GEOCHEMICAL AND NEOMORPHIC ALTERATION OF DOLOMITE: A REVIEW

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ABSTRACT: Many ancient dolomites are suspected of being alteration products of preexisting dolomite phases rather than being originally formed, unaltered dolomites. Such diagenetic alteration commonly results in changes in geochemistry and/or neomorphic changes in dolomite crystal sizes and textures. Hence, previous studies that have interpreted environments of initial dolomitization based on presumed preservation of diagnostic geochemical compositions and textures must be reevaluated because these parameters are known to reequilibrate during later diagenesis. The principal driving forces for neomorphism are the inherent thermodynamic instability of preexisting, non-stoichiometric dolomites, and to an unknown extent, the surface free energy-driven recrystallization of fine crystalline mosaics to coarser crystalline textures. The four inter-related criteria that are used commonly as collective evidence of alteration of preexisting dolomites are: (1) non-stoichiometric and poorly-ordered dolomites have an inherent tendency to transform to the more stoichiometric and better ordered phases typical of many ancient dolomites, a process that commonly is concurrent with (2) the neomorphic change from fine crystalline to coarse crystalline mosaics of either planar or nonplanar texture; (3) based on comparison to modern dolomites, depletion in ^{18}O isotopic composition and Sr and Na concentrations relative to presumed preexisting phases; and (4) homogenization of primary cathodoluminescent zonation that may have been present in the preexisting phase. Although certainly not unequivocal, the inference or recognition of such changes suggest the complexity of diagenetic modifications that have affected many ancient dolomites.

INTRODUCTION

Dolomites have received considerable attention over the past 200 years because of their scientific and economic significance. Published reviews on dolomites and dolomitization are numerous, the most recent of which include the contributions by Friedman and Sanders (1967), Land (1980, 1985, 1986), Zenger *et al.* (1980), Morrow (1982a, b), Machel and Mountjoy (1986), Given and Wilkinson (1987), Hardie (1987), Shukla and Baker (1988), and Usdowski (1989). These reviews and others were concerned primarily with various aspects of dolomite genesis, geochemistry and sources of magnesium, environments of formation, and abundance through time. In contrast, relatively little attention has been given to questions concerning the nature and extent of alteration of preexisting dolomites as related to interpretive studies of ancient dolomites.

Beginning essentially with the studies of Land (1980), and later, Gregg and Sibley (1984), there have been major advances in our knowledge concerning dolomite alteration, although our information on the subject is far from complete. The many papers published subsequently on this subject have affirmed five important concepts: (1) newly formed, unstable dolomites commonly are altered, sometimes rapidly, in various diagenetic environments; (2) this alteration can be manifested in modification of geochemical compositions relative to preexisting dolomites, and/or the development of neomorphic textures; (3) such altered dolomites likely are more common in the stratigraphic record than recognized previously; (4) diagenetic environments of many ancient dolomites inferred on

the basis of presumed preservation of primary texture and geochemistry therefore are suspect; and (5) the presence of altered dolomites can sometimes be recognized on the basis of comparative textural observations and geochemical data. There are many inherent complexities, however, that must be considered in interpretive diagenetic studies of dolomitization. Accordingly, much confusion and disagreement exist among petrologists as to the nature and significance of various processes involved and products of dolomite alteration.

This paper critically assesses fundamental aspects of the causative processes and products of dolomite alteration and various criteria for their recognition in ancient rocks. It considers two separate but commonly interrelated aspects of the alteration of newly formed dolomite: geochemical and neomorphic changes. The term "neomorphism" as used herein was applied to dolomite studies by Sibley and Gregg (1987) following the original definition of Folk (1965). It is preferred by them and others over the specific term "recrystallization", which refers to textural changes alone, because they believed the process typically involves mineralogic changes in unstable phases (notably, the transformation of poorly ordered, non-stoichiometric dolomite to more stable, ordered and stoichiometric dolomite) as well as textural changes.

PRESERVATION OR ALTERATION?

The notion that once formed, dolomites (and some limestones) remain unaltered compositionally or texturally in ancient rocks is or was once shared by several

researchers (Fritz, 1971; Moller et al., 1976; Morrow, 1978; Dunham and Olson, 1980; Dickson and Coleman, 1980; Bein and Land, 1983; Fairchild, 1985; McKenzie, 1985; Veizer, 1985). Many workers cited as supportive evidence for this contention the occurrence of presumably unstable (non-stoichiometric and poorly ordered) "protodolomites" in rocks as old as Precambrian (Graf and Goldsmith, 1956; Atwood and Fry, 1967; Richter, 1974; Lumsden and Chimahusky, 1980; Fairchild, 1985; Land, 1985). There is no doubt that unstable dolomites (as well as aragonites and high-magnesian calcites: e.g., Brand, 1989) can persist under certain circumstances, but such occurrences are relatively rare in nature. On the contrary, many ancient dolomites are much more stoichiometric and better ordered than these "protodolomites" and their analogous modern counterparts, although they rarely attain "ideal" composition and ordering (Land, 1980).

Following such a "preservationist" attitude, many authors had inferred various environments and/or environmental-related modes of dolomitization for ancient dolomites (e.g., sabkha, mixing-zone model, etc.) on the basis of certain petrographic and geochemical data which were considered to reflect essentially unaltered or only slightly modified original attributes of the rocks (see papers in Zenger et al., 1980). However, most did not adequately consider the possibility that present dolomite textures and geochemical compositions may actually be alteration products of preexisting dolomites; or at least, they could not recognize such alteration products at that time. As was discussed by Land (1980, 1983, 1985, 1986) and explicitly stated by Hardie (1987) with specific reference to recrystallization (neomorphism), ". . . we must take into account the strong possibility that the geochemical record has been rewritten by burial diagenesis." (p. 179). Likewise, the petrographic record in many ancient dolomites probably also has been overprinted by later diagenetic events. In fact, many petrologists (e.g., Land, 1980; Gregg and Sibley, 1984, 1986; Sibley and Gregg, 1987; and others cited in the following pages) have suggested that few if any ancient dolomites are original in the sense that they represent unaltered mosaics formed during single, short-lived diagenetic events (for a possible exception see Lee and Friedman, 1987). Rather, they are thought to be products of multi-stage diagenesis, and hence, most likely have been modified to various degrees by processes such as: (1) multiple episodes of replacement of precursor limestones or mineralogically unstable carbonate sediments by dolomite, (2) nucleation of additional dolomite on preexisting dolomite crystals, i.e., overgrowth, which may be part of the process involved in (3) the neomorphic and geochemical alteration of preexisting, generally finer crystalline dolomites. As discussed below, these processes are operative not only in the burial environment as suggested by Hardie (1987), but in the near-surface meteoric, mixed meteoric-marine, and essentially syndepositional marine environments as well. Hence, we must critically reevaluate earlier studies that inferred

certain environments of dolomitization based on assumed preservation of primary geochemical compositions and other textural criteria. Perhaps part of the divergence of opinions of the "preservationists" and "alterationists" results from the difficulty of recognizing (particularly in fine crystalline dolomites) distinct multiple dolomitization events, changes in geochemical compositions relative to inferred preexisting phases, and neomorphism in some dolomites and our limited knowledge of processes and certain geochemical parameters related to dolomitization in general. Despite such problems many studies, discussed below, have shown that geochemical and neomorphic alteration of presumed preexisting dolomites likely has affected many ancient dolomites.

A review of published studies on dolomite diagenesis suggests that there are four main textural and geochemical criteria, none of which individually is unequivocal, by which alteration can sometimes be recognized in dolomites: (1) an increase in the ordering and stoichiometry of crystals; (2) changes in crystal texture and increase in crystal size (neomorphism); (3) deductions from oxygen and strontium isotopes and major and trace element (primarily Sr and Na) compositions; and (4) cathodoluminescence characteristics. These criteria are discussed in detail in the following sections of this paper. Other criteria that have been proposed for the recognition of altered dolomites include studies of fluid inclusions (Hardie, 1987), isotopes of neodymium (Banner et al., 1988), and relative concentrations of elements such as Fe, Mn, Zn. Insofar as the utility of these methods either is presently uncertain (e.g., in the case of Nd), plagued with more severe problems than others (in the case of Fe, Mn, and Zn concentrations), or relies on a priori assumptions that neomorphism likely has occurred, these are either not discussed or are only summarily considered in this paper.

DOLOMITE NEOMORPHISM
Driving Forces

Dolomite neomorphism has been compared to the neomorphic alteration of limestones, particularly micrites, in terms of the driving forces and textural products of such alteration (Gregg and Sibley, 1984; Hardie, 1987; Sibley and Gregg, 1987; Gregg and Shelton, 1990). The presumed driving forces for dolomite neomorphism are:

(1) The inherent thermodynamic instability of poorly ordered, non-ideal dolomites. According to Graf and Goldsmith (1956), Goldsmith and Graf (1958), Land (1980, 1985, 1986), Lumsden and Chimahusky (1980), and others, an "ideal" dolomite is stoichiometric as well as ordered in the sense that calcium and magnesium are present in equal amounts and are segregated into alternating cation planes within the crystal lattice. Because of low free energies, ideal dolomites are thermodynamically the most stable and least soluble form of mixed Ca-Mg carbonates. Most ancient
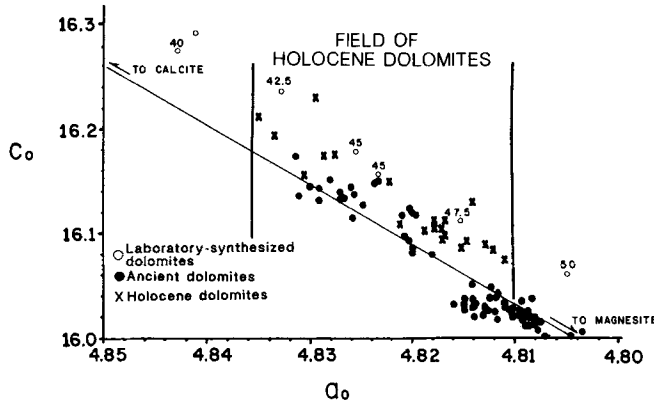
Figure 1. Unit cell measurements of modern and ancient dolomites; numbers refer to mole% $MgCO_3$ in laboratory-synthesized dolomites (modified from Land, 1985). The range of dolomite compositions is $Ca_{0.96-1.16}Mg_{0.84-1.04}(CO_3)_2$. As pointed out by G. M. Friedman (pers. comm., 1991), the relationship between composition based on XRD peak position and chemical analysis is not yet well understood. Therefore, these data require further attention.

sedimentary dolomites, however, approach but rarely attain ideal stoichiometry and ordering. In contrast, most Holocene and Cenozoic peritidal to deep-sea dolomites typically are even more poorly ordered and less stoichiometric (calcic, "protodolomites" of some workers) as determined for example by their unit cell parameters (Fig. 1). As a consequence of their poor ordering and nonstoichiometry such crystals have higher free energies and are therefore unstable and prone to dissolution and/or neomorphic alteration by a process of dissolution-reprecipitation (discussions in Carpenter, 1980; Land, 1980, 1983, 1985, 1986; Busenberg and Plummer, 1982; Hardie, 1987; Sibley, 1990). Such instability is probably the principal driving force in the rapid neomorphic alteration of newly formed dolomites, regardless of whether they are of syndepositional or of later diagenetic origin.

(2) The general dictum ("Ostwald ripening") that fine crystalline mosaics have high surface free energies (high entropy), and therefore, also are unstable and tend to recrystallize to coarser mosaics of lower free energies (low entropy). According to Sibley and Gregg (1987) and others, fine crystal size and accompanying high surface free energies alone likely are not an adequate driving force for neomorphism (in strict terms, recrystallization) except under epigenetic and metamorphic conditions and/or long periods of time (also Hardie, 1987). Fine crystal size, in combination with the poor ordering and non-stoichiometry typical of many newly formed (e.g., Holocene and Cenozoic) dolomites, however, should render them particularly susceptible to more rapid neomorphic alteration than better ordered and more nearly stoichiometric dolomites of equivalent crystal size. A recent study by Gregg *et al.* (in press) suggests that Holocene (<3,000 years old), fine crystalline, poorly-ordered, non-stoichiometric dolomites from Belize are already being recrystallized, presumably by this process.

(3) Strain recrystallization, that is, recrystallization driven by the energy of deformed crystal lattices, has also been discussed by Folk (1965) and Bathurst (1975) as a possible factor in limestone neomorphism. According to these workers its importance in the neomorphism of both undeformed dolomites and limestones likely is insignificant.

Petrographic Criteria for Recognition of Neomorphism in Dolomites

Increase in ordering and stoichiometry. —Many studies have assumed that neomorphism in some ancient and modern dolomites (perhaps excluding cements) must have occurred if they are now better ordered and more nearly stoichiometric, and more coarsely crystalline, then contemporaneous dolomites and presumed preexisting dolomites (Land, 1980, 1983; McKenzie, 1981; Gregg and Sibley, 1984; Sibley and Gregg, 1987; Banner *et al.*, 1988; Compton, 1988b; Moore *et al.*, 1988; Gregg and Shelton, 1990; and others). It is certain that such instability drives neomorphism via mineralogic transformation, and it is known to occur in newly formed dolomites regardless of their site and timing of formation or diagenetic environment (e.g., Land, 1980, 1983; McKenzie, 1981; Gregg and Sibley, 1984; Sibley and Gregg, 1987; Banner *et al.*, 1988; Burns *et al.*, 1988; Compton, 1988a, b; Lumsden, 1988; Moore *et al.*, 1988; Usdowski, 1989; Gregg and Shelton, 1990; Sibley, 1990). But not all newly formed dolomites are poorly ordered and non-stoichiometric, however, and there is evidence that factors such as salinity and fluid Sr/Ca and Mg/Ca ratios may exert a control on the initial composition of some primary dolomites. Several studies, for example, have inferred that some hypersaline dolomites formed under conditions of high Mg/Ca ratios in ambient fluids tend to be more stoichiometric than some normal marine dolomites; in comparison, low fluid Mg/Ca ratios tend to favor Ca enrichment and nonstoichiometry in dolomites (Lumsden and Chimahusky, 1980; Morrow, 1982b; Hardie, 1987; Sass and Bein, 1988). Vahrenkamp and Swart (1990) suggested that some late Tertiary, subsurface dolomites from the Bahamas are initially stoichiometric and formed from essentially unmodified sea water (although we cannot discount the possibility that these dolomites have been altered by ambient marine fluids). Hence, there may not be an inherent thermodynamic potential for some newly formed dolomites to alter neomorphically if they were stoichiometric initially. Furthermore, whether or not any dolomite compositional or structural reorganization may have occurred in originally unstable dolomites prior to a later, overprinting neomorphic event, and the extent of such, usually cannot be determined in ancient rocks. From McKenzie's (1981) study of Holocene sabkha dolomites from the Persian Gulf it seems likely that some amount of early, syndepositional increase in the degree of ordering and stoichiometry can be expected in some newly formed, unstable dolomites prior to any later neomorphism. Similar

conclusions were reached by Gregg et al. (in press) in their study of modern dolomites from Belize. On the basis of analogy to McKenzie's (1981) study Gregg and Shelton (1990), for example, proposed early dolomite formation and then an unknown degree of compositional and structural stabilization in quasi-marine fluids, followed by further neomorphism in the mesogenetic environment, in some Cambrian dolomites in Missouri (also Gregg and Sibley, 1986, and Shukla, 1986). As pointed out by Gregg and Shelton (1990), the suggestion of early, syndepositional neomorphism was merely a possibility, one that could not be proven because a preexisting dolomite phase could not be identified. Because of such limitations and the fact that dolomites can initially be ordered and stoichiometric, the occurrence in ancient rocks of ordered and stoichiometric dolomites alone does not necessarily indicate neomorphic alteration.

Crystal texture and size.—Gregg and Sibley (1984) proposed a model for textural and size changes resulting from dolomite neomorphism based on crystal growth theory and the inherent "neomorphic potential" (term modified from Hardie's [1987] "recrystallization potential") of unstable dolomites. Citing Jackson (1958a, b), Jackson and Gilmer (1976) and others, they noted that at low temperatures crystals grow by the layer-by-layer addition of atoms onto a crystal face, thereby resulting in the formation of smooth, faceted crystal faces and euhedral and subhedral crystals ("planar" texture of Sibley and Gregg, 1987, or "idiotopic" texture of Friedman, 1965, and Gregg and Sibley, 1984). Above a "critical roughening temperature" (CRT), however, atoms are added randomly to a crystal surface, the formation of faceted crystal faces is retarded, and the result is an interlocking mosaic of anhedral crystals ("nonplanar" texture of Sibley and Gregg, 1987 or "xenotopic" texture of Gregg and Sibley, 1984, the latter which is partly equivalent to "xenotopic" as defined by Friedman, 1965[1]). Based on experimental data and studies of a variety of naturally occurring dolomites, they estimated the CRT for dolomite to be between 50° and 100°C. They extended these theoretical considerations to dolomite formation by suggesting that dolomite crystal growth at temperatures below 50°C should produce mostly planar textures, whereas above this CRT (or 60°C according to Gregg and Shelton, 1990), nonplanar textures would be developed most commonly (i.e., in the burial environment).

According to Gregg and Sibley (1984), Sibley and Gregg (1987), and Gregg and Shelton (1990), neomorphic dolomites and dolomites that replaced limestones at high temperature (see Gregg, 1985, 1988) may be characterized by coarse crystalline, nonplanar textures (Fig. 2). The transition between a preexisting dolomite and its neomorphic alteration product may be coincident with the change from unimodal coarse skewed to a log-normal crystal size distribution (Fig.

3). Component crystals in neomorphic dolomites typically have highly irregular intercrystalline boundaries and, commonly, undulatory extinction and abundant inclusions, the latter resulting in "dirty" crystals (Fig. 2). Intercrystalline boundaries may be curved, lobate, serrated, or indistinct (Fig. 2), with rarely preserved crystal-face junctions (Fig. 4). Replacement crystals and pore-lining dolomite cements may include saddle dolomite (Radke and Mathis, 1980). Gregg and Sibley (1984), later modified by Sibley and Gregg (1987), proposed a classification of dolomite textures based on crystal morphology and crystal boundaries (Fig. 2). Because of their genetic implications, they make important distinction between planar-S and nonplanar-A dolomite textures (non-neomorphic versus neomorphic, respectively). Such distinction can be made qualitatively or, if necessary, on the basis of point counting the number of crystal-face junctions present (nonplanar textures generally contain less than 30% crystal-face junctions).

Application to dolomites that replaced limestones.— According to their model, newly formed dolomites that replaced limestones at temperatures below and above 50° to 60°C should be characterized by mostly planar and nonplanar textures, respectively (also Gregg, 1985, 1988). According to Gregg and Shelton (1990), these dolomites can resist later neomorphism if they are ordered and stoichiometric. If poorly ordered and nonstoichiometric, however, such dolomites would be unstable regardless of original textures (e.g., planar or nonplanar) and therefore prone to subsequent neomorphic alteration. As one particular corollary to these suggestions, the stabilization of unstable planar dolomites formed initially at temperatures below 50° to 60°C (the principal driving force being thermodynamic instability) to better ordered phases could result in the formation of somewhat larger euhedral crystals and retention of planar textures. This contention is supported by McKenzie's (1981) and Gregg et al.'s (in press) studies of Holocene calcic dolomites which appear to "age" in a few thousand years at ambient surface temperatures to larger, more perfect rhombohedral faceted crystals with increased degrees of ordering. Hence, they provided a viable model to explain the common occurrence in many ancient rocks of associated laminae of fine crystalline, planar (non-neomorphosed due to early stabilization) and coarse, nonplanar (altered) dolomites (see Gregg and Sibley, 1986; Shukla, 1986). But what about initially unstable nonplanar textures that formed at temperatures above (or lower than: discussed below) the critical CRT: what will be the effect of neomorphism on resulting texture and geochemical composition? There presently is no answer to this question.

There are other rather severe limitations in the recognition of neomorphic textures in ancient dolomites that presumably are replacive of limestones, even if we are to accept for the moment the CRT proposed by Gregg and Sibley (1984). The most important of these limitations are: (1) an inability to identify within

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[1] *The terminology followed in this paper will be that of Sibley and Gregg (1987).*
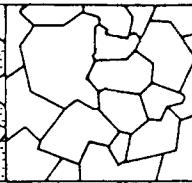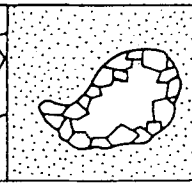
PLANAR DOLOMITES

(less than 50-60°C)

Planar-E: dolomite crystals mostly euhedral; crystal-supported with interxtall areas filled with another mineral or porous
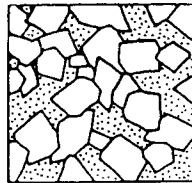
Planar-S: subhedral to anhedral crystals, low porosity and/or little interxtall matrix; straight compromise boundaries common, greater than 30% crystal-face junctions (= hypidiotopic and some xenotopic of Friedman 1965)

Planar-C: euhedral crystals lining pores or surrounding patches of another mineral (e.g., gypsum, calcite). May also be replacive dolomite, where undolomitized interior of allochem was later dissolved
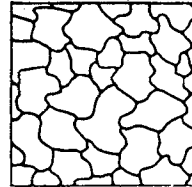
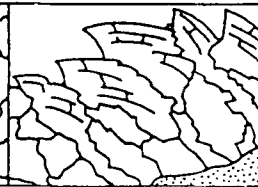Planar-P: porphyrotopic, scattered crystals in matrix (matrix-supported)
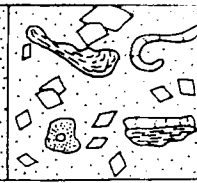
NONPLANAR DOLOMITES

(greater than 50-60°C)

Nonplanar-A: anhedral crystals with mostly irregular interxtall boundaries (less than 30% crystal-face junctions); crystals commonly with undulatory extinction, inclusions; also includes replacement saddle dolomite

Nonplanar-C: pore lining saddle dolomite cement crystals

Nonplanar-P: porphyrotopic, single anhedral crystals or patches of anhedral crystals, matrix-supported; crystals commonly with undulatory extinction
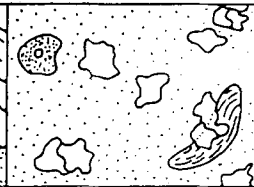

Figure 2. Textural and genetic classification of dolomites, and some characteristics of planar and nonplanar textures (modified from Gregg and Sibley, 1984 and Sibley and Gregg, 1987).
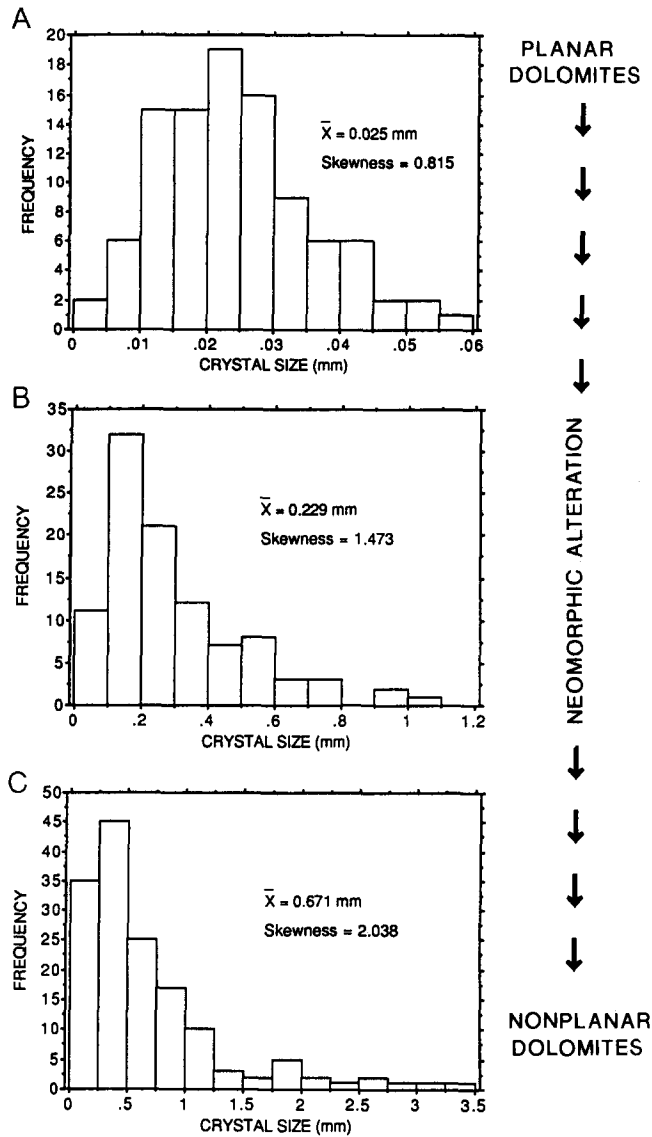
Figure 3. Examples of crystal size distributions in neomorphic and unaltered dolomites. A through C show increasing skewness toward coarser crystal sizes in non-neomorphosed and fine crystalline planar dolomites, transitional dolomites, and coarse crystalline and non-planar dolomites of neomorphic origin, respectively (from Gregg and Shelton, 1990).

Figure 4. Model of the formation of crystal-face junctions (from Gregg and Sibley, 1984).

presently coarse crystalline, nonplanar, stoichiometric dolomites the former existence of any intermediate dolomites, and hence, to determine their chemistry and texture; and (2) Gregg (1985, 1988) suggested that coarse crystalline, nonplanar dolomites at the base of the Cambrian Bonneterre Formation in Missouri replaced limestones at temperatures in excess of 50°C. Can we truly distinguish in massive dolomites those that replaced limestones and those that replaced preexisting dolomites above this temperature threshold? I don't believe such distinctions are always possible at this time. Zenger and Dunham (1988), for example, readily admitted this uncertainty in their study of Silurian-Devonian dolomites in New Mexico.
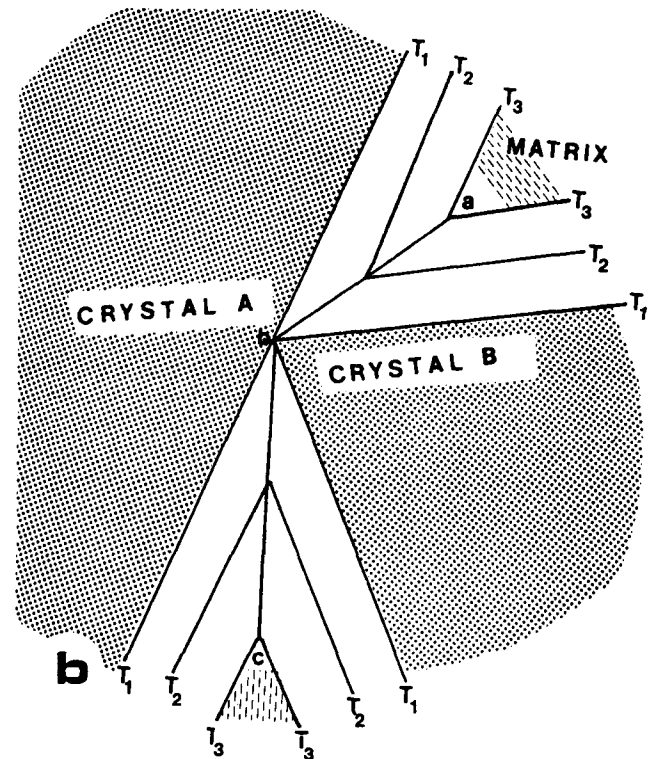
Application to alteration of preexisting dolomites. — According to Gregg and Sibley (1984), at temperatures exceeding the 50° to 60°C CRT, coarser crystalline and nonplanar dolomites should develop from the neomorphism of any preexisting unstable dolomites regardless of their original textures (Fig. 2). Such a model was applied subsequently to ancient rocks by other workers, who also suggested that textural changes presumably accompanied increases in dolomite ordering and stoichiometry (Banner et al., 1988; Compton, 1988b; Coniglio and James, 1988; Fischer, 1988; Gregg, 1988; Moore et al., 1988; Zenger and Dunham, 1988; Gregg and Shelton, 1990). Whereas this model likely is realistic, again the problem of actually identifying in ancient rocks the initial texture of the precursor dolomite or, for that matter, whether it was unstable or stable, remains to haunt us. The matter is simplified somewhat if we assume that the preexisting dolomite was fine crystalline and unstable as are many Holocene dolomites, but this is not always the case in young dolomites and cannot be demonstrated with certainty in ancient rocks.

Gregg and Sibley (1984) further suggested that the driving forces for the neomorphic alteration of preexisting dolomites are, as described previously, the inherent instability of poorly ordered dolomites and to a lesser degree, the tendency for fine crystalline mosaics to recrystallize to coarser mosaics. But let us consider the case of already stabilized dolomites. As noted earlier, recrystallization alone is believed to occur relatively slowly and only at elevated temperatures. Cer-

tainly some ancient, already stabilized dolomites regardless of initial texture must have been exposed subsequently to epigenetic conditions over long periods of time (e.g., as possibly reported by Sternbach and Friedman, 1986; Lee and Friedman, 1987; Gregg and Shelton, 1990). Hence, two additional questions must be addressed: (1) what are the relative roles of neomorphism and recrystallization in the development of alteration textures; and (2) can we distinguish on the basis of texture (and/or chemistry) those dolomites formed by neomorphism alone, those altered by neomorphism and recrystallization, and those altered by recrystallization alone? The study of Gregg and Shelton (1990) on some Cambrian rocks in Missouri was inconclusive in this regard. These considerations await further research.

Gregg and Sibley (1984) noted that the CRT of calcite likely is less than 25°C and, accordingly, neomorphic textures in limestones form diagenetically early, at corresponding lower temperatures and depths than dolomites. Insofar as substitution of Ca or Fe for Mg changes the enthalpy factor (which is the energy required to take an atom from the crystal and put it into the phase in which the crystal is growing: Jackson, 1958a, b) as well as entropies and free energies (Carpenter, 1980), some ferroan and calcic (non-stoichiometric and generally poorly ordered) dolomites likely have a lower CRT and corresponding lower neomorphic threshold, due perhaps to thermodynamic instability, than more stoichiometric dolomites (Gregg and Sibley, 1984). This aspect of neomorphism also remains to be examined in further detail.

Other factors controlling texture and crystal size.—Sibley and Gregg (1987) refined their earlier model of dolomite diagenesis by discussing other factors that control nucleation and crystal growth kinetics, and hence, textural variations in dolomites. They, and Gregg (1988), stated that neomorphic and high-temperature replacive dolomites should generally be more coarsely crystalline than low-temperature (and non-neomorphic) dolomites insofar as nucleation and crystal growth rates increase with temperature. They stressed, however, that the fundamental control on crystal size is not temperature alone, but rather, relative differences between temperature and nucleation and growth rates (Genck and Larson, 1972) such that at high temperatures: (1) relatively fine crystalline textures will develop if the nucleation rate increases faster than the growth rate; and (2) coarser crystalline textures will develop if the growth rate increases faster than the nucleation rate. Furthermore, unimodal crystal size distributions, which presumably are typical of many unaltered dolomites, may in fact develop in neomorphic dolomites as a result of single nucleation events, especially on homogeneously distributed nucleation sites under conditions of uniform growth rates. In contrast, polymodal crystal size distributions, presumably common in neomorphic dolomites, may develop in altered as well as neomorphic dolomites when there is a heterogeneous distribution of nucleation sites, mul-

tiple periods of dolomite nucleation, or variations in the local growth rate. Factors such as substrate mineralogy and crystal size, mode and/or environment of replacement, and supersaturation levels also may affect nucleation, growth kinetics, and resultant crystal size distributions (see Folk and Land, 1975; Bullen and Sibley, 1984; Morrow, 1982a, b; Compton, 1988b; Shukla, 1988; and others).

Although nonplanar textures may be typical of many high-temperature and neomorphic carbonates, dolomites formed above the CRT locally may develop mosaics of faceted (euhedral) crystals and planar textures if: (1) they are precipitated in pores; (2) growing dolomite crystals are in contact with non-carbonate minerals; in contrast, anhedral crystals and nonplanar textures develop typically when dolomite grows in contact with neighboring dolomite or calcite; or (3) crystal faces are stabilized during growth by organic material and/or clay mineral impurities. This relationship between impurities and dolomite texture was demonstrated by, among others, Gregg (1988) in his study of partial dolomitization of Cambrian shales in Missouri. In terms of the relationship between fluid supersaturation levels and temperature he suggested that dolomite formed under conditions of low supersaturation and/or temperature (below the CRT) would be characterized typically by layer-by-layer nucleation, and hence, the formation of faceted crystals and corresponding planar textures. At high levels of supersaturation, or above the critical CRT (50° to 100°C), non-faceted crystals and corresponding nonplanar textures develop instead by the random addition of atoms to growing crystal surfaces. Theoretically, however, nonplanar dolomite textures can also develop below the critical CRT at high supersaturation levels, but Gregg (1988) believed that such occurrences probably are rare in nature.

They also noted a relationship between texture and crystal size. Textures of sub-micron size crystals, for example, are typically nonplanar because surface free energy is dominant over other factors that promote faceting. As crystals become larger, however, the contribution of surface free energy to growth kinetics becomes less, and hence, faceted crystals and planar textures develop. Although they suggested that planar textures in fine crystalline mosaics may persist in dolomites that were stabilized early in their diagenetic history, we are unsure of the effects of recrystallization on such textures.

Inferences from cathodoluminescence petrography.—Several studies have examined the relationship between cathodoluminescence (CL) characteristics and dolomite types in ancient rocks. There appears to be no definitive correlation between the presence or absence of luminescence, allochem ghosts, and degree of neomorphism in dolomites. Neomorphic and limestone-replacive dolomites vary from non-luminescent to brightly luminescent (Lee and Friedman, 1987; Cander et al., 1988; Fischer, 1988; Gregg, 1988) depending on the relative concentrations of Fe (quencher) and Mn (activator) in the crystals (Fairchild, 1983). Ac-
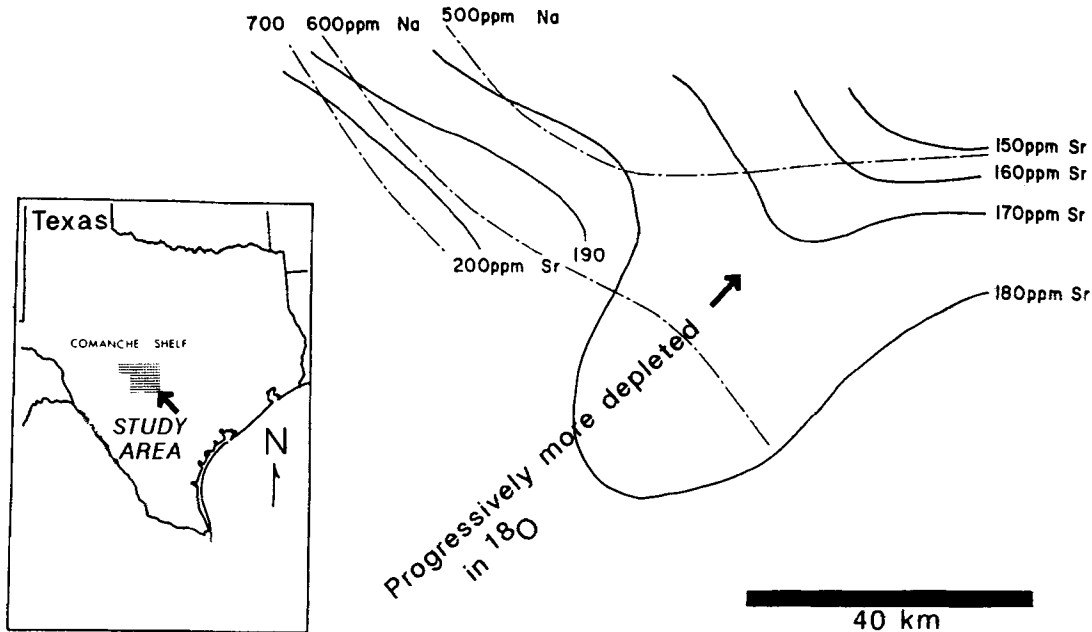
Figure 5. Updip depletion in Sr and Na concentrations and ¹⁸O in some Cretaceous carbonates of Texas, changes that presumably resulted from the post-depositional alteration of preexisting peritidal dolomites in an unconformity related, mixed marine-meteoric diagenetic setting (modified from Land, 1980).

cording to Coniglio (1986), Cander et al. (1988), and Holail et al. (1988), however, possibly a more distinctive signature of dolomite neomorphism is that any CL zoning that may have been present in precursor dolomites (if any!) usually is homogenized. Gregg and Sibley (1984) and Lee and Friedman (1987) suggested that the presence of allochem ghosts in a dolomite may be evidence of direct replacement of limestone rather than neomorphism of a preexisting dolomite. In contrast, the absence of allochem ghosts does not necessarily imply that neomorphic alteration has occurred. More work needs to be done on these subjects.

Of particular interest in dolomite studies is the observation that CL zoning commonly highlights the occurrence in many rocks of typically dusty, fine crystalline core crystals within larger crystals of dolomite. The presence or absence of such cores is significant in diagenetic interpretations regarding possible neomorphism. These cores may be detrital or authigenic (e.g., Coniglio and James, 1988) and, if the latter, are likely to be a preexisting dolomite. Banner et al. (1988), for example, showed that rhombic core crystals in Mississippian rocks were, in fact, precursor non-stoichiometric dolomites that were relatively enriched in Sr and ¹⁸O and later altered to coarser, stoichiometric, Sr-depleted and ¹⁸O-depleted dolomites (see also Holail et al., 1988). In this case, the presence of the core crystals was instrumental in identifying the neomorphic origin of the associated replacive dolomites. Such relationships can not be readily determined on the basis of geochemistry in other occurrences because the fine size of the core crystals precludes their separation from the surrounding matrix (e.g., Coniglio and James,

1988). The absence of such cores, however, poses additional restrictions on diagenetic interpretations. For example, where core crystals are not identifiable within relatively coarse crystalline dolomites of suspect origin, the questions that must be considered, and which presently can not be answered definitively, include: (1) was there a preexisting dolomite and, accordingly, is the present texture neomorphic after this preexisting phase, or (2) does it represent the replacement of a preexisting limestone; and (3) under what circumstances are preexisting core crystals preserved versus obliterated during neomorphism? These questions likewise await further study.

DOLOMITE GEOCHEMISTRY AND RELATIONSHIPS TO NEOMORPHISM

Changes in oxygen and strontium isotopic compositions and the concentrations of some incorporated minor and trace elements are common in dolomites, and these changes can sometimes be used with supportive petrographic observations as evidence of dolomite neomorphism. According to Land (1980, 1985, 1986), the initial geochemistry of dolomites is expected to be altered during later diagenesis, with or without accompanying observable neomorphic changes, however, because diagenesis rarely occurs in closed systems.

Oxygen Isotopes and Elemental Concentrations

Oxygen isotopes.—The early work of Land (1980, 1983) on the origin of some Cretaceous dolomites in central Texas set the tone for subsequent studies on
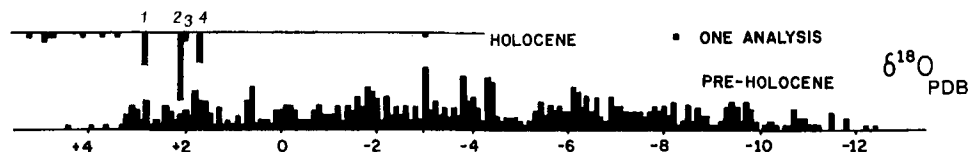
Figure 6. Range of oxygen isotopic compositions of some Holocene and ancient platform dolomites (modified from Land, 1980) with additional data on Holocene dolomites from McKenzie (1981), Carballo et al. (1987), Mazzullo et al. (1987), and Mitchell et al. (1987).

chemical alteration and neomorphism of dolomite. These rocks were believed to have been dolomitized syndepositionally in hypersaline peritidal environments. Based on analogy to modern dolomites, the dolomites were assumed to have been initially fine crystalline, poorly ordered, non-stoichiometric, and relatively enriched in Sr (perhaps not totally reasonable assumptions considering the foregoing discussions!) and Na, and with a possible $\delta^{18}O$ isotopic composition of approximately +4‰ PDB. The dolomites presently are coarse crystalline, better ordered and near-stoichiometric, depleted in Sr and Na, and have a $\delta^{18}O$ composition of approximately +1‰ PDB. Regionally, Sr and Na concentrations in the dolomites were found to decrease progressively in an updip direction, with corresponding depletion in ^{18}O in the same direction (Fig. 5). On the basis of these data, Land suggested that presumed preexisting, unstable peritidal dolomites were chemically and neomorphically altered as a result of post-depositional meteoric exposure. According to Land (1986) and others, Sr depletion accompanying stoichiometry enhancement, regardless of the specific diagenetic environment in which it may occur, is a result of the fact that the distribution coefficient of this element is less than unity, and the large Sr ion is not readily accommodated into the contracted lattice of more ideal dolomites where it substitutes mainly for Ca. In contrast, Sr is accommodated in the expanded lattice of poorly ordered dolomites. Some workers (e.g., Vahrenkamp and Swart, 1990), however have questioned the utility of using relative concentrations of Sr as diagenetic markers insofar as low-Sr dolomites may form as primary phases. Land (1980, 1983) went on to suggest that if positive $\delta^{18}O$ isotopic values of approximately +4‰ PDB (the average composition of many supposedly unaltered Holocene dolomites: Fig. 6) are preserved in ancient dolomites, then the implication is that chemical alteration has not occurred. He pointed out, however, that rarely are ancient dolomites so isotopically enriched. Instead, they typically are depleted in ^{18}O (Fig. 6), and if they are depleted by more than -2 to $-4‰$ (Land, 1980 and 1985, respectively), they therefore must have been either: (1) altered by ^{18}O-depleted fluids, or (2) altered by higher temperature fluids. Distinguishing the products of these processes in ancient rocks often is a difficult task.

Other studies similarly have documented and further refined our understanding of isotopic and trace and major element changes attendant with dolomite neomorphism. In a study of Mid-continent Mississip-

pian dolomites Banner et al. (1988), for example, recognized early formed dolomites, albeit partly altered by meteoric fluids soon after formation, that nevertheless remain non-stoichiometric, relatively enriched in Sr (106 ppm to 123 ppm), with $\delta^{18}O$ values that range from +2.5 to $-2.2‰$ PDB. In contrast, dolomites that presumably replaced these preexisting phases are more coarsely crystalline and more nearly stoichiometric, and are depleted in both Sr (53 ppm to 60 ppm) and ^{18}O (having values as low as $-6.6‰$ PDB). Studies such as these and others have indicated that perhaps the most definitive evidence for the geochemical alteration and neomorphism of dolomite in ancient rocks is on the basis of concurrent depletion in ^{18}O and Sr concentrations, increase in dolomite crystal size, ordering, and stoichiometry, and, if altered above the 50° to 60°C CRT, development of nonplanar textures. These criteria are most reliable when they can be compared relative to those parameters in a recognized preexisting, finer crystalline dolomite (Veizer et al., 1978; Land, 1980; Veizer, 1983; Gregg and Sibley, 1984; Sibley and Gregg, 1987; Gregg and Shelton, 1990; and numerous papers in Shukla and Baker, 1988) if such could be identified in the rocks (i.e., as described by Banner et al., 1988). Of course, evidence for alteration in those cases where we cannot recognize such preexisting phases, particularly in suspect dolomites with planar rather than presumed high-temperature nonplanar textures, ostensibly is less reliable. This is the situation we now face because, in terms of their oxygen isotopic compositions altered dolomites overlap and are not readily distinct from dolomites of other origin (Fig. 7). Similarly, whereas Holocene dolomites generally contain around 500 ppm to 800 ppm Sr (locally more), ancient dolomites of various origins, including altered ones, ubiquitously contain Sr concentrations of less than approximately 200 ppm (Weber, 1964; Land, 1980). So, interpretive problems remain.

Consider, for example, the situation depicted in Figure 8, which shows the geochemical compositions of some lower Permian, non-ferroan platform dolomites in the subsurface Midland Basin in Texas (Mazzullo and Ye, 1991). These dolomites occur in peritidal and shallow subtidal facies associated with evaporites and surfaces of subaerial exposure. Various lines of evidence (e.g., dolomitized intraclasts, synsedimentary evaporites having replaced dolomitized mudstones, etc.) suggest early syndepositional dolomitization. The rocks have been buried to depths where ambient temperatures were about 70°C. Fine crystalline (4–40 mi-
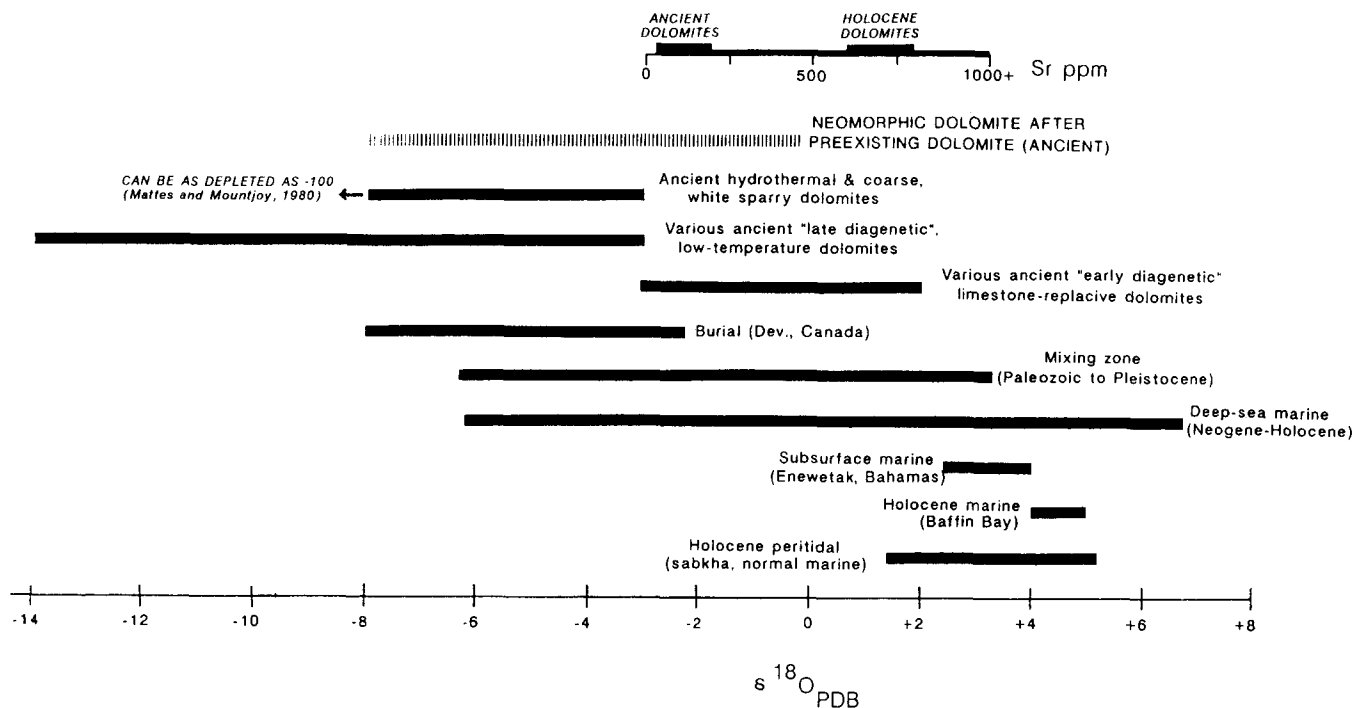
Figure 7. Range of oxygen isotopic and Sr compositions of some modern and ancient dolomites of known and less certain origin, including neomorphic dolomites. Data from the following sources: Choquette and Steinen (1980), Mattes and Mountjoy (1980), McKenzie (1981), Land (1983), Ward and Halley (1985), Carballo et al. (1987), Friedman (1987), Hardie (1987), Mazzullo et al. (1987), Mitchell et al. (1987), Banner et al. (1988), Holail et al. (1988), Lumsden (1988), Mullins et al. (1988), Machel and Anderson (1989), Gregg and Shelton (1990), and Vahrenkamp and Swart (1990). Major modes of Sr concentration (<200 ppm and 600–800 ppm) are range of averages for typical Holocene and ancient dolomites of various origins (from Weber, 1964; Land, 1980), the latter including neomorphic dolomites.

crons) type I dolomites in these rocks are characterized by planar and nonplanar textures, and have $\delta^{18}O$ isotopic compositions that are enriched by as much as 3‰ relative to lower Permian sea water; however, their isotopic composition becomes slightly depleted with increasing crystal size (Fig. 8A). These 4 micron-size dolomites may be a primary phase that formed initially in near-marine to slightly hypersaline fluids. Associated coarser crystalline (40–200 microns) type II dolomites are characterized by nonplanar textures, and have relatively depleted $\delta^{18}O$ isotopic compositions averaging about $-0.5‰$ (Fig. 8A). These dolomites and the 40 micron-size dolomites can be interpreted as the chemically altered, neomorphic equivalents of the 4 micron-size type I dolomites. However, whether the 40 micron-size crystals reflect early syndepositional neomorphic alteration of preexisting 4 micron-size crystals (e.g., McKenzie, 1981), or were formed later (e.g., perhaps by replacement in the burial environment) as a neomorphic product of or overgrowths on these finers crystals is uncertain.

What do the stoichiometry and Sr concentration of these dolomites tell us regarding possible alteration? The composition of the dolomites ranges from calcic to stoichiometric, and there is a definitive trend toward decreasing strontium concentration with increased

stoichiometry from type I to type II dolomite (Fig. 8B). Although such a trend often is taken as evidence of alteration it can not necessarily be cited as such because low-Sr, stoichiometric dolomites may form as primary phases (Vahrenkamp and Swart, 1990). Furthermore, because these dolomites are associated with evaporites we cannot necessarily even make the assumption that they all formed initially as non-stoichiometric phases (see discussions below). Although Sr concentrations decrease with increasing stoichiometry, there is a less than definitive trend between Sr concentration and oxygen isotopic composition in dolomite types I and II (Fig. 8A). If type II dolomites are of neomorphic origin, then we might expect to see a coincidence of increased stoichiometry and more depleted values of $\delta^{18}O$ between dolomite types I and II as would be expected if originally high-Sr, isotopically heavy, non-stoichiometric dolomites were altered to stoichiometric dolomites. The data in Figure 8C are inconclusive in this regard. Hence, type II dolomites could be alternatively interpreted as being of other than neomorphic origin.

Sodium. —Numerous studies have shown that generally, sodium concentrations also decrease as a result of the alteration of preexisting dolomites (Land, 1980, 1983; Holail et al., 1988; Moore et al., 1988). But there are mitigating factors that control Na concentrations
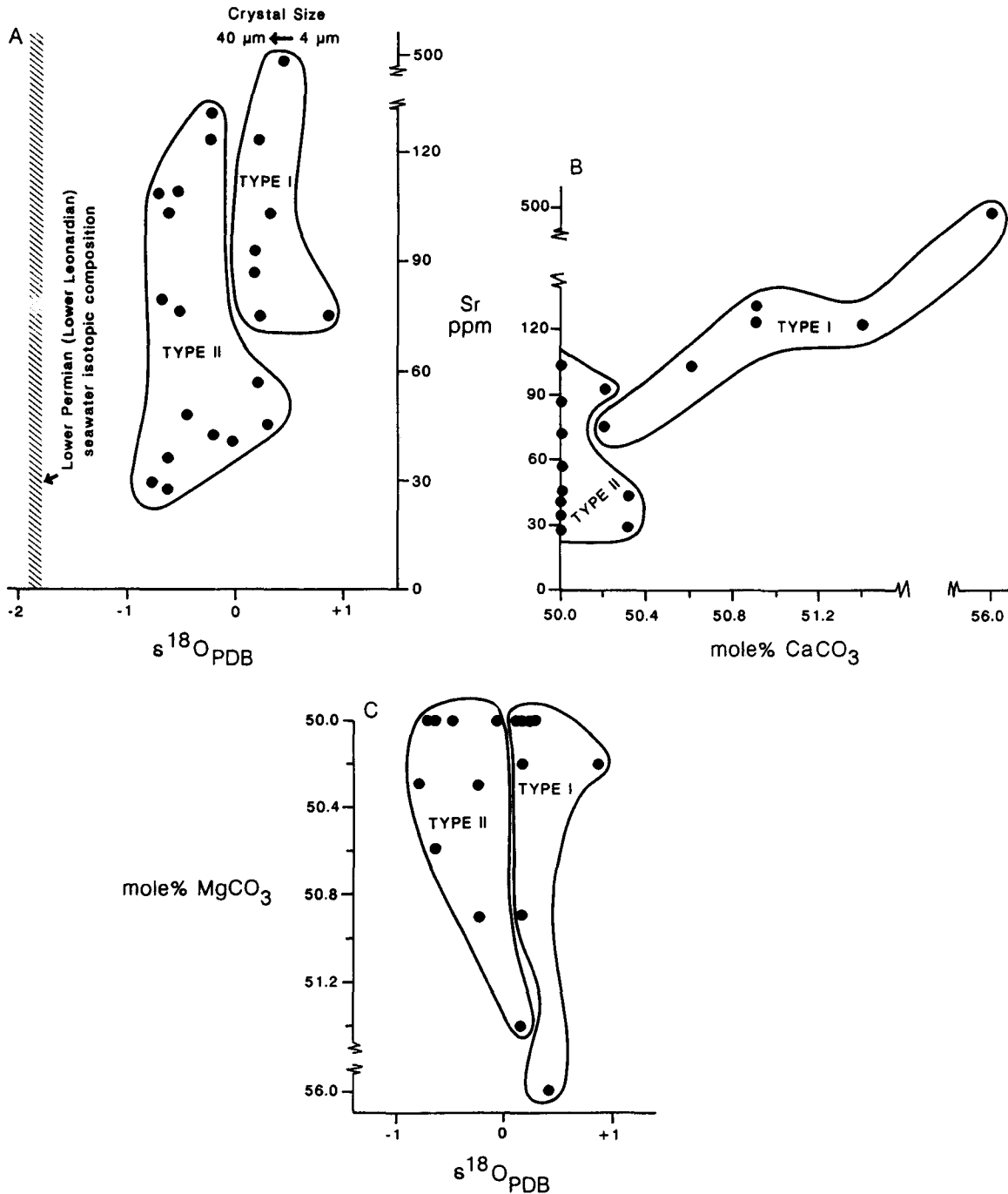
Figure 8. Geochemical data of dolomite types I and II in lower Permian (Lower Leonardian) platform dolomites, subsurface Midland Basin, Texas.

in dolomites. First, Na not only occurs within the lattices of crystals, but also as inclusions in crystals (Bein and Land, 1983). Distinguishing the relative contributions of Na from these different locations is important in geochemical studies, but is a difficult task (Bein and Land, 1983). Second, because many modern marine dolomites are non-stoichiometric and relatively enriched in Na, several workers have inferred that alteration must have occurred if dolomites are stoichiometric and have low Na concentrations. Such inter-

pretations must be tempered by the observation that newly formed dolomites may already by stoichiometric and relatively Na deficient. The studies of Lumsden and Chimahusky (1980), Morrow (1982b), Hardie (1987), and Sass and Bein (1988), for example, have shown that although Na concentrations in dolomites generally increase with salinity, some non-evaporative dolomites and those associated with gypsum vary from being initially stoichiometric to slightly calcian (57 mole % $MgCO_3$), with low (150 ppm to 350 ppm) and high

Figure 9. Relationship among Sr and oxygen isotopic compositions and Sr concentration in some Midcontinent Mississippian dolomites: EMD—estimated original marine dolomites; Dolomite I—marine dolomites that subsequently were slightly altered; Dolomites II and II'—progressively more neomorphically altered equivalents of Dolomite I (from Banner et al., 1988).

(as much as 2,700 ppm) Na concentrations, respectively. In contrast, dolomites associated with halite have almost ideal initial stoichiometric compositions and relatively low Na concentrations of 150 ppm to 270 ppm (Sass and Bein, 1988). Even though these aforementioned relationships are only gross approximations of the diagenetic behavior of these geochemical parameters, they nevertheless point out the fact that stoichiometric and low-Na dolomites can be primary rather than altered preexisting phases.

Another notable exception to the general relationship between high salinity and corresponding high Na concentrations in newly formed dolomites was discussed by Burns et al. (1988). They showed that Na concentrations in some Miocene deep-sea dolomites formed from interstitial fluids of normal marine salinity are comparable to those found in some recent, hypersaline dolomites (401 ppm to 1,840 ppm). Following Reeder (1981) and Busenberg and Plummer (1986), they presumed that such anomalously high Na concentrations were related to the fact that Na can be accommodated preferentially into the expanded lattices of poorly ordered and non-stoichiometric dolomites. Lastly, there may be certain relationships between initial Na concentration and mode of dolomitization, resulting fabric, and control by the chemistry of the replaced precursor in early formed dolomites (Shukla, 1988). More detailed study may reveal that such relationships are likely due in large part to the degree of alteration of these dolomites as well. Despite all these problems, Na nevertheless has been used in many instances as a diagenetic tracer in rocks and, in particular, as an indicator of paleosalinity (Land and Hoops, 1973; Veizer et al., 1977; Land, 1980, 1985; papers in Zenger et al., 1980; Bein and Land, 1983; Veizer, 1983; Sonnenfeld, 1986; Sass and Bein, 1988; papers in Shukla and Baker, 1988).
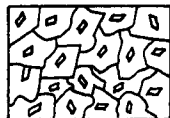
Iron and manganese.—Other elements such as Fe and Mn pose additional problems in studies of dolomite genesis. In studies of Mississippian and Jurassic dolomites Banner et al. (1988), Cander et al. (1988), and Moore et al. (1988), for example, reported that Fe and Mn concentrations, although they may be variable locally, generally increase in dolomites of likely neomorphic origin relative to preexisting dolomites. In contrast, Zenger and Dunham (1988), for example, re-

ported low Mn concentrations in possibly neomorphic dolomites of Silurian-Devonian age from New Mexico. According to Banner et al. (1988) and others, among the factors that affect the incorporation of Fe and Mn in diagenetic carbonates is the effect of redox control on locally derived supplies of Fe and Mn from sulfides, oxides, hydroxides, and silicates. These parameters vary greatly with respect to diagenetic environment, fluid chemistry, and the mineralogic composition of the dolomitized and surrounding rocks (see also Brand and Veizer, 1980, 1981). Whereas Fe and Mn are preferentially incorporated into dolomites because their distribution coefficients are greater than unity (Veizer, 1983), relatively high concentrations of these elements in diagenetic carbonates are expected in anoxic environments only (Land, 1986). Hence, the relative concentrations of Fe and Mn in precursor dolomites and their alteration products cannot be used as definitive criteria for the recognition of dolomite alteration. This is particularly true if one also considers the possible control on resultant dolomite chemistry of the geochemical composition of the precursor as was suggested recently by Holail et al. (1988) and Shukla (1988).

Strontium isotopes.—The Sr isotopic composition of dolomites reflects that of the fluids from which they were precipitated initially or subsequently altered (Burke et al., 1982). In those cases where marine fluids are involved in these processes, the timing of single or multiple episodes of dolomitization often can be inferred from the $^{87}Sr/^{86}Sr$ ratios in the dolomites upon comparison to curves prepared by Burke et al. (1982), DePaolo and Ingram (1985), Popp et al. (1986) and others. However, this relationship in itself can not necessarily be used to determine if alteration has occurred because similar Sr isotopic compositions are expected if, for example, dolomite formed initially in marine fluids and was altered subsequently in contemporaneous sea water. The later alteration of preexisting dolomites other than in contemporaneous fluids (such as in meteoric and mixed meteoric-marine waters or connate brines), however, can result in reequilibration of $^{87}Sr/^{86}Sr$ ratios in dolomites if, for example, radiogenic Sr in diagenetic fluids is derived from shales or more deeply-buried brines or non-radiogenic Sr is derived from other sources (Burke et al., 1982; Kesson et al., 1981; Chaudhuri et al., 1983; Banner et al., 1988).
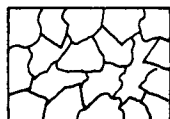
I. IN THE CASE OF PREEXISTING DOLOMITES

*THOSE WITH
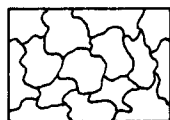IDENTIFIABLE CORES*

or

MASSIVE DOLOMITES

QUESTIONS/PROBLEMS

1. Where cores are present, are they detrital or authigenic? Can we in fact identify preexisting phases, particularly in massive dolomites?

2. In the case of either dolomites with core crystals or presently massive dolomites, were preexisting crystals (if present) metastable or stable?

3. To what degree, if any, were preexisting crystals stabilized early?

4. In what environment did any preexisting dolomites form -- early diagenetic (e.g., low-temperature) or later diagenetic (e.g., high-temperature)? Accordingly, were their textures planar or nonplanar?

5. If preexisting dolomites were stable or metastable, planar or nonplanar, in which environment(s) were they subsequently neomorphosed, if at all?

II. IN THE CASE OF DOLOMITIZATION OF PRECURSOR LIMESTONE

PLANAR TEXTURES

or

NONPLANAR TEXTURES

NEOMORPHISM → ALTERATION PRODUCT?

1. Can we determine if preexisting dolomites were present? Were they metastable or stable?

2. Metastable, originally planar textures that replaced limestone can be altered neomorphically to larger, stable crystals of planar texture below 50-60 degrees C; and originally metastable nonplanar textures that replaced limestone become stable but remain nonplanar if altered neomorphically at similar temperatures. If originally stable, however, there may be no further alteration except under epigenetic conditions over long periods of time. If crystals are now stable and either planar or nonplanar, can we determine if neomorphism has occurred, or even that the dolomite replaced limestone versus having replaced a preexisting dolomite?

3. What textures result from the high temperature (greater than 50-60 degrees C) neomorphic alteration of metastable nonplanar textures that originally replaced limestones?

III. WHAT IS THE ORIGIN OF GENERALLY COARSE CRYSTALLINE, NONPLANAR DOLOMITES?

Limestone → *High-temperature dolomitization*

Preexisting dolomite → *High-temperature neomorphism*

→ NONPLANAR TEXTURES

1. Can we truly determine if these textures have resulted from high-temperature neomorphism of a preexisting dolomite (metastable or stable) or are the products of dolomitization of limestones at high temperatures?

2. What is the timing and environment of such changes?

What is the effect on texture and geochemistry of recrystallization not driven by thermodynamic instability, and how can recrystallization versus neomorphism be recognized in ancient dolomites?

Figure 10. Some inherent difficulties in inferring neomorphic textures in dolomites.

Banner et al. (1988) interpreted essentially unaltered, non-stoichiometric, relatively Sr-rich replacement dolomites with near-marine Sr isotopic compositions as having formed shortly after deposition, from marine fluids. This initial phase was replaced by dolomites with better stoichiometry and depleted ^{18}O and Sr concentrations (Fig. 9), which were interpreted as being the result of alteration (neomorphism) in the burial environment. These altered dolomites had significantly higher $^{87}Sr/^{86}Sr$ ratios than the precursor dolomite (Fig. 9). They ascribed this new isotopic composition to nearly complete exchange of Sr in the preexisting dolomites with radiogenic Sr from deeper subsurface fluids during alteration. Other recent studies that have utilized Sr isotopic analyses to constrain the geochemical environment of dolomitization and alteration include those of Moore (1985), Moore et al. (1988), and Ruppel and Cander (1988). In a study of subsurface Jurassic carbonates from the Gulf Coast, Moore et al. (1988), for example, inferred that the elevated $^{87}Sr/^{86}Sr$ ratios of some platform dolomites were a consequence of either dolomitization of preexisting limestones or neomorphism of precursor dolomites in a meteoric fluid system.

In order to be useful, Sr isotopes must be incorporated into a diagenetic model that is based on supportive textural and other geochemical criteria such as changes in stoichiometry, relative oxygen isotope compositions, trace and major elemental concentrations (Fig. 9), and cathodoluminescence characteristics.

DISCUSSIONS AND CONCLUSIONS

So, where do we stand? The various petrographic criteria that have been proposed for the recognition of geochemically altered and neomorphic dolomites, for example, admittedly are individually equivocal and fraught with uncertainties (Fig. 10). Yet, many petrologists now feel that because of the inherent thermodynamic instability of most Holocene newly formed dolomites, by analogy geochemical and/or neomorphic alteration must have affected many ancient dolomites (although the role of recrystallization by itself remains unclear). The problem therefore lies not so much in attempting to define the causative processes of such alteration, but rather, to understand how to recognize the products of alteration in ancient rocks. There clearly is no unique solution to this problem. Based on presently available information it appears that four criteria, used collectively, offer persuasive although not necessarily definitive evidence of geochemical and neomorphic alteration, particularly in cases where the existence of a preexisting unstable dolomite phase can be demonstrated or inferred. These criteria are: (1) the transformation from non-stoichiometric to stoichiometric phases, concurrent with (2) the change from fine crystalline to coarse crystalline textures. If neomorphism occurred at temperatures below approximately 50° to 60°C, then the resulting texture of neomorphic dolomites may be mostly planar, whereas above these temperatures nonplanar textures may be most domi-

nant; (3) depletion in ^{18}O isotopic composition and Sr and Na concentrations relative to preexisting phases; and (4) homogenization of any primary CL zonation that may have been present in the preexisting phase.

The relative geochemical trends listed above are useful in identifying the presence of altered dolomites because diagenesis in open, fluid-dominated systems causes extensive exchange between preexisting phases and fluids, and results in marked differences in isotopic and elemental compositions between preexisting and secondary diagenetic minerals (Land, 1980, 1985, 1986). In fact, many of the examples of dolomite alteration cited in this paper have been from such diagenetic systems wherein altered dolomites can be more readily distinguished from unaltered dolomites. Of course, these geochemical tracers certainly may reflect modification of preexisting phases but they are, by themselves, not necessarily evidence of alteration. By contrast, diagenesis in systems that are partly closed to fluids, or rocks that are relatively poor in calcium carbonate, are rock-dominated wherein less fluid-mediated exchange occurs. Hence, the geochemical composition of secondary minerals may be similar to that of preexisting phases (see, for example, Baker and Burns, 1985; Mullins et al., 1988). In such cases alteration products may be less than readily evident. Because of these and other problems cited above, the answer to the question of whether or not some ancient dolomites have been altered both chemically and neomorphically often remains elusive (see Moore et al., 1988; Zenger and Dunham, 1988).

Based on recent studies it appears that dolomite alteration can occur in a myriad of diagenetic environments at various times in the history of sediments and rocks. The studies of McKenzie (1981), for example, have shown that Holocene dolomites are altered neomorphically in sabkha settings soon after their formation as non-stoichiometric phases. Similarly, early neomorphism of deep sea dolomites in shallow-burial interstitial fluids has been demonstrated by Burns et al. (1988), Compton (1988b), and Lumsden (1988). Likewise, later diagenetic alteration is known to occur post-depositionally, either upon exposure to meteoric or mixed meteoric-marine fluids in near-surface environments (Land, 1980, 1983; Moore et al., 1988), or in the mesogenetic environment associated with basinal brines (Gregg and Sibley, 1984; Sibley and Gregg, 1987; Banner et al., 1988; Gregg and Shelton, 1990).

The story of dolomite alteration is complex indeed. But we are now armed with just enough information that we can begin to recognize and critically assess the nature, extent, and significance of alteration in ancient dolomites.

ACKNOWLEDGMENTS

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