Geoscience Canada

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Volume 9, Number 1, March 1982

URI: https://id.erudit.org/iderudit/geocan9_1art02

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Publisher(s)

The Geological Association of Canada

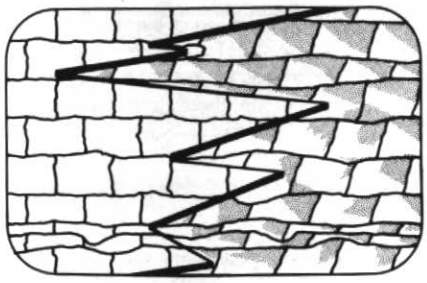
ISSN

0315-0941 (print)
1911-4850 (digital)

Explore this journal

Cite this article

Morrow, D. W. (1982). Diagenesis 1. Dolomite - Part 1: The Chemistry of Dolomitization and Dolomite Precipitation. *Geoscience Canada*, *9*(1), 5–13.



Diagenesis 1. Dolomite - Part 1: The Chemistry of Dolomitization and Dolomite Precipitation

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Introduction

Dolostones form a large part of the Proterozoic and Phanerozoic successions in many areas of Canada but are particularly abundant in lower Paleozoic strata (Fig. 1). These strata are predominantly carbonate unlike the overlying Mesozoic and underlying Proterozoic strata that are dominated by terrigenous sediments. This reflects the fact that during early Paleozoic time Canada was part of the Laurentian landmass that was situated in the tropical equatorial belt (Ziegler *et al.*, 1979). The economic importance of dolostones parallels their abundance in the stratigraphic record (Fig. 1). Dolostones form important reservoirs for oil (e.g., the Leduc Formation or D3) and gas (e.g., Manetoe Facies, Fig. 2) and are the main host rock in Canada for lead-zinc mineral deposits (e.g., the Presqu'ile Facies of the

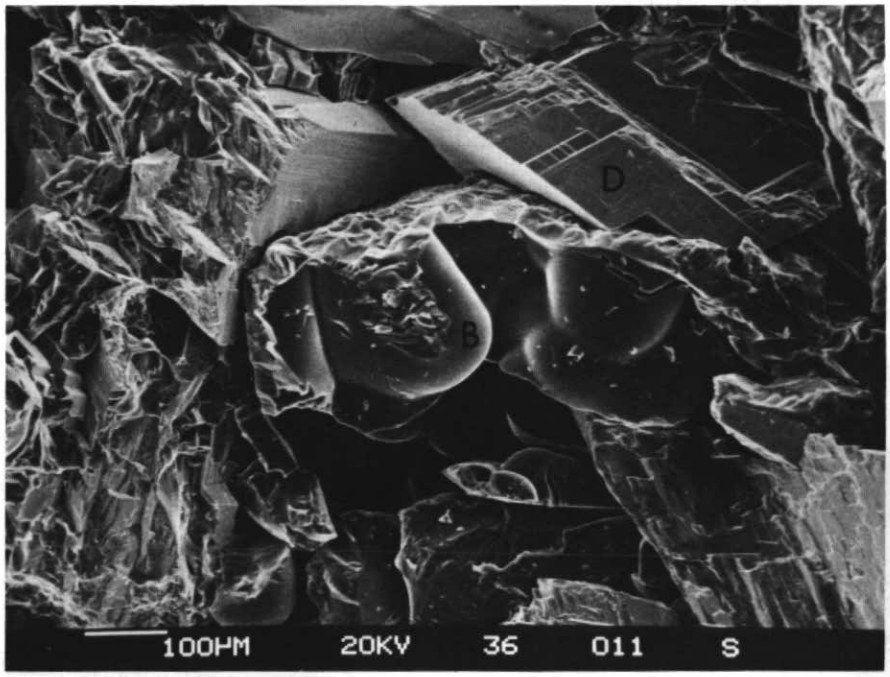

Figure 2 *An SEM photomicrograph of the gas-bearing dolomite of the Manetoe Facies in the Yukon and Northwest Territories. Well-formed (i.e. idiotopic) crystals of white dolomite (D) project into a vug that is lined in part by reniform bitumen (B). The surrounding dolomite has very low porosity and permeability.*

	WESTERN REGION		SOUTHEASTERN CANADA AND OFFSHORE	ARCTIC CANADA
TRIASSIC-JURASSIC	1 CHARLEY LAKE		1	
PERMIAN	1		(LODGEPOLE)	
MISS.-PENN.	5 TURNER VALLEY			
DEVONIAN	31 PRESQU'ILE, MANETOE, KEG RIVER, WINNIPEGOSIS, LEDUC, NISKU, GROSMONT, (SWAN HILLS), (PINE POINT)		2 (DUNDEE AND LUCAS)	3
SILURIAN	16	CANADIAN SHIELD	17 GUELPH	2 ALLEN BAY (BLUE FIORD)
ORDOVICIAN	9 WHITTAKER	2	9 (TRENTON) (ST. GEORGE)	2 (THUMB MOUNTAIN)
CAMBRIAN	11		6 THERESA	8
PROTEROZOIC	3+ unnamed parts of 4 groups	7+ unnamed parts of 5 groups	1	5 SOCIETY CLIFFS

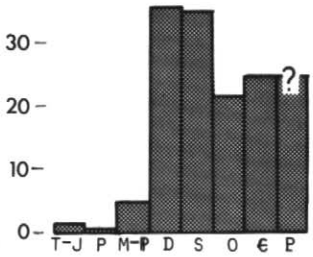

Figure 1 *A chart showing the numerical distribution of Canadian dolostones that have been formally named. Units that are named in the chart have economic importance both as reservoirs for oil and gas or as hosts for Pb-Zn deposits. Names in brackets are partly dolomitized limestone units in which the dolomite phase has economic importance.*

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Pine Point deposit). The importance of dolostones in Canada is a true reflection of the world wide importance of dolostones as reservoirs for hydrocarbons and as hosts for lead-zinc deposits (e.g., see Davies, 1979 and Macqueen, 1979).

Given the major, albeit indirect, role that the mineral dolomite has played in contributing to the well being and growth of the Canadian and world economies one might assume that the salient facts concerning the process of dolomitization and the precipitation of dolomite are well established. Unfortunately, although there is a considerable amount of experimental and theoretical data concerning the chemistry of the dolomitization process and the precipitation of the mineral dolomite from solution, no concensus exists regarding the general chemical conditions required for the dolomitization process. The absence of a widely accepted theory concerning the chemistry of dolomitization is due primarily to the difficulty in precipitating dolomite from appropriate solutions at temperatures less than 100° C. This has prevented direct interpretation of the physico-chemical conditions that prevailed during the precipitation of most dolostones in nature with the exception of those that were formed at high temperature. The inability to precipitate dolomite under controlled laboratory conditions constitutes the essence of the problem of the origin of dolomite.

The interpretation of the origin of a particular dolostone is therefore dependant upon inferences that are derived mainly from comparisons with a variety of dolomitization models, such as the Evaporative Pumping Model, the Reflux Model, the Coorong Model, the Solution-Cannibalization Model, the Mixed-Water or Dorag Model, the Compaction Model and other, less commonly encountered ones. These models will be discussed in a following paper on dolomite entitled *Dolomitization Models and Ancient Dolostones*. Taken together, they present a bewildering complexity of choice and it is commonly not apparent or universally agreed upon as to what are the essential features of these models that renders them agents of dolomitization (e.g., high Mg/Ca solution ratios, low salinities, high salinities, high [CO_3^{2-}], large organic content) or even why such features promote dolomitization. For example, does a lowering of salinity favour dolomitization from a kinetic standpoint (Folk and Land, 1975) or largely from a thermodynamic standpoint (Badiozamani, 1973)? It is not sufficient merely to state that a drop in salinity promotes dolomitization, we must know why and under what circumstances this is true if we are to make full use of this insight in our interpretations. In other words the formidable array of current models for dolomitization is not clothed by any certain or complete understanding of the precipitational conditions of the mineral dolomite and, like the emperor who had no clothes, it stands before us embarrassingly naked. In this review, I will assemble and stitch together like some demented tailor, the experimental, field and theoretical evidence concerning the chemistry of dolomitization into what I hope will pass as an example of sartorial elegance.

Dolomite Crystal Structure and Compositional Variability

The mineral dolomite has an ideal chemical composition of $CaMg(CO_3)_2$ and a symmetry structure $\bar{3}$ in the trigonal subsystem of the hexagonal crystal stystem. The unit cell is a rhombohedron elongate parallel to the "c" crystallographic axis (Fig. 3) similar to that of calcite but more highly ordered, and has a lower degree of symmetry because of the substitution of magnesium atoms for half of the calcium atoms. Like calcite, the dolomite crystal is built up of layers of cations (Ca^{2+}, Mg^{2+}) alternating with anions (CO_3^{2-}) perpendicular to the c-axis direction with the distinction that half of the cation layers are magnesium layers. It is this regular alternation of calcium and magnesium layers with intervening carbonate layers that uniquely characterizes the mineral dolomite.

Dolomite crystals in nature and those synthesized experimentally are better represented by the formula $Ca_{(1+x)}Mg_{(1-x)}(CO_3)_2$ and commonly depart considerably from an ideal composition and structure. Three distinct factors contribute to this departure.

The degree of order of a compositionally ideal (i.e., stoichiometric) dolomite crystal is affected by the degree to which calcium and magnesium are segregated into their respective layers. If calcium atoms from calcium layers are inter-

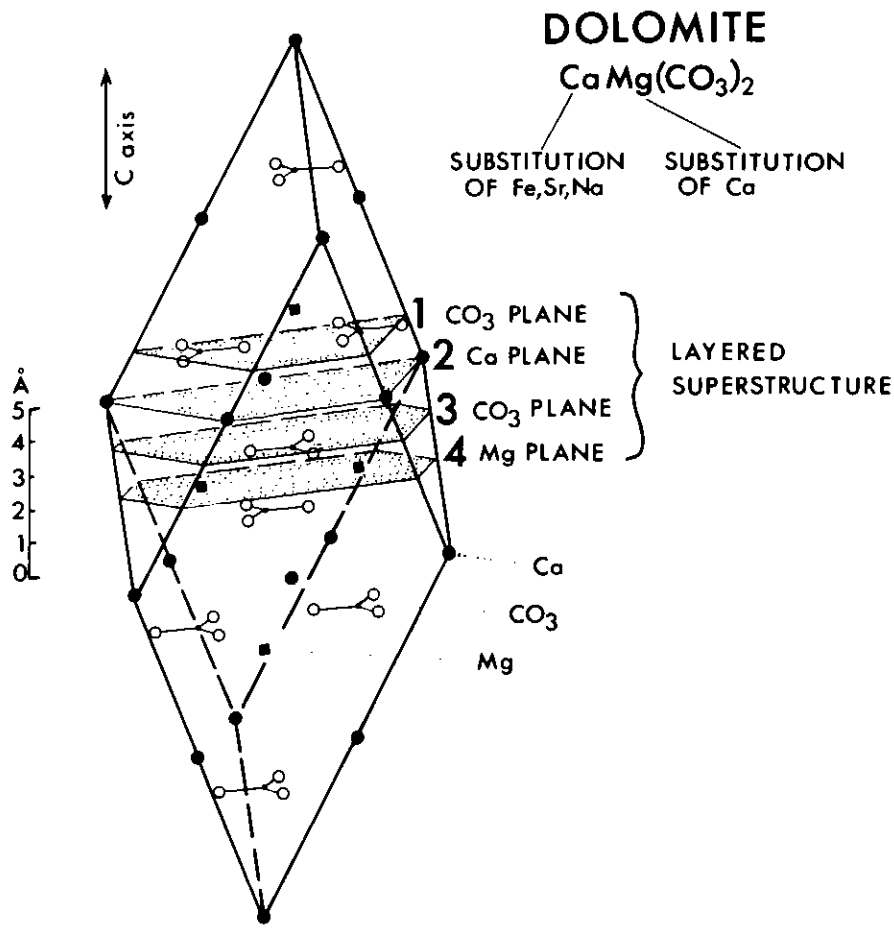

Figure 3 *Diagram of four rhombohedral unit cells of dolomite showing its layered superstructure perpendicular to the "c" axis direction composed of regularly alternating sheets of calcium, magnesium, and carbonate. Commonly Ca and Mg are incompletely segregated into their respective layers and there is an excess of calcium. Also many foreign ions substitute for calcium. These defects affect the thermodynamic properties of dolomite.*

changed with an equal number of magnesium atoms from magnesium layers the degree of order of the crystal is lowered although its composition is unaffected. Most natural dolomites display some degree of mixing of calcium and magnesium between cation layers (Goldsmith and Graf, 1958; Carpenter, 1980). Secondly, dolomites commonly depart from a stoichiometric composition because of an excess of calcium which is accomodated in the magnesium layers (Goldsmith and Graf, 1958; Lumsden and Chimahusky, 1980). Finally, a multitude of cations, primarily Fe, Sr, Na and Mn, substitute for calcium in many dolomites (e.g., Veizer *et al.*, 1978). Iron in particular may be present in concentrations of up to 4 or 5 mole per cent in ferroan dolomites.

These departures from the ideal composition also diminish the ordering of the crystals (Carpenter, 1980). Intracrystal variations in composition and degree of order are also common, particularly in larger crystals (e.g., Fritz and Katz, 1972). There is even some evidence that compositional variations have influenced the shape of the coarse crystals with curved faces that are common in some late diagenetic dolostones (Radke and Mathis, 1980). The degree of disorder and of departure from stoichiometry also affects the unit cell dimensions and the solubility of dolomite (Land, 1980).

Many authors have applied the name protodolomite or even pseudodolomite (e.g., Gaines, 1977, 1978; Deelman, 1978; Gidman, 1978) to dolomites that are not ideal in structure or composition. Such names tend to obscure the similarity of these non-ideal dolomites to ideal dolomite and Land (1980) suggested retaining the name dolomite for all such phases that have a composition near $CaMg(CO_3)_2$ and display evidence, such as superstructure reflections in x-ray patterns, of the degree of order characteristic of dolomite.

The Stability of Dolomite in Natural Environments

Minerals that have survived unchanged for long periods of time in natural environments do so for one of two reasons. The mineral may be stable thermodynamically, which is to say it will not be affected by small changes in the environment, or the mineral is unstable thermodynamically but is inert. Inert minerals are in the process of change to other species that have a lower free energy of formation, but the process may be extemely slow, as, for example in the conversion of diamond to graphite on the earth's surface. Such compounds are commonly called metastable to indicate the fact that they exist for variably long periods of time within the stability field of other compounds of similar composition.

The appropriateness of the terms 'metastable' and 'inert' are obviously dependant on the period of time over which a reaction is being considered, which in this case, is geologic time.

The factors (e.g., catalysts, temperature and concentration) that influence the speed of a chemical reaction are known collectively as reaction kinetic effects. The dolomite-calcite relationship is one of the more spectacular natural examples of the influence of kinetic factors. Under a wide range of surface and near-surface conditions dolomite is favoured thermodynamically over coexisting calcite so that at equilibrium in solution the dolomitization reaction, as it is commonly expressed (e.g., Bathurst, 1975)

$$2\,CaCO_3 + Mg^{2+} \rightleftharpoons Ca\,Mg\,(CO_3) + Ca^{2+} \quad (1)$$

is characterized by a free energy change of $\Delta G^\circ_r = -1.83$ kilocal/mole for the transformation of aragonite to dolomite of ideal composition and structure (Table I p. 11), which indicates that this reaction has a thermodynamic drive towards dolomitization.

We may use the relationship $\Delta G_r = \Delta G^\circ_r + RT \ln Q$ (Q = activity ratio of Ca^{2+}/Mg^{2+}, R = the gas constant, and T = absolute temperature), to derive a value of 21.96 for the activity ratio Ca^{2+}/Mg^{2+} for reaction (1) at equilibrium. Solutions with smaller values of Q will favour the replacement of aragonite by ordered dolomite. Seawater is one such solution with a Q value of only 0.16 (Garrels and Thompson, 1962; Wigley and Plummer, 1976) indicating a strong thermodynamic drive towards the replacement of aragonite and calcite by dolomite in the worlds oceans. What perversity of nature has left the vast present day submarine blankets of aragonite undolomitized?

The Mg^{2+} in equation (1) is necessarily supplied in solution to the reaction site from an external source. Lippman (1973) has emphasized that dolomite precipitates from ions in solution and that the $CaCO_3$ must dissolve before dolomite can form if the Ca^{2+} and CO_3^{2-} ions are derived from the $CaCO_3$ alone. It is also possible that part of the CO_3^{2-} in dolomite may have been supplied by the solution from an external source and Lippman (1973) has proposed the reaction

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

in which the CO_3^{2-} anions as well as Mg^{2+} are supplied by solution to the reaction site as an alternative to the traditional equation of reaction (1). For the dolomitization of aragonite, the free energy for reaction (2) at equilibrium is $\Delta G^\circ_r = -13.24$, favouring the formation of ordered dolomite even more strongly than reaction (1). Reaction (2) also has the advantage that the calcium liberated by dissolution of $CaCO_3$ is removed entirely from solution by dolomite whereas dolomitization by reaction (1) poses the problem of Ca^{2+} removal from the reaction site. If this evolved calcium is not removed its presence will raise the Ca/Mg ratio of solution and lower the thermodynamic drive towards dolomitization.

It may be assumed that, like other diagenetic reactions involving carbonates, dolomitization is entirely a wet chemical process (see Lippman, 1973; Bathurst, 1975; Land, 1980). Solid state reactions between carbonate minerals in the absence of an aqueous phase proceed prohibitively slowly at temperatures less than several hundred degrees centigrade (e.g. Fyfe and Bischoff, 1965). The existence of calcium-rich, non-stoichoimetric dolomite with compositions that fall in the region of the immiscibility gap between calcite and dolomite (Fig. 4) is evidence of slow reaction rates. However, recent work has shown that there may be some stable phases of intermediate composition between the low

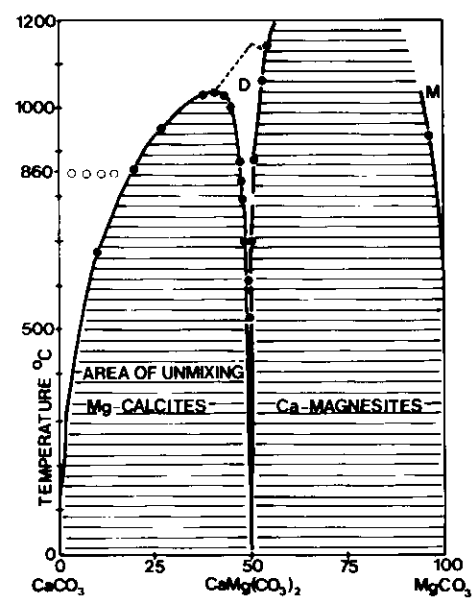

Figure 4 *Phase diagram of (water-free) $CaCO_3$, $CaMg(CO_3)_2$ (dolomite), and $MgCO_3$ (Magnesite) at temperatures between 0° and 1200° C. Only pure dolomite and calcite are thermodynamically stable at earth surface temperatures (after Deelman 1978; Goldsmith and Graf, 1958; and Goldsmith and Heard, 1961.). Recent work by Reeder and Wenk (1979) may cause some modification of this simple scenario.*

temperature calcite and dolomite stable end members (Reeder and Wenk, 1979).

Water of various compositions occupies even submicron-sized lamellar spaces between adjacent crystals in carbonate rocks and participates in their diagenesis (Pingitore, 1976; and Wardlaw, 1976). Most of these natural solutions are mixtures of waters of meteoric and marine origin modified by burial processes and commonly are supersaturated with respect to dolomite even when undersaturated with calcite, except for dilute solutions undersaturated in both phases (Fig. 5).

In summary we can state that dolomite is stable in most natural solutions and that the existence of aragonite and calcite in these solutions is a metastable condition.

The Role of Kinetic Effects on the Crystallization of Dolomite

Several kinetic factors that impede the precipitation of dolomite from supersaturated solution have been identified. These factors involve the molecular mechanics of precipitation and difficulties associated with the formation of the regularly alternating sheets of calcium and magnesium atoms in growing dolomite crystals. Many of these kinetic effects interlock and it is difficult to separate cause and effect. However, there are three major underlying kinetic barriers to the precipitation of dolomite:

1) Rapid crystallization from supersaturated, concentrated (i.e., saline) solutions impedes the segregation of calcium and magnesium ions into their respective layers so that magnesium layers are contaminated by calcium atoms and vice versa and disordered Ca-Mg carbonates are formed (Folk, 1979; Folk and Land, 1975; Lippman, 1973, p. 179);

2) Pronounced differences in the hydration behavior in aqueous solution of the constituent ions of dolomite promote precipitation of calcium-rich phases (Lippman, 1973); and

3) The low activity or concentration of CO_3^{2-} relative to Ca^{2+} or Mg^{2+} in most natural solutions inhibits the precipitation of magnesium-bearing carbonate minerals in general (Lippman, 1973).

Some have argued that the growth of dolomite crystals is predominantly by the sequential addition of successive cation-anion layers (e.g., Deelman, 1975, but see also Towe, 1975). However, in modern evironments of dolomite formation, dolomite is invariably present in the sediment as rhombs that range in size from less than 1μm to about 10μm. No crystals have been caught in the act of adding layers as planar sheets perpendicular to the c-axis. Instead dolomite crystals appear to grow as rhombs at more or less equal rates in all directions in spite of its layered construction (Fig. 3).

The speed of crystallization influences the degree of order because ions that adhere to incorrect lattice positions on the surfaces of rapidly growing crystals are more likely to be entombed in these positions than if the crystals grow slowly. Slower growth permits a longer period of exposure to the solution of an incorrectly situated ion. This increases the likelihood that it will be displaced by an ion of proper type for this lattice site. Calcium and magnesium ions are easily interchanged in dolomite's crystal lattice because of the small differences of lattice energy that are involved (Folk and Land, 1975).

The strength of the electrostatic ion of magnesium to water molecular bond is about 20 per cent greater than that of its calcium counterpart and much greater than that of the carbonate ion (Lippman, 1973, Table 20). The relatively strong attachment of the magnesium ion to its water of hydration shell (Fig. 6), is even more evident in the data of Samoilov (1965, see Horne, 1969, p. 106) in which magnesium is cited as being about 40 times as likely to carry its water of hydration sheath with it during migration through the liquid. The multitude of mestastable, naturally occurring hydrous magnesium carbonates, such as hydromagnesite or nesquehonite, that crystallize in the thermodynamic stability field of anhydrous magnesite, is also evidence of the relative strength of the hydration sheath of the magnesium ion. Magnesite, like dolomite, is highly super-saturated in seawater and many environments of modern dolomite formation, such as the Persian Gulf sabkhas or ephemeral lakes associated with the Coorong Lagoon in Australia (Alderman, 1965; Patterson, 1972), are accompanied by magnesite precipitation (plus assorted hydrous magnesium carbonates).

Calcium ions, which are less strongly hydrated than magnesium ions, are more readily incorporated into a growing Ca-Mg carbonate and will tend to occupy sites within magnesium layers as well (Fig. 3).Again, rapid rates of crystal growth reduces the time available for magnesium ions in solution to displace errant calcium ions before these defects are buried by continued crystal growth. Thus, more rapid crystal growth or crystallization rates favour the development of more calcium rich phases.

Another important kinetic effect related to the strength of the magnesium ion hydration sheath, is the inability of the relatively unhydrated carbonate ion to batter its way through this hydration barrier and come in contact with the crystal surface (Fig. 6). Only a part of the total CO_3^{2-} in solution has sufficient energy of motion (translational or vibrational) to break through the hydration barrier surrounding magnesium ions on the surface of a growing dolomite crystal. This low activity of the CO_3^{2-} ion compared to the activities of the Ca^{2+} and Mg^{2+} ions in many neutral and acid

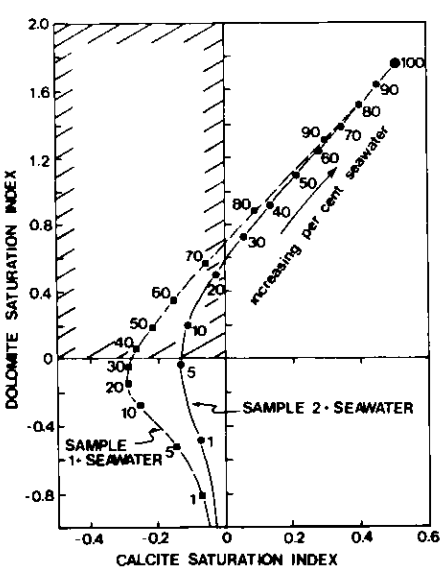

Figure 5 *Calcite and dolomite saturation index changes for mixing of sample 1 ($PCO_2 = 10^{-2}$ atm; broken line) and sample 2 ($PCO_2 = 10^{-3}$ atm; solid line) with sea water. Shaded region is where Badiozamani (1973) and others have argued that dolomitization is favoured (diagram after Wigley and Plummer, 1976).*

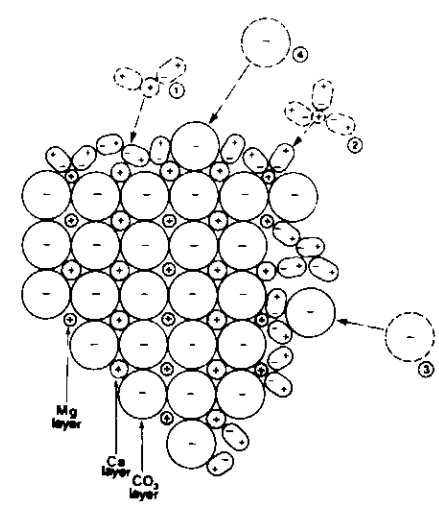

Figure 6 *A dolomite structure, showing water molecules preferentially bonded to the cations of the crystal surface. Calcium ions (1) are less strongly hydrated than magnesium ions (2) so calcium ions tend to be incorporated into magnesium layer positions causing the growth of a disordered Ca-rich carbonate. Carbonate ions are unhydrated but must have sufficient energy to displace the water molecules adjacent to the cation layer (e.g. 3 and 4). For simplicity an NaCl type of crystal structure is shown (after Lippman, 1973, Fig. 32).*

natural solutions, such as in sea water, is therefore a kinetic hindrance to the formation of dolomite although the thermodynamic solubility product of dolomite is exceeded by a wide margin (Lippman, 1973, p. 158-161).

The three main parameters that will affect the kinetics of the growth of dolomite are the Mg^{2+}/Ca^{2+} ratio, the salinity, and the CO_3^{2-}/Ca^{2+} ratio. The block diagram shown in Figure 7 is a plot of these solution parameters and the dolomite-calcite field boundary is shown as a plane separating a dolomite field on the near side and a calcite field on the far side. This plane represents a generalized kinetic boundary that lies entirely within the region of thermodynamic stability of dolomite. The lower surface is the bivariate plot of Folk and land (1975). A solution in the calcite field can move into the dolomite field by increasing its Mg/Ca ratio, decreasing its salinity or by increasing its CO_3^{2-} content.

An increase in the solution's Mg/Ca ratio favours the uptake of magnesium into a precipitating Mg-Ca carbonate. This is because an increase in the amount of magnesium in solution probably increases the number of magnesium ions relative to calcium ions that are energetic enough to shed their water of hydration and be incorporated into a growing Ca-Mg carbonate (Fig. 8). The laboratory syntheses by Glover and Sippel (1967) and Erenburg (1961) of magnesium calcites containing progressively greater mole per cent $MgCo_3$ contents with increasing Mg/Ca ratios in solution, constitute a good illustration of the effect of independently varying the Mg/Ca ratio of the solution. The sabkha environment of the Persian Gulf is a natural setting where the influence of the solution Mg/Ca ratio on dolomitization of aragonitic sediments is particularly well documented (e.g., Kinsman, 1965 and Patterson, 1972). At high temperature (> 100° C) the rate of dolomite precipitation is increased by higher Mg/Ca ratios up to an optimum value (Gaines, 1980). This may apply also at lower temperatures.

The disordering effect caused by rapid precipitation may be overcome by a reduction in the rate of precipitation by dilution of these solutions. This is difficult to verify by laboratory experiments, because of the slowness of crystallization from solutions more dilute than sea water, but has been inferred from natural examples such as modern dolomitization from brackish waters in the Floridan Aquifer (Hanshaw *et al.*, 1971; Fanning *et al.*, 1981), in the sediments of Lake Balaton, Hungary (Muller *et al.*, 1972), and from Pleistocene examples where the geologic history is known with a high degree of certainty (e.g., Land, 1973a, 1973b).

Calculations of the thermodynamic stability of various carbonate minerals in mixtures of sea water and fresh groundwater show that there is a large region in the mixing continuum in which calcite is undersaturated but dolomite remains supersaturated (Badiozamani, 1973; Wigley and Plummer, 1976; and Fig. 5). Badiozamani (1973) speculated that the replacement of calcite by dolomite would be considerably easier within this mixing region because of the thermodynamic drive causing calcite to go into solution.

It is certainly true that mixing a wide variety of solution compositions can induce limestone dissolution. However, it is less clear why this fact in itself should induce dolomitization. The dissolution of aragonite and precipitation of dolomite takes place in solutions that are saturated or supersaturated with both phases in settings such as the sabkha environment (Kinsman, 1964) or evaporite lagoons or ponds (Morrow, 1978; Friedman, 1980) because of an appropriate rise in the solution Mg/Ca ratio through the precipitation of gypsum. It seems likely therefore, that the undersaturation of calcite that results from the mixing of saline with dilute solutions is not an important factor for dolomitization. The dilution of saline solutions favours dolomite precipitation simply because of kinetic effect of the attendant decrease in the rate of precipitation.

An increase in the CO_3^{2-} ion concentration of the solution, particularly in excess of the Ca^{2+} concentration, may also be an important variable for promoting dolomitization in that a greater number of CO_3^{2-} ions with sufficient energy to shoulder aside the hydration shield of magnesium ions would be present. A variety of laboratory experiments by Lippman (1968a) and Davies *et al.* (1977) have indicated the importance of the CO_3^{2-} concentration. Liebermann (1967) also synthesized dolomite from artificial solutions more saline than sea water and with a Mg/Ca ration approximately that of sea water but with a relatively high pH and CO_3^{2-} concentration.

Sources for naturally occurring alkaline solutions containing high CO_3^{-2} concentrations include continental groundwaters that have been involved in the weathering of siliceous rocks or that have dissolved continental alkalic carbonate minerals, or marine and con-

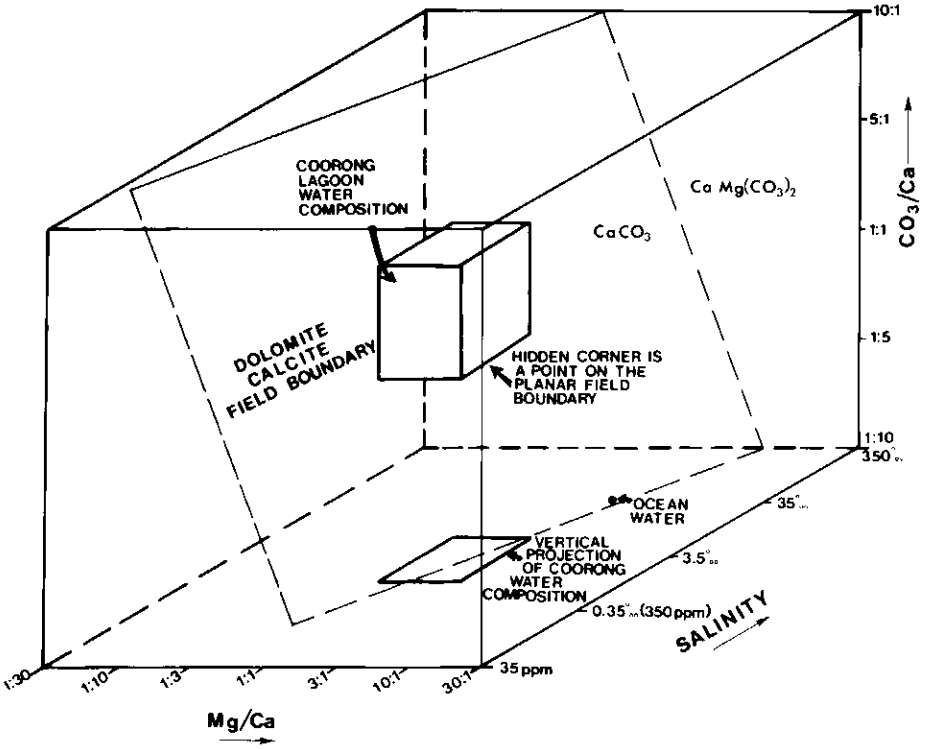

Figure 7 *Block diagram showing the effect of variation in the three parameters, the Mg/Ca solution ratio, the salinity, and the CO_3/Ca solution ratio. The plane represents the kinetic boundary between dolomite and calcite or aragonite and it includes the hidden corner of the Coorong Lagoon waters as a point on the plane. The basal plane is after Folk and Land (1975). Note that the vertical projection of Coorong Lagoon waters falls largely on the calcite-aragonite side of the stability boundary on the basal plane. A decrease in salinity, an increase in the Mg/Ca ratio or an increase in the CO_3/Ca ratio favours the precipitation of dolomite.*

tinental waters that have been involved in anaerobic bacterial sulphate reduction (Lippman, 1973). The Coorong Lagoon is the best documented modern occurrence of dolomitization under the influence of continental groundwater (Von der Borch, Lock and Schwebel, 1975; Von Der Borch, 1976; Von der Borch and Lock, 1979).

The composition of groundwater in the Coorong Lagoon Area is shown in Figure 7. Note that the projection of this solution composition onto the Folk and Land (1975) bivariate diagram falls largely outside the region of dolomite kinetic stability. This may be an indication that the high CO_3^{2-} concentration in the Coorong ground waters also promotes the precipitation of dolomite and Figure 7 has been constructed on this basis.

Generation of CO_3^{2-} by anaerobic sulphate reduction may have occurred in many burial environments from depths less than a metre to several hundred metres below the sediment-water interface. This process has been suggested as a factor in the dolomitization of some recent burrow fillings (Brown and Farrow, 1978). A supply of SO_4^{2-} ions in excess of the Ca^{2+} concentration is probably necessary because the initial rise in alkalinity will precipitate $CaCO_3$ before proceeding to dolomitization (Lippman, 1973).

Other Factors Controlling the Rate and Extent of Dolomitization

Most of the major models for dolomitization such as the Sabkha Model, the Reflux Model, the Mixed-Water Model and the Coorong Model may be explained in terms of the parameters shown in Figure 7, but other parameters under specific circumstances may be important. An increase in temperature such as occurs during burial will reduce the kinetic inhibitions to dolomitization (see Gaines, 1974; Mattes and Mountjoy, 1980). The length of time and the supply of magnesium available for dolomitization will govern the amount of dolomite formed (Hanshaw *et al.*, 1971). These problems will be discussed in relation to specific models of dolomitization in following paper.

The relative ease of dissolution of the various polymorphs of $CaCO_3$ is also an important rate-determining step in the dolomitization process (Gaines, 1974). The dolomitization of aragonitic sediments proceeds considerably more rapidly than for calcitic sediments (e.g., Schmidt, 1966). The rapid conversion of aragonite to low-magnesian calcite in humid climates has been cited as a factor in the resistance to dolomitization of Pleistocene shelf limestones exposed during low stands of sea level (Sibley, 1980).

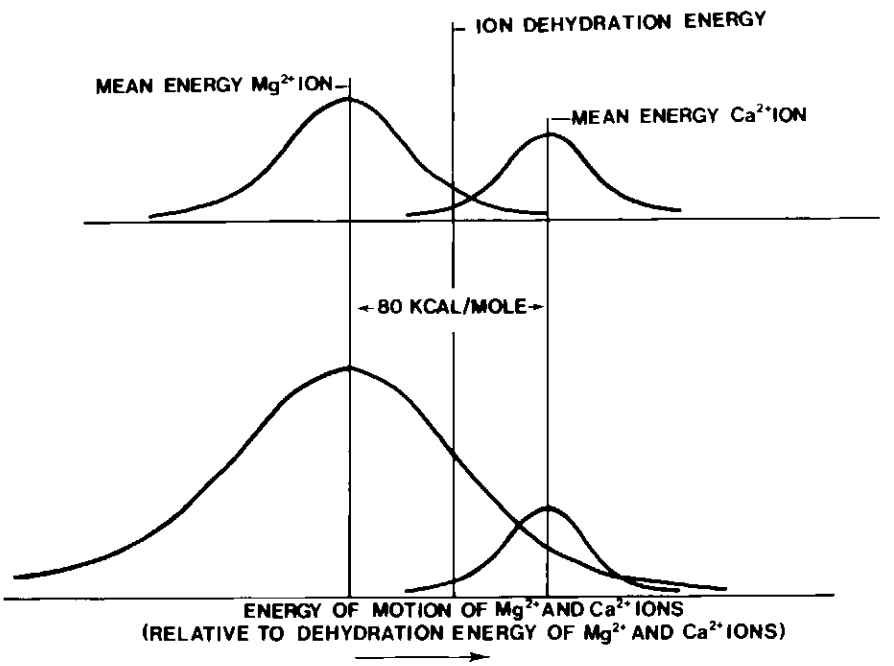

Figure 8 *Diagram showing energy (of motion) distribution of Mg^{2+} and Ca^{2+} ions in solution relative to the ion dehydration energy. It is possible to have an equal number of Mg^{2+} ions with energies exceeding the dehydration barrier by increasing the amount of Mg^{2+} in solution relative to the amount of Ca^{2+} in solution. A similar argument also applies to the CO_3^{2-} ion in solution. A normal distribution of ion kinetic energies is shown here for simplicity. The true shape of the distribution of the kinetic energies of molecules in a liquid is not known and is probably unique for each ion in solution but probably lies somewhere between a normal distribution and the assymetric Boltzman distribution for the energies of molecules in a gas.*

The presence of certain cations, such as lithium and possibly iron, have a catalytic effect on the precipitation of dolomite (Carpenter, 1980; Gaines, 1980). Carpenter (1976) has also suggested that because the proportion of strongly hydrated magnesium ions decreases markedly with increasing salinity, dolomitization should be favoured by high salinities and it does appear that dolomites that have formed under conditions of higher salinity and higher solution Mg/Ca ratios tend to be less calcium-rich and hence more stoichiometric (Fuechtbauer and Goldschmidt, 1966; Glover and Sippel, 1967). But the degree of disorder introduced by the faster rate of precipitation from more saline solutions overshadows the effect of the diminution of the hydration barrier of the magnesium ion with increasing salinity so that, although the Ca/Mg carbonates that are formed approach a dolomite composition, they tend to be disordered (Glover and Sippel, 1967; Folk and Land, 1975; Morrow, 1978). More experimental data is needed to separate the effects of precipitation rate versus the Mg/Ca ratio of the solution.

Dolomitization and the Volume Problem

The chemical reaction for dolomitization is most commonly given in the form shown in reaction (1) in which a mole of dolomite replaces two moles of calcite. The alternative dolomitization reaction given in reaction (2) was proposed by Lippman (1973, p. 180) largely because of the advantages of a high CO_3^{2-} concentration in solution. In reaction (1) the dolomitizating solution supplies the Mg^{2+} required and removes the Ca^{2+} released to solution, whereas in reaction (2) the solution supplies both Mg^{2+} and CO_3^{2-} but is not required to remove any reaction products.

Both of these equations involve considerable volume changes. A loss of volume of 6% to 13% (aragonite or calcite replacement) accompanies dolomitization according to reaction (1), a circumstance commonly cited by workers in the oil industry. On the other hand, dolomitization according to reaction (2), if applied literally, involves a tremendous volume gain of about 75% to 88% (Lippman, 1973, Table 28).

However, most dolomitized rocks do not appear to have undergone volume changes during dolomitization indicating a volume for volume replacement rather than a mole for mole replacement (Friedman and Sanders, 1967). Depositional fabrics such as those displayed by algal laminites (Gebelein and Hoffman, 1973) or by oolitic sediments (Powers, 1962) are not

disrupted by dolomitization. The increase in permeability that accompanies total dolomitization may be related to the idiomorphic shape and uniformity of size of the dolomite crystals (Wardlaw, 1979).

The conservation of volume during the dolomitization reaction may be an important constraint. For a volume-for-volume reaction the net dolomitization reaction may be written

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

where x = 0.11 and 0.25 for the dolomitization of aragonite and calcite respectively. Any departure from a volume for volume replacement will result in changes in these numbers which represent the net exchange of ions between the solution and the solid phases. Reaction (3) is characterized by a free energy change at equilibrium of $\Delta G^\circ_r = -3.085$ for dolomitization of aragonite (Table I) which is intermediate between the free energies of reaction of (1) and (2). Reaction (3) is a composite of reactions (1) and (2) which may be regarded as end members of a series of reactions dependant on the degree to which there is a gain or loss of rock volume during dolomitization.

Patterson (1972, p. 325) has proposed the reaction

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

based on chemical mass balance considerations for dolomitization of sabkha sediments which is similar to reaction (3) except that carbonate is supplied in the form of bicarbonate because of the slightly acid diagenetic environment of the sabkha. Patterson suggested that the average value of x in reaction (4) is close to 0.1 based on the organic content of the sabkha sediments. This value of x also satisifies the conservation of volume criterion.

Reaction (3) implies that the equilibrium constant for dolomitization depends on the CO_3^{2-} concentration as well as the Mg^{2-} and Ca^{2+} concentrations. But, because of kinetic factors, the concentrations of Mg^{2+} and CO_3^{2-} in the solution must be higher than that necessary merely to satisfy the thermodynamic requirements of dolomitization and the dolomitizing solution must play an active role as a transporter of ions to and from the reaction site. This has important implications for carbon and oxygen stable isotope studies of dolostones.

The release of Ca^{2+} to solution during dolomitization can lead to the local precipitation of gypsum as has been documented in Persian Gulf sabkhas (Patterson, 1972). This may be an alternative explanation also for the minute gypsum or anhydrite crystal inclusions in the coarsely crystalline white dolostones of the Mississippi Valley and Pine Point Districts which Beales and Hardy (1977, 1980) suggested were remnants of former evaporites.

The Dolomitization Process - Conclusions

1) Dolomite is thermodynamically stable in most natural solutions at earth surface conditions and a thermodynamic drive exists for the conversion of calcite and aragonite to dolomite.

2) The precipitation of dolomite is hindered by kinetic factors that are a consequence of the high degree of order of the dolomite crystal lattice and of the differences in hydration behavior of the Ca^{2+}, Mg^{2+} and CO_3^{2-} ions.

3) The extent to which these factors inhibit dolomitization appear to be governed largely by the interplay of three critical parameters: a) The rate of crystallization governs the degree of order of precipitating Ca-Mg carbonates. Dilution of supersaturated natural solutions is one method of reducing the crystallization rate; b) the Mg/Ca ratio of the solution determines the degree to which Mg^{2+} is incorporated into precipitating Ca-Mg carbonates. This ratio commonly rises during the precipitation of gypsum and/or anhydrite to a level favourable for dolomitization; and c) A CO_3/Ca ratio greater than one will aid in the precipitation of dolomite. This ratio may rise in ground water involved in weathering of igneous rocks or where anaerobic bacterial reduction of sulphate occurs.

4) A conservation of volume constraint implies a reaction of the form:

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

where x equals 0.11 or 0.25 for dolomitization of aragonite or calcite respectively. All three of the constituent ions of dolomite are exchanged between the solution and the solid phases emphasizing the role of fluid movements and compositions during dolomitization.

It is hoped that this review has succeeded in providing a coherent synthesis of evidence and theories specifically concerning the chemistry of the dolomitization process. The main kinetic factors controlling dolomite precipitation may have been identified but a more determined effort should be made to precipitate dolomite in the laboratory in quantities large enough to verify the influence of these kinetic effects and perhaps even to gain a degree of quantitative understanding of them. Only then will we be in a position to fully understand the significance of the isotopic composition and of the trace element contents of dolostones because of their dependence on the chemistry of the dolomitization process. Knowledge of the chemical environment of dolomitization also provides a clearer insight into the process of dolomitization in specific models for dolomitization.

Acknowledgements

Douglas Kent of the University of Saskatchewan and Alan Kendall of Amoco Canada Ltd. critically read the manuscript. I particularly wish to thank Kendall for his assistance in clarifying some of the ideas presented here and Ian McIlreath, the editor of this series, for his comments and encouragement.

Table 1 *Free Energies of Dolomitization Reactions (1), (2) and (3) at Equilibrium*

	ΔG°_r calcite (kilocal/mole)	ΔG°_r aragonite (kilocal/mole)
Reaction (1)	-1.38*	-1.83
Reaction (2)	-13.01	-13.24
Reaction (3)	-4.29	-3.08

* Calculation of free energies from data of Helgeson *et al.* (1978) using fully ordered dolomite. These numbers vary depending on the degree of order of the dolomite, but ordered dolomite is the most favoured phase thermodynamically.

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MS received November 27, 1981