

**THE DOLOMITE PROBLEM:
STABLE AND RADIOGENIC ISOTOPE CLUES**

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The "dolomite problem" is a classic geological enigma: we cannot explain, to the satisfaction of a great number of scientists, many rocks composed dominantly of dolomite. Although numerous Holocene examples, possibly analogous to some ancient deposits, have been described and are still being described, no analog exists to massive stratal dolomites common in the geologic past. Considering the brevity of the shallow water "platform-like" Holocene record, it is unlikely such analogs will ever be found. To compound the problem, dolomite has yet to be synthesized in the laboratory under earth-surface conditions. Practically, this means that we cannot test quantitative measures of dolomite behavior such as trace element distribution coefficients and isotopic fractionation factors.

Another complicating factor, which is also true of virtually all other chemically-generated sedimentary phases, is that the mineral which forms during or immediately following sedimentation is almost never preserved without chemical modification. Limestones provide an excellent parallel. Modern carbonate sediments are composed of the minerals aragonite and Mg-calcite, yet limestones are composed of calcite. The metastable "precursor" phases aragonite and Mg-calcite are transformed stepwise during diagenesis, according to Ostwald's rule, to a more stable configu-

ration. Primary chemical signatures are either irrevocably lost, or modified to the point that we are not yet able to untangle the original from the secondary. Dolomite behaves similarly.

Most Holocene dolomite is Ca-rich, very fine-grained, and is characterized by numerous crystallographic imperfections (e.g. Wenk et al., 1983). Aragonite and Mg-calcite, the precursor phases to limestones, are replaced by calcite as limestones form, and early-formed dolomite is similarly replaced during diagenesis by more stable dolomite phases. Our goal in utilizing isotopic data to understand dolomite (or any other chemically precipitated sedimentary phase) should be not only to characterize the primary sediment, or characterize the water from which it formed, but to understand the history of the sediment, from its chemical inception through its subsequent modification. We should not be surprised or disappointed if we are unable to deduce conditions of genesis, which remains only one (elusive) goal of sedimentology. In the case of dolomite, isotopic data have proven more useful than many other kinds of observations in documenting the geologic history of various kinds of dolomite.

Dolomite, $\text{CaMg}(\text{CO}_3)_2$, contains major cations (Ca and Mg), minor cations (e.g., Sr, Fe, Mn, and Rare Earth Elements), major anions (C and O), and possibly minor anions like borate and sulfate, all of which can substitute into the crystal lattice (as opposed to being adsorbed, or trapped in fluid inclusions). The potential number of isotopic systems which bear on the mineral dolomite is clearly very large! Only a few of the potentially useful isotopic systems have been utilized, however. All dolomite crystals are precipitates whether they "replace" other phases or form primary sediment or cements. Solid state reactions are precluded at the temperatures characteristic of sedimentary basins. Because dolomite precipitation from aqueous solution involves vast amounts of oxygen, oxygen isotopes have proven most useful in elucidating dolomite geochemistry. Carbon isotopes, though less useful, have the capacity to document both redox conditions and secular changes in ocean chemistry. One of the most nagging problems of dolomite genesis has been the source of sufficient amounts of Mg to account for large volumes of dolomite.

Of the "cation-tracers", Sr isotopes are proving to be of great utility in constraining the Mg source. Each of these isotopic systems, for which considerable data exist, will be treated in turn. A final section is devoted to the remainder, and to speculations about useful paths for future research.

OXYGEN ISOTOPES

Like most oxygen-bearing minerals, we presume there exists a temperature-dependent equilibrium relationship between the oxygen isotopic composition of a growing dolomite crystal and the water from which it precipitates. We cannot currently precipitate dolomite in the laboratory under earth-surface conditions, and therefore the relationship we seek must be approximated. Two methods of approximation have evolved, and, fortunately, they are in reasonable agreement. The first determines the needed relationship at sufficiently high temperatures so the reaction takes place in the laboratory on a reasonable time scale, and extrapolates the results to earth-surface temperatures, and the second utilizes natural examples. Before investigating the results of these two approaches, however, we must understand how analytical methodology bears on our results.

Methodology

When Urey first recognized the potential utility of carbonate minerals to determine past earth surface temperatures, he also recognized the difficulty of simply extracting the oxygen isotope ratio from these minerals. At that time, fluorination techniques were not available, and it was quickly recognized that the decomposition reaction:



yielded CO_2 (the preferred gas for analysis) whose isotopic composition depended on numerous uncontrollable variables (surface area, heating rate, crystal defect density, trace element composition, etc.). Fortunately, Urey's student, McCrea, recognized that anhydrous phosphoric acid could be used to release CO_2 reproducibly, albeit not quantitatively, from carbonates. But if we only analyze two of the O atoms in carbonate minerals with this technique, how do we relate the isotopic composition of the mineral (all three O atoms) to the isotopic composition of water (as a function of temperature)? The answer is that we must know the fractionation factor (known as the phosphoric acid fractionation factor) between the oxygen in the mineral (all three O atoms), and the oxygen in CO_2 released from the mineral (as a function of temperature). Just as each carbonate mineral has a unique mineral-water fractionation factor, each carbonate mineral has a unique phosphoric acid fractionation factor.

A further complication has developed because of the use of two different standards, SMOW (Standard Mean Ocean Water) and PDB (Pee Dee Belemnite). Urey chose a natural skeletal calcite for a standard (not wisely, in hindsight) and used the $^{18}\text{O}/^{16}\text{O}$ of the CO_2 released from that calcite in phosphoric acid for a reference. To complicate matters, he was also unable to determine the $^{18}\text{O}/^{16}\text{O}$ of H_2O . Instead, Urey recognized that the reaction between CO_2 and H_2O proceeds reasonably rapidly in the laboratory, and so if he added a small amount of CO_2 (sufficient for analysis) to a large amount of H_2O , and allowed equilibrium to be obtained, analysis of the $^{18}\text{O}/^{16}\text{O}$ in the CO_2 would be proportional to the $^{18}\text{O}/^{16}\text{O}$ in the H_2O . The proportionality is, of course, the fractionation factor. Urey's classic "paleotemperature equation" relates the $^{18}\text{O}/^{16}\text{O}$ in CO_2 evolved from calcite in anhydrous phosphoric acid at 25°C to the $^{18}\text{O}/^{16}\text{O}$ of CO_2 equilibrated with water at 25°C . In order to convert to the SMOW scale we need three fractionation factors (Fig. 1): (a) the relation between the $^{18}\text{O}/^{16}\text{O}$ of calcite and the $^{18}\text{O}/^{16}\text{O}$ of CO_2 evolved by reaction of calcite in anhydrous phosphoric acid at 25°C , (b) the relation between the $^{18}\text{O}/^{16}\text{O}$ in water and the $^{18}\text{O}/^{16}\text{O}$ in CO_2 in equilibrium with water at 25°C , and (c) the relation between the two CO_2 samples (1 and 2) when the calcite and water are in equilibrium with each other.

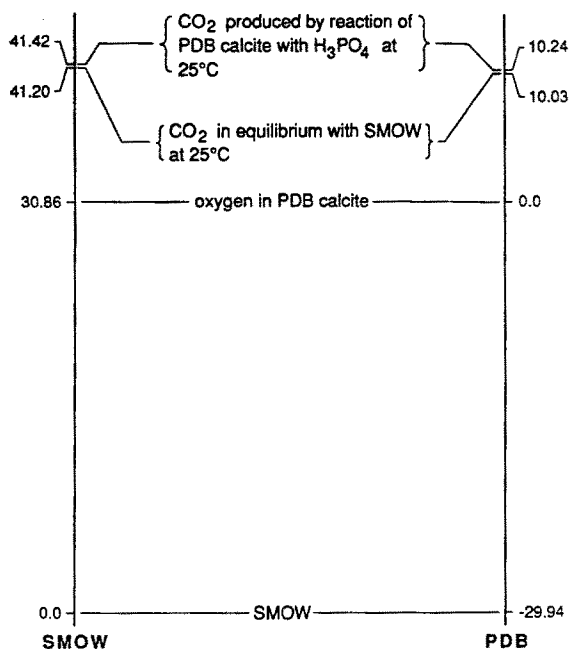


Figure 1: Graphical representation between SMOW and PDB scales (after Land, 1980, his figure 6)

If we are interested in minerals other than calcite (like dolomite), then all relations must be known for each mineral. Because different researchers may have used different methodology (e.g. different standards, different reaction temperature, etc.), we must be certain to understand what each investigator actually measures and reports, in making comparisons and in interpreting the analyses.

High Temperature Studies

Surprisingly, only five studies have been made of dolomite water fractionation at elevated temperature (Fig. 2), and none in almost 15 years! None of these early studies characterized the microstructure of the dolomite which was synthesized, or examined the reaction products carefully with the electron microscope to document the petrographic nature of the precipitates. Nevertheless, we can be quite certain that dolomite is enriched in ¹⁸O by 3 ± 3 per mil at 25°C relative to calcite precipitating

under the same conditions of $\delta^{18}\text{O}$ and temperature. This is often expressed by the statement that the "delta" value (the difference in the δ -values between calcite and dolomite) is about 3 per mil.

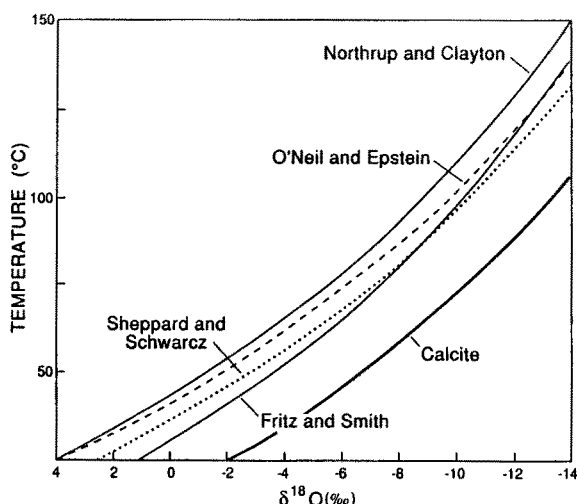


Figure 2: Four available equations for dolomite-water fractionation as a function of temperature for water having a $\delta^{18}\text{O}$ of 0 per mil (SMOW; after Land, 1983 his Fig. 4-1)

Natural Examples

New examples of modern dolomite are being found and described almost every year. Most examples are marine, ranging in salinity from hypersaline to normal marine, but many examples of dolomite forming in playas are also known. The problem in using modern examples is that the dolomite is rarely forming at the actual time of sampling, and therefore the $\delta^{18}\text{O}$ of the water and the temperature must be assumed for the recent past. Additionally, the dolomite often replaces precursor Ca-carbonate phases, and although Ca carbonate and dolomite coexist, they are not commonly cogenetic. These are difficult problems in the case of an environment like a playa, where conditions can be very ephemeral. But they are less difficult in the case of marine and marine hypersaline environments where sufficient sedimentological study has been accomplished to constrain past conditions. Table 1 lists modern environments where the $\delta^{18}\text{O}$ of water, $\delta^{18}\text{O}$ of dolomite, and temperature are all known. A Δ value is then calculated by

subtracting from the analyzed dolomite value the value of calcite which should precipitate under the observed conditions of $\delta^{18}\text{O}$ water and temperature. Recognizing that ranges of values are characteristic of all environments which have been studied so far, the conclusion from the high temperature studies that $\Delta = 3 \pm 3$ per mil can be further constrained to 5 ± 2 per mil.

Table 1

Locality	$\delta^{18}\text{O}$ water	$\delta^{18}\text{O}$ dolomite	Temperature (°C)	Δ
Jamaica (Mitchell et al., 1987)	+0.8	+2.0	26-29	4.2
Baffin Bay (Behrens and Land, 1972)	+2.0	+4.8	24-30	2.9
Florida (Carballo et al., 1987)	+0.9	+2.8	30-32	5.6
Gulf of Elat (Aharon et al., 1977)	+11.0	+9.0	49-57	6.7
Persian Gulf (Mackenzie, 1981)	+3.9	+2.1	32-39	3.0
Deep Springs (Clayton et al., 1968)	-2.1	+2.5	15-25	6.0

$\delta^{18}\text{O}_{\text{PDB}}$ was converted to $\delta^{18}\text{O}_{\text{SMOW}}$ using the equation: $\delta^{18}\text{O}_{\text{SMOW}} = 1.03086 \times \delta^{18}\text{O}_{\text{PDB}} + 30.86$. $\delta^{18}\text{O}$ calcite was calculated using the equation from Friedman and O'Neil (1977): $10^3 \ln \text{calcite-water} = 2.78 \times 10^6 T^{-2} - 3.39$ where T is in degrees Kelvin ($^\circ\text{C} + 273.16$). Δ is $\delta^{18}\text{O}_{\text{observed dolomite}} - \delta^{18}\text{O}_{\text{calculated calcite}}$

To a first approximation, if the measured $\delta^{18}\text{O}$ of dolomite is made 3.8 per mil more negative (3 per mil because of the Δ value between calcite and dolomite, and 0.8 per mil because of different phosphoric acid fractionation factors between the two minerals), and the fractionation between calcite and water is used (see Table 1), then a satisfactory approximation for the equilibrium relations between dolomite and water, as a function of temperature, can be made. Future work may refine this approximation, probably upward, but it seems to be sufficiently accurate that useful conclusions can be reached. More experimental work, and more analyses of existing natural examples, are clearly needed. Figure 3 graphs the above relationship and presents, as a histogram at the top, a summary of dolomite values from the literature as of about 1979. Quite clearly, few described samples

could have precipitated from seawater (or hypersaline seawater) at earth-surface conditions. Either most dolomite did not form under earth surface conditions, or dolomite is "reset" during diagenesis to more ^{18}O -depleted values. Considerable support can be advocated to support the latter supposition.

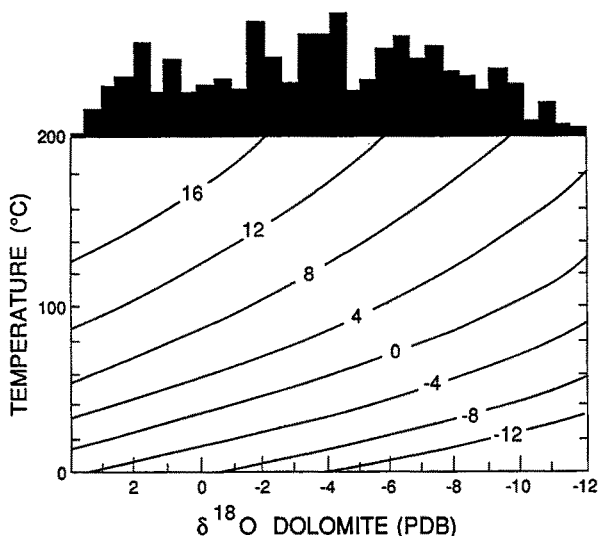


Figure 3: Graphical representation of the oxygen isotopic composition of dolomite (PDB scale), $\delta^{18}\text{O}$ water (SMOW scale), and temperature. At the top of the diagram is a summary of data obtained on sedimentary dolomite as of about 1979 (after Land, 1985, his Fig. 9)

Modern dolomite is trace element rich, and forms small crystals with numerous imperfections (e.g. Mitchell et al., 1987). Ancient dolomites are typically trace element depleted (or contain abundant Fe, an element rare in modern carbonates), and form large crystals characterized by simple, more nearly ideal microstructure. Stepwise stabilization of metastable precursor phases is the most likely explanation for these observations, and is substantiated by oxygen (and Sr) isotopic analyses. More stable phases are typically depleted in ^{18}O (e.g. Fritz and Jackson, 1972), and can be either enriched or depleted in ^{87}Sr (Gao, 1990), due to stabilization during burial at elevated temperature by solution-reprecipitation (replacement).

If we consider the amount of oxygen in a carbonate sediment relative to the amount of oxygen in the pore fluids, we can

demonstrate that the ratio of those two "reservoirs" (the rock/water ratio) is the lowest of almost any isotopic or trace element system we can conceive. For example, using 40% porosity as a reasonable value for unconsolidated sediments (and typical modern carbonate sediments in seawater for subsequent calculations), the ratio of the number of O atoms in the minerals to the number of oxygen atoms in the water (the rock/water ratio) is 2.2. If replacement takes place (by dissolution-precipitation, since solid state processes can be ignored at earth surface temperatures), then the oxygen isotopic composition of the secondary mineral can easily be changed because subequal numbers of O atoms are present in both the minerals and the pore fluids. This suggests a "test" for unaltered minerals. If any trace component (including isotopes) having a rock/water ratio higher than oxygen has been altered, then the oxygen isotopic composition of the mineral must have been altered as well. It needs not to have changed from its original composition, by pure happenstance, but it must have been altered. As a corollary, if components with higher rock/water ratios than oxygen have not been altered, that does not prove that the oxygen isotopes are unaltered also. Because the rock/water ratio for oxygen is so small, a very small amount of replacement can affect the oxygen isotopic composition of a mineral without causing measurable changes in other components. Dolomite formed in a sabkha (say $\delta^{18}\text{O} = +4$ per mil PDB) can be replaced (in meteoric lenses, for example) by a more stable phase, shifting the $\delta^{18}\text{O}$ to, say -3 per mil, without any measurable effect on the C or Sr isotopic composition (but with a large effect on the Sr concentration). For this reason, the use of oxygen isotopes along with other isotopic (and trace element) systems provides a potentially much more powerful tool than the use of oxygen isotopes alone.

CARBON ISOTOPES

Barring small effects due to the solubility of CO_2 in phosphoric acid, the $^{13}\text{C}/^{12}\text{C}$ ratio of the CO_2 released on

digestion of carbonate minerals in phosphoric acid is presumed to be identical to the $^{13}\text{C}/^{12}\text{C}$ ratio in the mineral. Equilibrium relationships between calcite, dissolved carbon (mostly HCO_3^- at the pH's typically encountered in water in contact with carbonate rocks), and CO_2 gas, are reasonably well known (Fig. 4). But unfo-

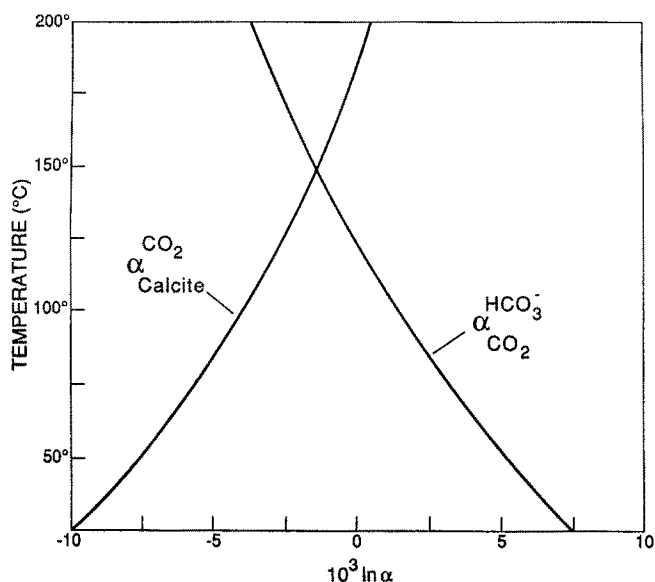
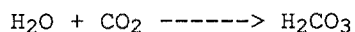


Figure 4: Fractionation between calcite and CO_2 , and between bicarbonate and CO_2 as a function of temperature (after Friedman and O'Neil, 1977). Given an atmospheric CO_2 value of -7 per mil at 25°C , equilibrium bicarbonate should be about +0.5 per mil and calcite +3 per mil

rtunately, we also know that precipitation rate can affect the carbon isotopic composition of calcite (and presumably dolomite), something which has not been (and hopefully never will be!) demonstrated for oxygen. The situation is similar to the uptake of trace elements in that rapidly precipitating crystals simply sequester the component of interest ($\text{CO}_3^{=}$ in this case) from solution so rapidly that equilibrium processes, limited by the slowest reaction (in this case the isotopic exchange that takes place via the reaction:



cannot prevail. As a result (see Fig. 4), rapidly precipitated calcite (and presumably dolomite) can be depleted in ^{13}C relative to an equilibrium precipitate.

Assuming that water in contact with carbonate rocks contains about 200 mg HCO_3^-/l (3.3 millimoles C/l), then a carbonate sediment or rock ($36.94 \text{ cm}^3/\text{mole}$) having 40% porosity has a rock/water ratio of about 12,000. Appreciable changes in the carbon isotopic composition of carbonate sediments during replacement by dolomite will, therefore, be very difficult to achieve. If approximately 1000 pore volumes of seawater are sufficient to completely dolomitize a sediment (e.g. Land, 1985), and if the carbon isotopic composition of the water were to differ from the sediment by 10 per mil (an extreme case!), then the dolomite which formed would still be no more than about 1 per mil different from the precursor sediment. Carbon isotopes, therefore, have been of less use than oxygen isotopes in interpreting the origin and diagenetic history of dolomite, and only few authors have systematically considered them.

Aerobic and anaerobic microbial processes during early sediment burial, aerobic oxidation during subareal exposure, and thermal maturation of kerogen during deep burial all release ^{13}C -depleted carbon from organic matter, which may be incorporated in carbonate phases. Dolomite depleted in ^{13}C relative to expected normal marine values is known from a variety of environments, including lithified supratidal crusts associated with subareal exposure (Carballo et al., 1987), generally poorly lithified deposits associated with extensive sulfate reduction of organic-rich sediments (Behrens and Land, 1972; Garrison et al., 1984), and late stage dolomite cements associated with hydrocarbon emplacement (Woronick and Land, 1985). Distinguishing these various environments in the rock record on the basis of carbon isotopes alone is impossible, but used in conjunction with sedimentary structures and textures, and in the context of sequence stratigraphy, carbon isotopes can be useful in confirming depositional environments. For example, an upward trend toward depleted ^{13}C values as one approaches an exposure surface would provide support for subareal exposure and the development of a

soil cover (Allen and Matthews, 1982). In the absence of petrographic, stratigraphic, or paleogeographic evidence of exposure, however, depleted carbon values could be explained in many other ways.

Both extremely enriched and extremely depleted carbon isotopic values do, however, seem to be diagnostic of specific sedimentary environments and processes (see figure in companion paper of Holser). $\delta^{13}\text{C}$ values in carbonates in excess of about +6 per mil seem to require a process commonly known as "fermentation". Taking place microbially (and therefore at temperatures less than about 80°C) after elemental O_2 and oxygen from compounds like Fe-oxides, Mg-oxides, and dissolved sulfate have been consumed, $^{12}\text{CO}_2$ is preferentially utilized by bacteria as an O source, leaving behind a reservoir of CO_2 enriched in ^{13}C . Nodules are able to record evolving carbon diagenesis, beginning with oxidation and sulfate reduction at shallow burial depths (meters or tens of meters), which are characterized by depleted $\delta^{13}\text{C}$ values, and proceeding into the zone of methanogenesis (Irwin et al., 1977). At the other end of the spectrum, carbon isotopic values more depleted than about -28 per mil seem to be indicative of methane oxidation, since methane is the only natural C-containing compound known to contain such depleted carbon. Little dolomite has been documented from such environments.

With few exceptions, most dolomite is characterized by carbon isotopic values between about +6 and -2 per mil, values characteristic of marine limestone precursors. Although some data suggest dolomite should be enriched in ^{13}C relative to calcite by about 2 per mil (Sheppard and Schwarcz, 1970), little confirmatory evidence has emerged from the study of modern examples. Dolomite rocks associated with hypersaline environments are commonly relatively ^{13}C -enriched, in keeping with the inorganic (rather than skeletal) nature of the precursor sediments and the paucity of abundant organic matter in highly evaporitic environments. Absolute values should never be used as diagnostic of any particular environment without reference to the petrography of the rocks themselves, and their age must be kept in mind since secular

variations in marine carbon of approximately 4 per mil have been determined and are well documented (Fisher and Arthur, 1977).

STRONTIUM ISOTOPES

Strontium is the most abundant trace element in carbonate sediments and most carbonate rocks. Reasons for the abundance of Sr include the fact that it is the ninth most abundant ion in seawater (not counting H and O), and it is preferentially incorporated in many skeletal and inorganic precipitates of aragonite up to, and even exceeding concentrations of 10,000 $\mu\text{g/g}$. Most modern carbonate sediments are deposited from marine water and contain aragonite as a primary phase. Even Holocene marine dolomite, whether of normal marine or hypersaline marine origin, contains about 800 $\mu\text{g/g}$ Sr. Therefore, the reservoir of Sr in primary carbonates is quite large, about 1250 times the reservoir of Sr in the pore fluids in a primary marine sediment. But this is less than the rock/water ratio for carbon previously discussed by about a factor of ten, so Sr will be about ten times more sensitive than carbon to early diagenetic modification. The situation is very different during late diagenetic modification, however, when porosity is much lower (say about 10%). The rocks no longer contain Sr-rich phases like aragonite (typical limestones contain only about 200 $\mu\text{g/g}$ Sr), and saline pore fluids can be quite Sr-rich (about 2000 $\mu\text{g/g}$). In this case the rock/water ratio is about 2.4, less than that of O (which is 13.2) under the same circumstances. So under subsurface conditions, if the rock is out of ionic equilibrium with its pore fluids, and dissolution-reprecipitation takes place, Sr isotope ratios can be more easily altered than O isotope ratios.

Carbonates contain too little Rb to be good candidates for Rb-Sr age dating, but Sr isotopes still can provide some extremely useful information. The reason for this is that we know that the $^{87}\text{Sr}/^{86}\text{Sr}$ of seawater has varied over a range more than one hundred times larger than our ability to measure that ratio (see

companion paper of Holser in this volume). The driving forces for the secular change include changes in continental runoff and hydrothermal circulation through ocean ridges, both processes being driven by variations in plate dynamics. The Sr isotopic system represents a fascinating and productive way to study these processes. But our emphasis here is on understanding how to use the Sr isotopic system to understand dolomite paragenesis. Therefore, we want to use the secular variation in seawater without necessarily having to understand it. But first we must be certain that we understand how the $^{87}\text{Sr}/^{86}\text{Sr}$ of seawater has changed with time. How can we do this if the recorded ratio in the rocks has been modified by post-depositional changes? The answer is that we must always proceed on parallel paths of investigation. We must understand diagenesis, using as many tools as possible, in order to document both the primary conditions of deposition, and to quantify subsequent changes. Because the rock/water ratio is usually relatively large, and barring extensive burial modification (which would be evidenced by depleted $\delta^{18}\text{O}$ values) documenting the $^{87}\text{Sr}/^{86}\text{Sr}$ (and $^{13}\text{C}/^{12}\text{C}$) ratio of ocean water is much easier than documenting the $^{18}\text{O}/^{16}\text{O}$ of ancient oceans.

Heavy isotopes like Sr (we are concerned with masses 86, 87, and 88) do not fractionate in the same way as is observed with light isotopes like oxygen and carbon. There simply isn't sufficient mass difference for ^{86}Sr to fractionate from ^{88}Sr as processes like mineral precipitation take place. So the mineral (dolomite in this discussion) always bears the same isotope ratio as the fluid from which it precipitates. If dolomite formed in, say, mid-Ordovician time from coeval seawater, it might have a $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7085 (see seawater curve in Holser's companion paper). If the $^{87}\text{Sr}/^{86}\text{Sr}$ "age" of a dolomite agrees with its stratigraphic "age", then contemporaneous dolomitization by seawater is logical. Of course we must always be careful to examine other evidence as well. For example, a mid-Ordovician dolomite having a $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7085 could also have formed from mid-Silurian, early Devonian, or even early Miocene (see seawater curve in Holser's companion paper) seawater, or have been reset by groundwater which had flowed through strata of these ages. Given the stratigraphic constraints and the Sr isotopic data we would

need to assess, on geological grounds, whether or not post-Ordovician seawater having a $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7085 was a possible agent of dolomitization.

Conversely, if we know from paleontological or other evidence that a certain dolomite replaced lower Cretaceous rocks, and we measured a $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7098 on the dolomite (again, see the seawater curve in Holser's companion paper), we could be quite certain that if the dolomite formed contemporaneously with deposition, it must have been subsequently modified by a fluid other than seawater. Alternatively, the dolomite did not form from seawater in the first place. Saller (1984) used similar reasoning to conclude that dolomite found in Eocene rocks of Enewetak Atoll was formed by circulation of Middle Miocene or younger seawater through the atoll. He measured a $^{87}\text{Sr}/^{86}\text{Sr}$ between 0.7086 and 0.7090 on the dolomite, eliminated all other possible reservoirs of Sr (easy to do in this Pacific Ocean setting), recognized that seawater is the only source of mobile Mg at the earth's surface, documented a reasonable way to circulate seawater through the buried sediments (by low temperature hydrothermal convection), and thus destroyed previous dogma (Berner, 1965).

Obviously, Sr isotopes can provide powerful constraints, but constraints which depend on accurate knowledge of variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater, and the assumption that the world ocean always had a uniform Sr isotopic composition. The latter assumption is certainly true today (based on actual measurements), and supported by knowledge that the residence time for Sr in the ocean (the time it would take for all the Sr in the ocean to be replaced by continental discharge, hydrothermal circulation, and diffusion of Sr out of sediments undergoing burial diagenesis) is relatively short, on the order of 4 million years. But the world ocean today is very well connected because of the continent distribution and is being very actively circulated on a time scale of only a few thousand years because of our present "ice-house" climate. In the past, neither of these requirements may have been met, and although variations in $^{87}\text{Sr}/^{86}\text{Sr}$ between coeval ocean basins or within a single stratified ocean basin has not yet been demonstrated, we must consider that possibility.

If we can demonstrate that a given dolomite is characterized by an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio inconsistent with coeval dolomitization by seawater, then what information is provided? The first hypothesis we should test is that dolomitization was caused by seawater subsequent to deposition of the rocks (as Saller concluded). Because it provides such a ready source of Mg, seawater should always be the solution of "first choice" for dolomitization. Because of the complex nature of the secular variation of seawater $^{87}\text{Sr}/^{86}\text{Sr}$, the Sr isotopic composition of dolomite could be either higher or lower than the composition of coeval seawater. If geologic constraints eliminate such an hypothesis (or the $^{87}\text{Sr}/^{86}\text{Sr}$ of the dolomite falls outside the range of seawater variation), then we must conclude that the dolomite has been "reset", or it did not form from seawater in the first place. Using our conclusions from the oxygen isotopic composition of dolomite (Fig. 3), replacement of metastable dolomite by ^{18}O -depleted, more stable phases, is most easily caused by meteoric water, or by increased temperature during burial (Gao, 1990). In both cases, sources of ^{87}Sr from Rb-bearing silicates tend to elevate the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. We know that modern rivers and modern formation waters exhibit wide ranges in $^{87}\text{Sr}/^{86}\text{Sr}$ (see companion papers by Chaudhuri and Clauer, this volume), so once we are sure that the measured Sr isotope ratios do not record coeval or younger seawater, interpretation of absolute values will be very difficult.

Although absolute values may be hard to interpret, spatial variation, as in the case of the other isotopic systems, may be extremely useful. If rock chemistry is changed by import of allochthonous material (as opposed to autochthonous "cannibalization" by stylolitization), then an ancient flow system must have existed. Systematic changes in isotope ratios (and trace element concentrations) can define the direction of flow assumed by diagenetic fluids and "point to" the source of the diagenetic fluids themselves. For example, suppose a dolomite formation displayed typical "marine" isotope ratios in one area, depleted ^{13}C , and ^{18}O , and more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ in another area, and systematic intermediate values in between. A possible interpre-

tation might be that the formation once behaved as an aquifer, and hot, ^{13}C -depleted, radiogenic basinal fluids invaded the aquifer and "reset" an early generation of dolomite. Quantitative modelling of the different isotopic systems (accompanied by other geochemical and petrographic measurements) could constrain not only the direction of fluid flow, but the composition and volume of fluid involved. Although these types of calculations are in their infancy (e.g. Land, 1980, his Appendix III; Banner et al., 1988, their Fig. 14), they hold great promise.

OTHER ISOTOPIC SYSTEMS

The oxygen, carbon, and strontium isotopic systems just discussed are only three of the potentially useful isotopic systems that have been extensively investigated. Continued improvement in mass spectrometers and in the chemistry involved in sample preparation suggests that many more isotopic systems will be utilized in the future. Ca and Mg are both major elements which have natural stable isotopes which may prove to be of use. Measurable natural fractionation of Mg may or may not occur between ^{24}Mg and ^{26}Mg . It has been shown that natural fractionation as much as 2.5 per mil can affect the $^{40}\text{Ca}/^{44}\text{Ca}$ ratio (Russell et al., 1978), but whether or not useful conclusions will result from the study of dolomite remains to be demonstrated. Sulfur and boron isotopes also have potential application if substitution for carbonate in the dolomite lattice takes place, or if sufficient amounts of either element are incorporated in fluid inclusions.

Recently, a few analyses of dolomite involving the Sm-Nd system have been accomplished. Rare earth elements are vanishingly soluble in water so that rock/water ratios are extreme, typically around 10^6 (Banner et al., 1988). The Mississippian dolomites studied by Banner et al. apparently record the Ce-depleted signature of oxidizing seawater, and Nd isotopic analyses can be interpreted (not unequivocally, however) as being controlled by

late Paleozoic seawater. Considerably more data will be needed, however, before application of rare earth isotopic systems to dolomite is fully understood.

CONCLUSION

At what time(s) in the history of a sediment did dolomite form? What kinds of solutions were involved? Were conditions (e.g. temperature, ocean composition) at the earth's surface different than they are today? Isotopic analyses are just one tool which can be used to constrain answers to these important questions. But isotopic data alone are almost never unequivocal, and a single isotopic system rarely useful. Isotopic data must be obtained within a sedimentologic and petrographic framework, and used in conjunction with elemental analyses and quantitative models. Only in this way can these powerful tools be wisely used.

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