside of the fractures). If such fluids are undersaturated with respect to dolomite, which is not uncommon, they will lead to dissolution and recrystallization of pre-existing dolostones that make up the wall rocks, analogous to the case of deep burial dissolution and recrystallization in the squeegee system discussed by Montañez (1994). A good example of this type of hydrothermal alteration originating from fault systems is in Devonian carbonates of western Canada (Lonnee & Machel 2004).

Texturally, most high-temperature and hydrothermal dolomites are distinct. First, most dolomite replacing limestone at temperatures in excess of about 60 °C is medium–coarse crystalline, nonplanar and/or planar with a relatively narrow size distribution. As Sibley & Gregg (1987) and Gregg (2004) pointed out, similar textures and crystal size distributions also result from recrystallization of older, low-temperature dolomites. Hence, these textures by themselves are not indicative of limestone replacement or dolomite recrystallization. However, textures such as those shown in Figures 11 and 12 may be taken as evidence for high-temperature dolomitization, rather than dolomite recrystallization. This is because high-temperature replacement of limestone, whether hydrothermal or not, tends to be fabric-obliterative, as discussed previously. Furthermore, much if not most high-temperature dolomite, especially when grown as

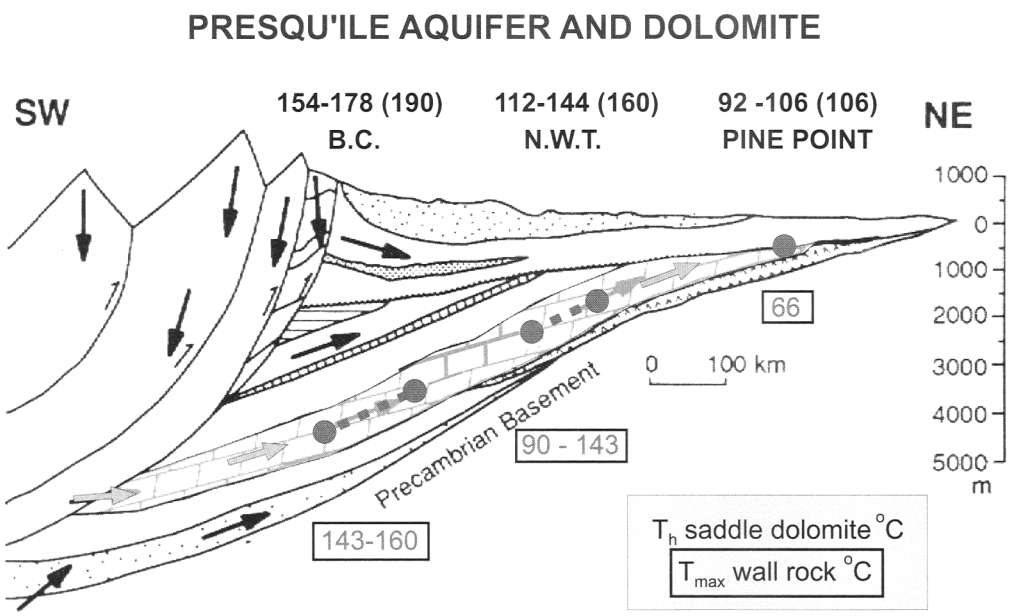

Fig. 24. Hydrothermal Presqu'ile saddle dolomite aquifer. The figure is modified from Qing & Mountjoy (1992, 1994).

cement into macropores, is saddle dolomite. This does not mean, however, that all saddle dolomite is hydrothermal. It can be formed in at least three ways: i.e. from advection (fluid flow); local redistribution of older dolomite during stylolitization; and as a by-product of thermochemical sulphate reduction in a closed or semi-closed system, as discussed above. Only the first and the last of these possibilities have a chance of being hydrothermal.

Reimer & Teare (1992) and Reimer *et al.* (2001) proposed that breccias cemented with saddle dolomite encased in limestone formed in a so-called 'HTD-furnace' ('hydrothermal dolomite furnace'), and that thermochemical sulphate reduction (TSR) initiated and promoted such dolomitization. This 'TSR–HTD model' is partially based on the notion that TSR is exothermic (Reimer & Teare 1992; Reimer *et al.* 2001). However, such saddle dolomite bodies are likely to be hydrofrigid where associated with TSR, and TSR did not initiate such dolomitization. First, it is not justified to assume that all or even most TSR settings are hydrothermal. Simpson *et al.* (1996) and Simpson (1999) have shown that TSR is probably endothermic in many, if not most, cases. Secondly, most TSR settings are closed or nearly closed hydrodynamically (e.g. Machel 2001), whereas dolomitization requires an open system because of the requirement to deliver Mg. At best, TSR may coincide with dolomitization in such a setting and add some oxidized carbon to the saddle dolomite. On the other hand, where brecciated dolomite bodies such as those discussed by Reimer & Teare (1992), Reimer *et al.* (2001), and seen in many MVT occurrences (Gregg 2004), formed without the involvement of TSR, and where dolomitization was caused by fluid flow ascending through faults, saddle dolomite bodies are commonly hydrothermal.

Secular distribution of dolostones

The relative abundance of dolostones that originated by the replacement of marine limestones appears to have varied cyclically through time. Early data suggested that dolomite was most abundant in rocks of the early Palaeozoic systems and decreased in abundance with time (van Tuyl 1914, table 1, with a reference to Daly 1909). Relatively recent reassessments of the dolomite distribution throughout time reveal discrete maxima of 'significant early' dolomite formation, i.e. massive early diagenetic replacement of marine limestones, during the Early Ordovician–Middle Silurian and the Early Cretaceous (Given & Wilkinson 1987). Furthermore, it is well known from geologically young carbonate platforms, such as the Bahamas Bank,

that marine carbonate rocks younger than about the late Pliocene are almost devoid of dolomite.

The reason(s) for the secular variations in dolostone abundance throughout the Phanerozoic are much debated. Various explanations have been proposed, including periods of enhanced 'early' dolomite formation related to or controlled by plate tectonics that changed the compositions of the atmosphere and seawater, such as increased atmospheric CO_2 levels, high eustatic sea levels, low saturation states of seawater with respect to calcite, changes in the marine Mg/Ca ratio or low atmospheric O_2 levels that coincided with enhanced rates of bacterial sulphate reduction (see discussions in Stanley & Hardie 1999; Burns *et al.* 2000). It appears possible that a combination of two or more of these factors were involved. Perhaps the most elegant explanation was recently provided by Nordeng & Sibley (2003) who interpreted the notable absence of dolomite in carbonates younger than late Pliocene in the Bahamas Bank as a result of the lengthy induction period for dolomite formation. According to Nordeng & Sibley (2003), Bahamas carbonates older than late Pliocene are dolomitized because they remained in contact with the dolomitizing solution (seawater) long enough to exceed the induction period. On the other hand, carbonates younger than late Pliocene have not been in contact with seawater long enough, and any metastable precursors to dolomite that may have formed were readily destroyed by freshwater diagenesis during several intervening periods of exposure. This interpretation, if true, may also explain the secular variations in dolomite in the earlier Phanerozoic. Mesozoic and Palaeozoic variations in marine dolomitization may simply reflect periods of seawater contact longer or shorter than the induction period.

Summary and conclusions

(1) The thermodynamic conditions of dolomite formation are well known. The kinetics of dolomite formation are relatively poorly understood, although it is clear that there are significant kinetic barriers to formation below about 50 °C.

(2) Mass-balance calculations necessitate advection for extensive dolomitization, and this is why all models for the genesis of massive dolostones are essentially hydrological models. The exceptions are natural environments where carbonate muds or limestones can be dolomitized by diffusion of magnesium from seawater rather than by advection.

(3) The replacement of shallow-water limestones, the most common form of dolomitization, results in a series of distinctive textures that often form in a sequential manner with progressive degrees of dolomitization.

(4) Many dolostones have higher porosities than limestones, and this may be the result of several processes. There also are several processes that destroy porosity and which vary in importance from place to place. The evolution of permeability during dolomitization is also variable. Generalizations are difficult.

(5) A wide range of geochemical methods may be used to characterize dolomites and dolostones, and to decipher their origins. Of particular interest are those methods that can be used to identify the direction of fluid flow during dolomitization.

(6) Dolomites that originally form very close to the surface and/or from evaporitic brines tend to recrystallize with time and during burial. On the other hand, those that form at several hundred to a few thousand metres depth are not, or hardly, prone to recrystallization.

(7) Penecontemporaneous dolomites commonly form only small amounts (a few per cent) of microcrystalline dolomite. Many, if not most, penecontemporaneous dolomites appear to form through the mediation of microbes.

(8) Virtually all volumetrically large, replacive dolostones are post-depositional and form during some degree of burial.

(9) In its original form the mixing model of dolomitization does not provide a viable explanation for the formation of massive dolostones.

(10) Dolomitization can occur in hypersaline environments and below, either via reflux in subtidal environments (reflux model) or via reflux and/or evaporative pumping in intertidal–supratidal environments (sabkha model).

(11) Seawater dolomitization is not an independent model. Rather, the various possibilities of dolomitization by seawater form a group of models that have seawater in common as the principle source of Mg.

(12) Thermal convection in open half-cells (Kohout convection) can form massive dolostones only under favourable circumstances. Thermal convection in closed cells cannot form massive dolostones.

(13) Compaction flow cannot form massive

dolostones, unless it is funnelled. The latter may be more common than is generally recognized.

(14) Neither topography driven nor tectonically induced flow (squeegee-type) are likely to form massive dolostones, except under highly unusual circumstances.

(15) The regionally extensive dolostones of the Bahamas (Cenozoic), Israel (Mesozoic), western Canada and Ireland (Palaeozoic), can be classified both as seawater dolomites and as burial dolomites. This apparent ambiguity is a consequence of the historical evolution of dolomite research.

(16) Hydrothermal dolomitization is not an independent model. Rather, hydrothermal fluids may occur in a variety of overlapping diagenetic settings.

(17) The secular distribution of dolostones that replaced shallow-marine limestones is uneven throughout the Phanerozoic. The reasons for this phenomenon are not clear.

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