

DEPOSITIONAL AND DIAGENETIC HISTORY OF LIMESTONES:
STABLE AND RADIOGENIC ISOTOPES

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Carbonates represent one of the dominant rock types in the sedimentary shell of this planet. They contain a wealth of information about the nature of sedimentary environments, their temporal evolution and their post-depositional history. Carbonates are also commonly repositories of mineral wealth, including metals, hydrocarbons, and water, and they are also the major resource for production of cement aggregate and building stones. Information contained in these rocks, if properly deciphered, goes beyond what we usually perceive as geology sensu stricto. Carbonates reflect the evolution of the ocean-atmosphere system over geologic time and permit to decipher its nature and variability prior to the advent of man as a geological agent. Environmental questions are emerging as perhaps the most important political issue of our times and they may dominate the forthcoming research agenda. If properly understood and applied, the isotope techniques discussed briefly in the subsequent section can serve as powerful tools for study of problems with scientific as well as economic and environmental overtones.

ISOTOPE SYSTEMATICS APPLIED TO CARBONATE ROCKS

Carbonate sediments and carbonate rocks contain a plethora of isotopic tracers that can be utilized either for dating (absolute or relative) or for tracing of processes involved in their formation and post-depositional stabilization.

The isotope systematics for dating purposes include the ^{14}C and the so called U-series disequilibrium methods, all utilized for dating of Holocene sediments up to several hundred thousand years old. These geochronometers are not the subject of the present chapter, but their overview is available in Faure (1986) and Bernat and Church (1989). In addition, the last few years witnessed an effort by several laboratories (e.g. Jahn et al., 1990) to utilize the U-Pb geochronometer for absolute dating of carbonates. This geochronometer has a potential for dating of old, particularly Precambrian, carbonate rocks, because their ages are often so poorly constrained that, even with large uncertainties, the technique may provide useful data.

The present chapter will concentrate instead on techniques that are applicable to tracing of processes involved in production of carbonate components and in their subsequent inversion into limestones. Such tracers include the isotopic ratios of $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$. In specific situations, these tracers can be utilized also for "Isotopic Stratigraphy", that is for correlation and dating purposes.

INCORPORATION OF ISOTOPES INTO CARBONATE MINERALS

The bulk of modern carbonate sediments originate in the marine realm. This has been even more the case for ancient limestones, because lake sediments have a low preservation potential due to the ease of their erosional dispersal. I shall therefore concentrate

on isotopic properties of marine carbonates. A good review of isotopic properties for non-marine environments is available in Buchardt and Fritz (1980) and Talbot (1990).

Carbonate components formed in sea water are orthorhombic aragonite (A) and rhombohedral calcite, the latter further subdivided into low-Mg calcite (LMC) with <4 mole % MgCO_3 (Chave, 1954, a,b), intermediate-Mg calcite (iHMC) with 4-12 mole % MgCO_3 and high-Mg calcite sensu stricto (hHMC) with 12-28 mole % MgCO_3 (Milliman, 1974, p. 267). The molar Mg/Ca ratio for present-day sea water is 5:1 and inorganically precipitated phases should be either A or HMC with about 7 mole % MgCO_3 (Fig. 3.1 in Morse and Mackenzie, 1990). LMC in marine environments is known mostly from intracellularly precipitated shells of some organisms, such as pelagic foraminiferans, that manage to retard the diffusion of Mg^{2+} through cellular tissue during shell secretion. Other organisms have shells composed of various combinations of A, HMC and LMC. On average, the shallow marine carbonate sediments, containing inorganically precipitated phases and skeletal debris, are composed of variable mixtures of HMC and A. As a generalization, the Mg content of HMC correlates with temperature and thus declines with latitude and/or depth (Mackenzie et al., 1983). Deep-sea oozes, on the other hand, consist almost exclusively of pelagic skeletal material (e.g. coccoliths and foraminiferans) and are predominantly LMC. Thus, primary minerals which compose the sediment become exposed to the influence of meteoric waters and/or are subjected to higher pressures and temperatures during burial, rendering the original mineralogical assemblages unstable and converting them into a monomineralic limestone (LMC) or dolostone (Land, this volume).

The incorporation of O and C isotopes into carbonate minerals is summarized well in O'Neil (1986). It is governed by the so called fractionation factor:

$$R_s = \alpha_{s-w} R_w$$

where R is the ratio of relative abundances of isotopes, in this instance $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$, the subscript S represents the solid carbonate phase, and W stands for water (and its solutes, such as

carbon species). Since α -values are close to unity and their variations are mostly in the third decimal place, the difference in α_{s-w} is better expressed in whole units as per mil ($0/0_0$). Thus,

$$\Delta_{s-w} = [(R_s/R_w) - 1] \times 10^3 = (\alpha_{s-w} - 1) \times 10^3.$$

For reasons connected with the design of mass spectrometers, it is easier to compare the measured isotope ratio of an unknown sample R_s to a standard with known R , and to express the measured difference as

$$\delta_s = [(R_s/R_{\text{standard}}) - 1] \times 10^3$$

Similarly, δ_w can be expressed as a difference relative to the same standard. The fractionation factor can be obtained from the measured δ 's (Hoefs, 1980) as

$$\alpha_{s-w} = \delta_s - \delta_w \approx \Delta_{s-w} \approx 10^3 \times \ln \alpha_{s-w}.$$

For oxygen and carbon isotope studies in carbonate rocks, the standard usually utilized is the PDB (Bellefleuritella americana from the Cretaceous Peedee Formation of South Carolina; McCrea, 1950). This standard is no longer available and most laboratories utilize secondary standards calibrated relative to PDB. For oxygen, the results are frequently reported also relative to the SMOW standard (Standard Mean Ocean Water; Craig 1961). The conversion equations between V-SMOW (Vienna SMOW) and PDB are (Coplen et al., 1983):

$$\delta^{18}O_{V-SMOW} = 1.03091 \times \delta^{18}O_{PDB} + 30.91$$

and

$$\delta^{18}O_{PDB} = 0.97002 \times \delta^{18}O_{V-SMOW} - 29.98.$$

The equilibrium isotopic fractionation factor is inversely proportional to temperature and the relationship takes the form:

$$\ln \alpha = AT^{-2} + BT^{-1} + C$$

where A, B, and C are constants determined experimentally and T is

absolute temperature in Kelvins. At surficial to high temperatures, the term BT^{-1} becomes negligible and the fractionation factor α is proportional to T^{-2} (Bigeleisen and Mayer, 1947).

Carbon Isotopes

The temperature dependence of α for C isotopes is relatively small. Gaseous CO_2 that diffuses into sea water, dissociates, and can finally precipitate as a CaCO_3 mineral, with fractionation involved at each step. The temperature dependencies of fractionation factors between CO_2 (gas) and the CO_2 (aq) (α_1), HCO_3^- (α_2), CO_3^{2-} (α_3) and calcite (α_4), respectively, are as follows (Emrich et al., 1970; Deines et al., 1974):

$$\begin{aligned} 1000\ln \alpha_1 &= 0.0063 (10^6 T^{-2}) - 0.91, \\ 1000\ln \alpha_2 &= 1.099 (10^6 T^{-2}) - 4.54, \\ 1000\ln \alpha_3 &= 0.87 (10^6 T^{-2}) - 3.4, \text{ and} \\ 1000\ln \alpha_4 &= 1.194 (10^6 T^{-2}) - 3.63. \end{aligned}$$

The overall variations in $\delta^{13}\text{C}$ of natural calcites induced by temperature are usually less than the scatter caused by other factors (about 0.04 per mil per 1°C). Theoretically, the CaCO_3 should be enriched by about 1-3 per mil in ^{13}C relative to the total dissolved C, because bicarbonate is the dominant C species in natural waters. In addition, aragonite should be somewhat enriched in ^{13}C relative to calcite. At 25°C , the theoretical calculations yield about 0.9 per mil enhancement, whereas the observed experimental enrichment has been about 1.8 per mil (Rubinson and Clayton, 1969).

Oxygen Isotopes and Paleothermometry

In contrast to C, O isotope fractionation is strongly temperature dependent. As a rule of thumb, the $\delta^{18}\text{O}$ become depleted by about 1 per mil for every 4°C at near-surficial temperatures. The actual α is, however, somewhat dependent on the mineralogical and chemical form of the CaCO_3 phase. The pertinent equation for calcite (O'Neil et al., 1969) is:

$$1000 \ln \alpha_{C-W} = 2.78 (10^6 T^{-2}) - 3.39.$$

Aragonite should be enriched, up to 1 per mil, in ^{18}O relative to calcite, and for Mg-calcites the enrichment is about 0.06 per mil, for every mole per cent of MgCO_3 (Tarutani et al., 1969). The above equation can be modified to permit a temperature estimate in $^{\circ}\text{C}$ (Epstein et al., 1953; Craig, 1965; Hays and Grossman, 1991).

$$T(^{\circ}\text{C}) = 15.7 - 4.36 (\delta^{18}\text{O}_C - \delta^{18}\text{O}_W) + 0.12 (\delta^{18}\text{O}_C - \delta^{18}\text{O}_W)^2,$$

where $\delta^{18}\text{O}_C$ and $\delta^{18}\text{O}_W$ are in PDB and SMOW, respectively (Anderson and Arthur, 1983). This is the basis of oxygen isotope paleothermometry and a grid of combinations of T , $\delta^{18}\text{O}_C$ and $\delta^{18}\text{O}_W$ is given in figure 1. For aragonite, the equation is slightly different (Grossman and Ku, 1986), but has a similar slope.

$$T(^{\circ}\text{C}) = 19.0 - 3.52 (\delta^{18}\text{O}_A - \delta^{18}\text{O}_W) + 0.03 (\delta^{18}\text{O}_A - \delta^{18}\text{O}_W)^2.$$

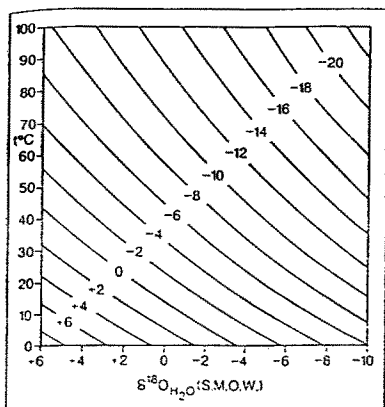


Figure 1: A grid of equilibrium relationships between $\delta^{18}\text{O}_W$ (SMOW), temperature ($^{\circ}\text{C}$) and the $\delta^{18}\text{O}_{\text{calcite}}$, the latter expressed in per mil PDB on diagonal lines. Modified from Tucker and Wright (1990)

The equations contain three unknowns, so that one needs to measure the $\delta^{18}\text{O}$ of a mineral and water to utilize this paleothermometer. In most cases, the ambient water is no longer available. For marine minerals, the SMOW value of 0 per mil is usually substituted, but this is not without problems as will be discussed later. Alternati-

vely, it is theoretically possible to utilize a cogenetic mineral phases in a manner similar to that of high temperature studies (see Faure, 1986; O'Neil, 1986; Valley, 1986). In this case, the $\delta^{18}\text{O}$ of ambient water is, by definition, the same for all minerals and this enables calculation of the formation temperature. Unfortunately, for most mineral phases in question - carbonates, phosphates, cherts - the $\Delta^{18}\text{O}$ (mineral A-B) changes little with temperature and this renders such pairs inapplicable for paleotemperature studies in sedimentary systems. In addition, although the minerals coexist frequently, their cogenetic nature is almost always questionable.

Disequilibrium Phenomena

In nature, observed isotopic ratios often deviate from calculated equilibrium values because of kinetic factors. Of these, perhaps the rate of precipitation of solid phases is the most important variable. Usually the faster the rate, the closer is the α to unity (e.g. Turner, 1982). The situation is still more complex if biomineralization is involved. Secretion of carbonate skeletons may proceed under equilibrium conditions or result in non-equilibrium fractionation of isotopes (O, C or both), known as biogenic fractionations or vital effects (Figs. 2 and 6). Such effects may be a consequence of biochemical processes that influence the kinetics of shell formation or, particularly for C, result from incorporation of metabolic CO_2 into CaCO_3 (Land, 1969; McConnaughey, 1990a,b). When this deviation is systematic, as for some foraminiferan species, it can be corrected for. A detailed review of these phenomena is available in Williams et al. (1988). In other cases, the degree - but not necessarily the sign - of disequilibrium is random. It is also possible, and by no means exceptional, to see different parts of the same skeleton having different isotopic composition.

The above discussion is not intended to discourage the potential user, only to point out that the rigorous theory has to serve only as a framework for practical applications. Nature obeys these rules to the extent of statistical approximations.

Strontium Isotopes

In contrast to O and C, the isotopes of Sr, ^{87}Sr and ^{86}Sr , are incorporated into carbonate minerals with no measurable isotope fractionation, because their mass difference is only 1.1%. The $^{87}\text{Sr}/^{86}\text{Sr}$ values are usually reported in absolute ratios of 0.70XXX and can now be reliably measured into the fifth decimal place. This usage is a consequence of the design of mass spectrometers. The 0

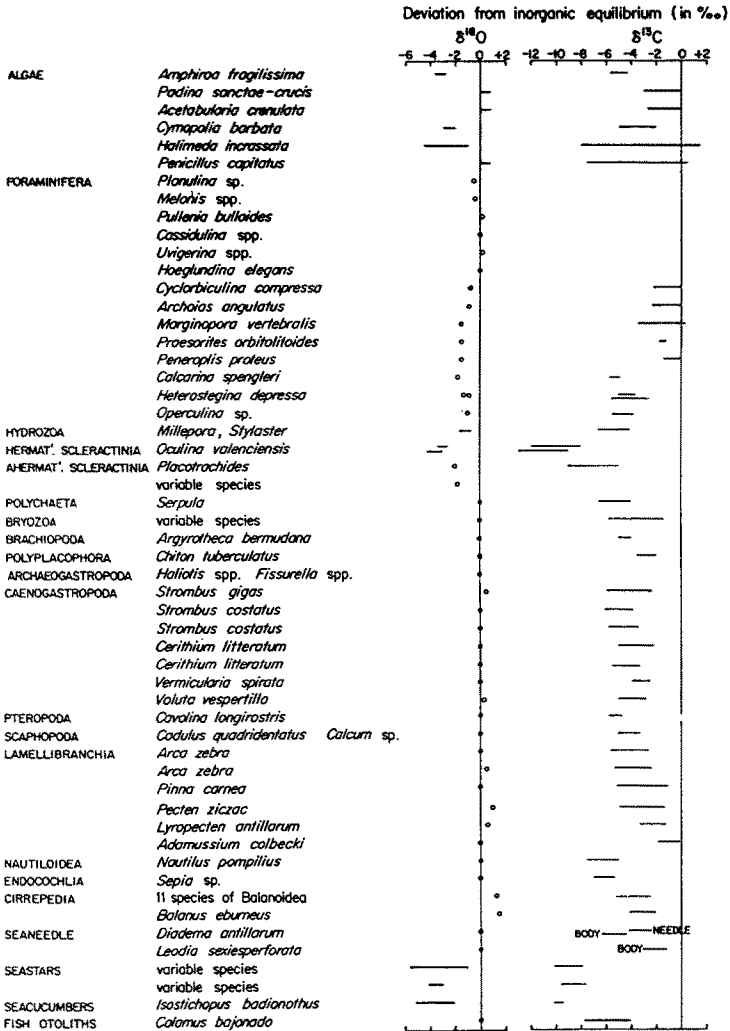


Figure 2: $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ departures from equilibrium values due to vital effect. Modified from Wefer (1983) and reproduced from Veizer (1983a)

and C isotopes are measured on CO₂ gas that is introduced into the source of ionization through a capillary. The passage through this capillary is accompanied by kinetic fractionation effects. For this reason, the measurement of an unknown sample must be immediately followed by a standard CO₂ gas with known isotopic composition that is introduced into the source via an analogous capillary. Isotopic values, if reported as δ (sample minus standard), selfcorrect for such kinetic factors. Sr samples, on the other hand, are introduced into the source of the mass spectrometer as solids, but the results - even among leading laboratories - differ in the fifth decimal place. They must be therefore normalized to a somewhat arbitrary value recommended for a given standard. Usually it is the Eimer and Amend SrCO₃ with an accepted ⁸⁷Sr/⁸⁶Sr ratio of 0.70800. Other standards include the NBS Sr carbonate (SRM 987), the USGS Tridachna shell (EN-1), and sea water. The results on carbonate samples are increasingly often reported in a way similar to that of the stable isotopes:

$$\delta^{87}\text{Sr} = [(\text{}^{87}\text{Sr}/\text{}^{86}\text{Sr}_{\text{sample}}/\text{}^{87}\text{Sr}/\text{}^{86}\text{Sr}_{\text{sea water}}) - 1] \times 10^5.$$

Since the ⁸⁷Sr/⁸⁶Sr of ocean sea water is uniform within analytical capabilities, the $\delta^{87}\text{Sr}$, reported relative to measurements of sea water (or EN-1) by the same laboratory, selfcorrects for interlaboratory differences. Further background to Sr isotope systematics is available in Faure and Powell (1972) and Faure (1986).

ISOTOPE CHARACTERISTICS OF NATURAL WATERS

Carbonate minerals, in one way or another, reflect the variability inherent in the composition of their parent solutions. It is therefore necessary to understand the isotopic patterns observed in natural waters and the dynamics that is involved in creation, maintenance, evolution, and dispersal of such patterns. The situation is much simpler for Sr than for O and C. The ⁸⁷Sr/⁸⁶Sr distribution in natural waters will therefore serve as a starting point of discussion.

Strontium

Present-day sea water contains about 8 $\mu\text{g/g}$ Sr with a uniform isotopic composition. As already pointed out, the actual value varies somewhat between laboratories. For example, MOBIL (Burke et al., 1982), Cambridge (Elderfield, 1986), USGS (Ludwig et al., 1988), UCLA (DePaolo, 1986), Florida (Hodell et al., 1990) and our Bochum laboratory reported the following values: 0.70907, 0.70924, 0.70925, 0.70923, 0.70917 and 0.70914, respectively. These minute differences are not solely of academic interest because, as will be shown later, they are important for the so called "high resolution isotope stratigraphy". For future work, it is therefore advisable to report the Sr isotopic ratios in ^{87}Sr units.

In contrast to sea water, the Sr concentrations and isotopic compositions of rivers and lakes are highly variable. Nonetheless, most rivers and lakes have about two orders of magnitude lower Sr concentrations and they are enriched in radiogenic ^{87}Sr (Palmer and Edmond, 1989). The global average river flux has $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.711, with Sr concentrations of 60 pg/g .

The residence time of Sr in the ocean is perhaps 2-4 million years (Holland, 1984; Hodell et al., 1990). Whatever the correct estimate, the input of extraneous Sr into the ocean is much slower than the oceanic mixing rate of some thousand years. This is the same reason why, at any given time, the open ocean water has a uniform Sr isotopic ratio. This ratio is a conservative property for even the most marginal marine environments, because the entire Sr endowment in any reasonable mixture of dilute riverine and salty sea water derives dominantly from sea water (cf. Veizer, 1989).

Oxygen

The variation in O isotopic composition of sea water is illustrated in figure 3. In the open ocean, the spread is at least 1.5 per mil. This range can even be exceeded in marginal seas and lagoons. High evaporation rates cause ^{18}O enrichment, while hyposaline and brackish situations, mostly caused by riverine influx,

result in ^{18}O depletion. Usually the slope is approximately 0.1 per mil $\delta^{18}\text{O}$ for each 1 per mil salinity change between 0 and about 80 per mil (Ferronsky and Brezgunov, 1989; Anati and Gat, 1989).

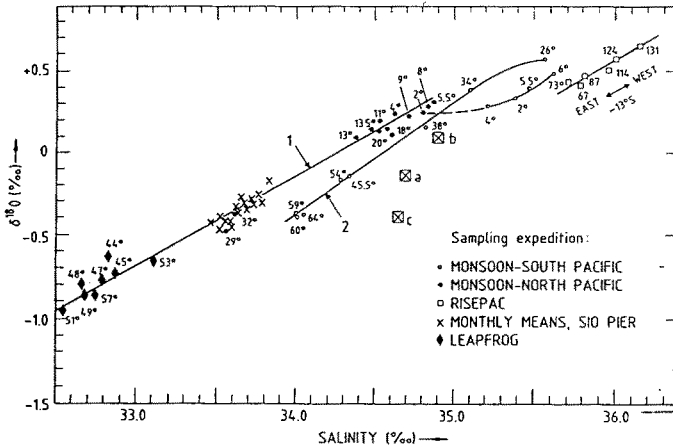


Figure 3: Variation of O isotopic composition in sea water. Modified from Ferronsky and Brezgunov (1989) and based on the data of Craig and Gordon (1965)

For low-latitude surficial waters of the open oceans, the loci of the bulk of carbonate production today, the $\delta^{18}\text{O}$ variations are usually less than those illustrated in figure 3 and they correlate positively with the net evaporation/precipitation (and runoff) balance in a given region. The ^{18}O depletion of deep waters, and of the circum-Antarctic surface waters (Fig. 3), is due to the dilution by cold and thus dense glacial melt waters that - for the reasons discussed below - are very depleted in ^{18}O . A complete melting of the present polar ice caps would decrease the $\delta^{18}\text{O}$ of the entire ocean by some 0.8 to 1.3 per mil (Savin and Yeh, 1981). This may have been the situation in the geological past.

The O isotopic composition of meteoric water is controlled by the process of evaporation/precipitation. As sea water evaporates at low-latitudes, the vapor is depleted in ^{18}O . This is because the $\alpha_{\text{vapor-water}}$ is inversely proportional to temperature. Subsequently, as the vapour diffuses across the surficial diffusion layer, additional kinetic fractionation occurs. The combined kinetic enrichment factor $\Delta\epsilon$ (Gonfiantini, 1986) can be expressed as:

$$\Delta\epsilon^{18}\text{O} \text{ (per mil)} = 14.2^{(1-h)}$$

where h is the relative humidity normalized to the surface temperature of the liquid. Cooling and condensation of the water vapor results in a reverse equilibrium fractionation. In this case, it is the heavy ^{18}O that is preferentially incorporated into condensing droplets. As the clouds move to higher, and colder, altitudes and latitudes, they and the precipitation become progressively more depleted in ^{18}O (Fig. 4).

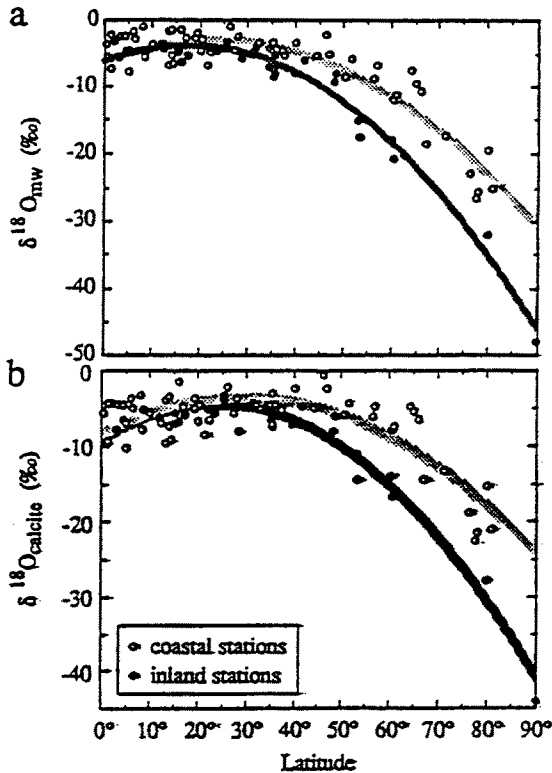


Figure 4: Mean $\delta^{18}\text{O}$ values of atmospheric precipitation (a) and equilibrium $\delta^{18}\text{O}$ values of calcite (b) vs. latitude for coastal and inland stations. Reproduced from Hays and Grossman (1991). The $\delta^{18}\text{O}$ is in SMOW and PDB for water and calcite, respectively

This process, known as Rayleigh distillation, can be expressed as:

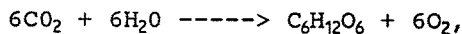
$$R_t = R_0 f^{(\alpha-1)}$$

where R_t is the $\delta^{18}\text{O}$ at time t , R_0 is the initial $\delta^{18}\text{O}$, f is the fraction of vapor remaining in the cloud, and x is the fractionation factor. The depletion gradient is somewhat steeper over the continents than over the oceans (Yurtsever, 1975; Gat, 1980; Hays and Grossman, 1991).

The net result of the above dynamics is that most, except some highly evaporated, meteoric waters are depleted in ^{18}O relative to sea water. Yet, in the low-latitudes that are the loci of carbonate production, the depletion is moderate, usually within 6 per mil (Fig. 4). Calcites precipitating in equilibrium with such meteoric waters should therefore have $\delta^{18}\text{O}_{\text{PDB}}$ of about -5 ± 2 per mil.

Carbon

The two dominant exogenic reservoirs of C are carbonate rocks and organic matter in sediments. They are linked in the carbon cycle via atmospheric CO_2 and the C species dissolved in the hydrosphere. The $\delta^{13}\text{C}$ for the total dissolved C (TDC) in sea water is about $+1 \pm 0.5$ per mil (PDB), with surficial waters generally heavier and deep waters lighter than this average (Kroopnick, 1980; Tan, 1989). Atmospheric CO_2 in equilibrium with TDC of marine surface water has $\delta^{13}\text{C}$ of about -7 per mil. CO_2 is preferentially utilized by photosynthetic plants for production of organic C cau-



sing further depletion in ^{13}C . Most land plants utilize the so called C_3 , or Calvin pathway that results in tissue with $\delta^{13}\text{C}_{\text{org}}$ of about -25 to -30 per mil. In contrast, aquatic plants and tropical grasses with the C_4 (Hatch-Slack or Kranz) pathway have $\delta^{13}\text{C}$ of some -10 to -15 per mil. A third group that combines these two pathways, the CAM plants (algae and lichens), has intermediate $\delta^{13}\text{C}$ values. In detail, the nature of the discussed variations is far more complex (Deines, 1980; Sackett, 1989) and depends on the type of organic compounds involved. For our purposes, however, it is only essential to realize that C_{org} is strongly depleted in ^{13}C . This

organic matter, which is very labile, is easily oxidized into CO_2 that inherits the ^{13}C -depleted signal.

Deep oceanic circulation during glacial times, such as the Quaternary, is dominated by production of cold, salty and dense waters at high latitudes. As these O_2 -rich waters sink and migrate, their aging is accompanied by an increase in TDC and PO_4^{2-} and a depletion in dissolved O_2 (Fig. 5); all a consequence of oxidation of the "raining" planktonic matter from the surficial water layer.

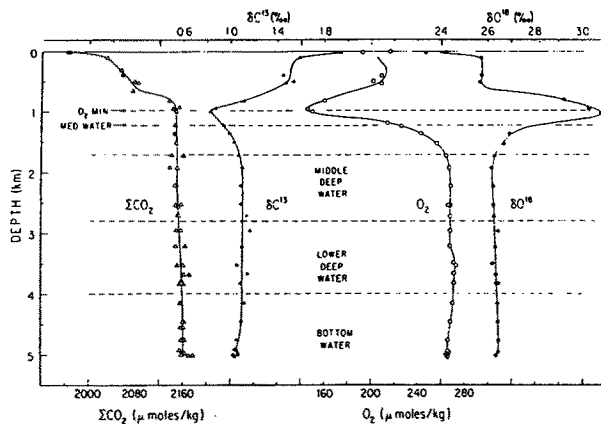


Figure 5: Changes in $\delta^{13}\text{C}$ of TDS (CO_2) and $\delta^{18}\text{O}$ of dissolved O_2 with depth for the North Atlantic Ocean. The $\delta^{13}\text{C}$ minimum at shallow depth is associated with oxygen minimum. The large $\delta^{18}\text{O}$ increase in the oxygen minimum zone is due to preferential consumption of ^{16}O by bacteria (Kroopnick and Craig, 1976). $\delta^{18}\text{O}$ in SMOW, $\delta^{13}\text{C}$ in PDB. From Kroopnick et al. (1972)

The addition of this "organic" CO_2 is the reason for the ^{13}C depletion of TDC in the deeper water column. However, the dynamics of the oceans may have been considerably different during times of warm, presumably non-glacial, climatic intervals, such as the Cretaceous. In this case, the dense waters may have originated not from cooling and ice formation, but from large degree of evaporation. Such waters would be O_2 poor and, as a result, the oceans may tend towards a greater degree of anoxia, retarding the oxidation of "raining" C_{org} . The oceans, however, are characterized not only by vertical, but also by horizontal gradients in $\delta^{13}\text{C}$ of TDC. In locations with carbonate deposition, these are typically within ± 0.5 per mil. The lighter values are characteristic of upwelling

regions and the heavier ones of mid-latitudes; a result of a net balance between organic productivity, rates of upwelling and sinking of waters, CO₂ invasion and evasion, and temperature (Kroopnick et al., 1977; Tan, 1989).

The $\delta^{13}\text{C}$ of TDC in meteoric waters is highly variable. It is determined (Anderson and Arthur, 1983) by the relative contribution to the overall TDC of C from sources such as: (1) degradation of C_{org} ($\delta^{13}\text{C}$ about -25 per mil), (2) dissolution of carbonates (+2 per mil), (3) diffusion from the air (-7 per mil) that results in TDC of +1 to +2 per mil, and (4) the extent of ¹²C withdrawal into organic matter. The resulting $\delta^{13}\text{C}_{\text{TDC}}$ may range from positive values (in carbonate buffered water masses) to highly negative ones. In most natural situations, however, the TDC of meteoric waters is depleted in ¹³C relative to sea water (Burchardt and Fritz, 1980).

RECENT MARINE CARBONATES

The components of Recent marine carbonates include skeletal parts, chemical and/or biochemical precipitates and early marine cements. Low-latitude shallow water assemblages, called Chlorozoan are dominated by aragonitic corals and green algae, frequently accompanied by marine precipitates (whittings, ooids, peloids) and having ubiquitous early marine cements of HMC and A mineralogy. In contrast, carbonates of temperate zones, and of deeper slope settings in tropical regions, the Foramol assemblage, contain mostly skeletal remains with Mg-calcitic mineralogy. The dominant contributors are molluscs, foraminifera and bryozoans (Lees and Buller, 1972). Early marine cements in this assemblage are rare and of Mg-calcitic composition. Finally, the off-shore assemblage of pelagic organisms, such as calcitic foraminifera and coccoliths as well as aragonitic pteropods accumulate above their respective carbonate compensation depths to produce deep sea oozes on the ocean floor. Rare cementation is mostly by Mg-calcite cements that have been discovered on some seamounts and guyots in semi-enclosed basins. A more detailed description of the subject is available in

Milliman (1984) and James and Choquette (1990a). The wide spread in O and C isotopic compositions (Fig. 6) of Recent marine carbonates reflects this complexity and the relative proportions of constituent components.

As already pointed out (Fig. 2), certain groups of organisms (some molluscs, foraminifera) secrete their shells in approximate isotopic equilibrium with the ambient water, while others (e.g. articulate algae, scleractinian corals, echinoderms) produce strongly ^{18}O and/or ^{13}C depleted skeletons. The wide spread of isotopic values in O/C space (Fig. 6a; Morrison and Brand, 1986) is a direct reflection of this state of affairs. Bulk typical sediments (Fig. 6c) show less scatter than for individual components (Fig. 6a) due to the averaging effect of their mixing. Temperate assemblages and deep sea oozes have usually ^{18}O enriched signal due to colder ambient water temperatures.

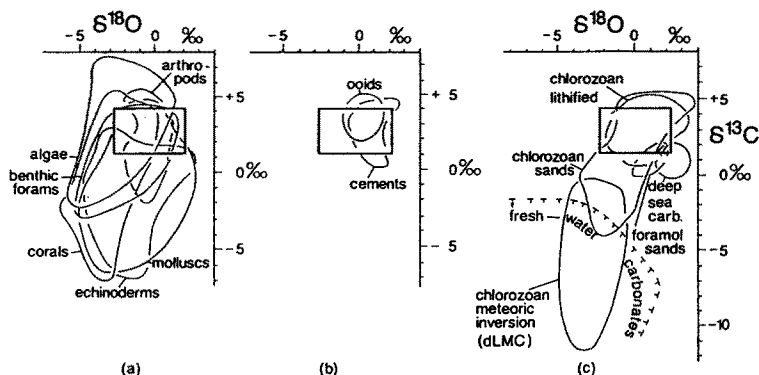


Figure 6: Generalized distribution of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in carbonate components and bulk sediments of Quaternary age. Box represents an approximate equilibrium range for CaCO_3 precipitated from shallow marine water. Domains of isotopic distribution in (a) marine skeletons, (b) precipitates, and (c) bulk sediments. Based on the data summarized by Land (1989), Milliman (1974) and James and Choquette (1990a and b)

The precipitates, such as ooids and early marine cements, tend to fall much closer to expected equilibrium values (Fig. 6b). In detail, however, they may be characterized by slight ^{13}C and/or ^{18}O enrichment (Milliman, 1974) and, if so, biochemically mediated processes may be involved in their precipitation.

ISOTOPIIC COMPOSITION OF ANCIENT SEA WATER

The discussion of the dynamics of modern ocean and of superimposed inorganic and biological factors is reflected in the complex isotopic patterns of Recent marine carbonate sediments. While modern isotopic patterns may serve as a starting point for discussion of ancient carbonates, the task is not that simple, because the isotopic composition of sea water has evolved in the course of geologic history.

Strontium Isotopes

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio evolved from mantle-like non-radiogenic values of about 0.703 in the Archean to its present day value. The dominant control of Sr isotopic composition in sea water is exercised by two fluxes, the riverine input ($^{87}\text{Sr}/^{86}\text{Sr}$ of 0.711 at present) and the circulation of sea water through hydrothermal systems in the young oceanic crust (≤ 0.703). The first order trend therefore reflects the transition from an ocean dominated by hydrothermal "mantle" buffering into an ocean dominated by riverine flux (Veizer, 1989). Due to waning and waxing of these two fluxes, the second and higher order oscillations are superimposed on the first order trend and they have been resolved for the Phanerozoic (Fig. 7b). This "curve" (Burke et al., 1982) approximates the $^{87}\text{Sr}/^{86}\text{Sr}$ evolution for the past 500 million years, but is better considered to be a band rather than a line. The width of the band decreases with decreasing age and it is particularly steep and well defined for the Cenozoic (Fig. 7c). This part of the curve is therefore frequently utilized for dating of unknown samples, by measuring their $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and comparing it with the sea water curve. The approach is known as "high resolution isotope stratigraphy" (e.g. Elderfield, 1986). Theoretically, it is also possible to utilize other steep slopes in the Phanerozoic curve for similar purposes. The mitigating factor is the width of the band, which cannot be constrained any better than the available dating precision for the

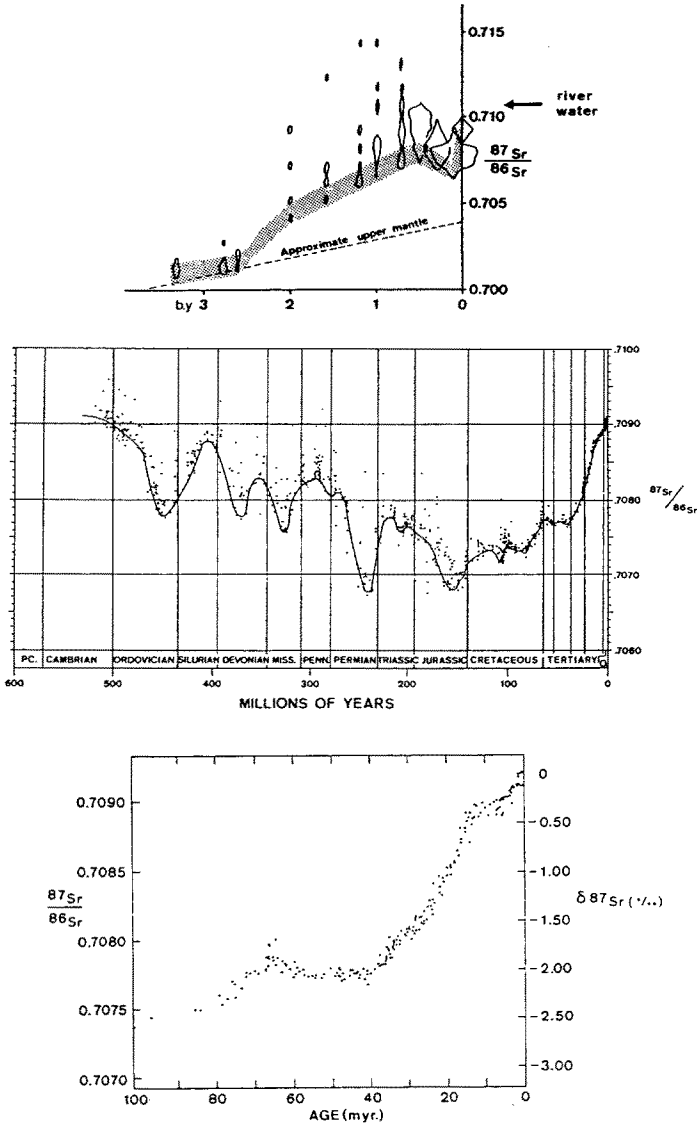


Figure 7: Sr isotopic evolution of sea water during geologic history. (a) First order trend on 10^9 years time scale, (b) Phanerozoic variations, and (c) details of variations for the Cenozoic. Reproduced in modified form from Veizer (1989), Burke et al. (1982) and Elderfield (1986)

samples that serve as calibration for the curve. Even if we could constrain all factors and exclude all post-depositional phenomena that alter the original signal, there will be a limit on the attainable resolution. It is apparent, that the time signal represents a hierarchy of wiggles and with each advance in resolution a set

of higher order wiggles emerges. It may be that the structure of the curve approximates the so called fractal geometry (Mandelbrot, 1983). The secular curve will thus always represent a band, albeit of progressively smaller width with improving resolution. Whatever the arguments, the starting point of discussion for studies of ancient carbonates must be the $^{87}\text{Sr}/^{86}\text{Sr}$ of the contemporaneous ocean and not its modern value.

Carbon Isotopes

The $\delta^{13}\text{C}$ of past oceans varied mostly within a 0 ± 3.0 per mil band since at least 3.5 billion years ago (Schidlowski et al., 1983). As in the case of Sr isotopes, superimposed on this first order trend are higher order wiggles. The generalized Phanerozoic variations are given in figure 8. These oscillations are probably caused by the relative proportions of C sequestered into carbonates and organic matter, respectively. At times of large production and storage of C_{org} in sediments, ^{12}C is depleted in the marine reservoir and the dissolved bicarbonate becomes isotopically heavy (Veizer et al., 1980). Alternatively, the ^{12}C depleted C can be stored in the deep water body of a stratified ocean, causing the shallow water layer to be ^{13}C enriched (Hoffman et al., 1990). Whatever the cause, local phenomena (e.g. evaporation, photosynthetic drawdown) or vital fractionation effects are superimposed as a scatter on this general trend. As already discussed, oceanic circulation

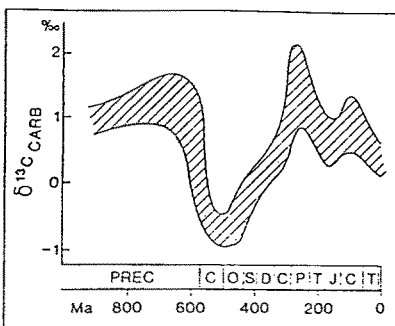


Figure 8: $\delta^{13}\text{C}$ variations in Phanerozoic carbonates. Reproduced from Tucker and Wright (1990) and based on the data summarized in Veizer et al. (1980)

^{18}O . My personal preference is for the alternative (c), perhaps complemented by the other factors, but the interpretation of this trend is still open to discussion. The pros and cons are summarized, for example, in Veizer et al. (1986).

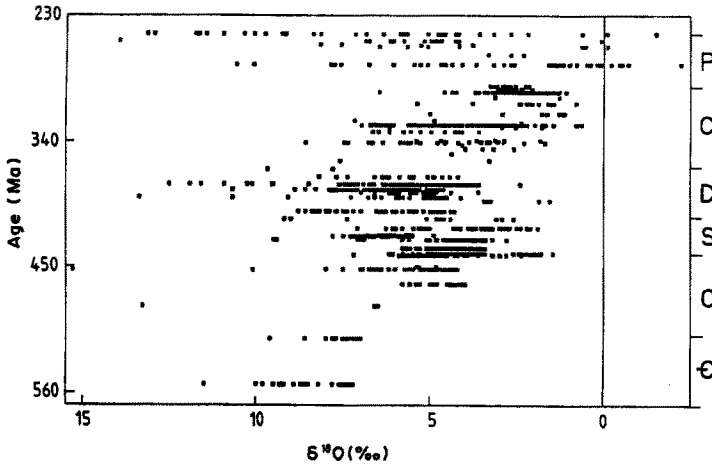


Figure 10: $\delta^{18}\text{O}$ variations in Paleozoic brachiopods. This summary represents 1428 samples and is reproduced from Wadleigh and Veizer (1992), who also list the sources of data

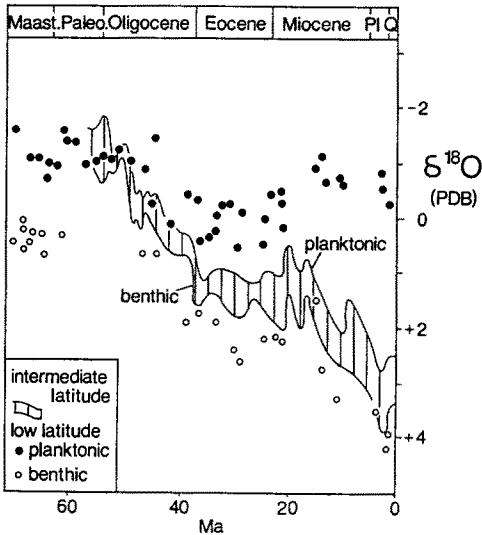


Figure 11: Oxygen isotopic composition of planktonic and benthic foraminiferans. Modified from Berger (1979) and based on the data of Shackelton and Kennett (1975) and Douglas and Savin (1975)

Whatever the case for the Paleozoic, the Mesozoic and Tertiary $\delta^{18}\text{O}$ of sea water fluctuated in the vicinity of SMOW value, yet the results, particularly for the foraminiferans, indicate overall cooling since the Mesozoic (Fig. 11). At intermediate latitudes this is recorded by both the planktonic species at the surface and the benthic ones at depth. Note, however, that at low latitudes it is mostly the benthic organisms that follow this trend, with $\delta^{18}\text{O}_{\text{benthic-planktic}}$ reaching about 15°C (4 per mil) in the Quaternary. This increasing temperature/depth gradient at low latitudes results from initiation and expansion of the "glacial" type of ocean circulation, with production of deep water masses increasingly from dense cold waters from high latitudes.

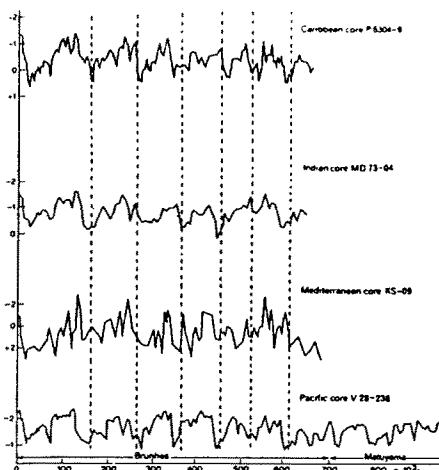


Figure 12: Oxygen isotopic compositions of foraminiferal tests in four cores from the Caribbean Sea, the Indian Ocean, the Mediterranean Sea and the Pacific Ocean. The $\delta^{18}\text{O}$ in PDB. Reproduced from Odin et al. (1982), who list sources of data

Superimposed on the overall cooling trend are higher level oscillations, culminating in the zig-zag pattern of $\delta^{18}\text{O}$ in Quaternary planktonic foraminiferans (Fig. 12; Emiliani, 1955; Shackleton and Opdyke, 1973; Williams et al., 1988). These fluctuations record glacial/interglacial cycles. However, the ^{18}O depletions are due to both, higher temperatures and melting of ^{16}O -rich polar ice caps. The relative proportions of these two causes at a specific time are difficult to disentangle. It is widely believed that these, the so called Milankovitch cycles, are driven by orbital parameters of the

earth (Imbrie and Imbrie, 1980). This is the standard explanation based on the concepts of linear dynamics. Alternatively, one is dealing with a non-linear dynamic system and the wiggly time series is a fractal structure that represents only a one dimensional projection from an attractor embedded in a four dimensional space (Nicolis and Nicolis, 1984). In plain language, at least four parameters (including the orbital ones) would be required to explain the observed pattern. As in the case of Sr and C, the secular $\delta^{18}\text{O}$ curve can be utilized as a chronostratigraphic tool and for correlation purposes in post-Paleozoic sediments.

DIAGENETIC OVERPRINT

Diagenetic modification of freshly deposited sediments begins on the sea floor with breakdown (mechanical and biological) of the carbonate components and their binding by cements. This process of rock generation from a loose sediment continues via two major subsequent pathways, designated here as meteoric and burial diagenesis (Bathurst 1975; James and Choquette, 1990a,b; Choquette and James, 1990; Hesse, 1990). These two pathways converge with time and some overlaps are possible even in the early stages of diagenesis.

Meteoric Pathway

Carbonate sediments deposited originally in shallow marine environments are, as a result of tectonics, sediment progradation or eustasy, exposed to the influence of meteoric waters. Such waters are frequently charged with CO_2 and thus highly corrosive. The original unstable marine mineralogical assemblage (aragonite and Mg-calcite) transforms into a monomineralic low-Mg calcitic limestone via sequential dissolution-reprecipitation. The dissolution-reprecipitation process is driven by the degree of undersaturation that decreases from Mg-calcite with more than 12 mole % MgCO_3 , to aragonite, to Mg-calcite with 12-4% MgCO_3 , to low Mg-calcite. Usually the process begins with dissolution of the most

soluble phase accompanied by its reprecipitation as diagenetic low-Mg calcite (dLMC). When this phase is obliterated the next most soluble phase maintains supersaturation with respect to dLMC, etc. But the differences in solubility, or the so called diagenetic potential, are not controlled solely by mineralogy and chemistry of the mineral phases, but also by factors that influence kinetics. For example, fine-grained sediments with large surface area and easy access from fluids (high porosity) dissolve faster than coarse grains of the same mineralogy and chemistry. This dissolution-reprecipitation process proceeds in a meteoric flow regime that is comprised of two components, regional flow and diffusion. The latter is relatively slow, of the order of $10^2\text{m}/10^6\text{a}$, whereas the former can vary considerably. At high flow rates the system is water-dominated. With high rates of dissolution, the resulting product becomes mineralogically, chemically and isotopically rather monotonous, albeit with possible gradients down-flow. At slow flow-rates, local dissolution-reprecipitation gradients, maintained by diffusion and local physical parameters, are not entirely dissipated. This is a rock-dominated system, where the precursor phases play a considerable role in controlling the chemistry and isotopic composition of waters in the microenvironments and thus of the locally precipitated successor dLMC. Depending on the relative rates of flow vs. diffusion and on the nature of the confining solid framework, all permutations are possible. But in most natural cases we deal with a partially rock dominated system, characterized by intermediate water/rock ratios. Note, however, that the same physical system may result in vastly different water/rock ratios for different chemical or isotopic constituents involved (see Banner and Hanson, 1990 and Land, this book). In the case of limestones, this will particularly be the situation for C and O isotopes. While C in the waters of the microenvironment originates mostly from the precursor carbonate phases, the proportion of O from this source - as opposed from the intervening water - is negligible. Thus the same physical system may yield an apparent low water/rock ratio for C and a high one for O isotopes.

For Sr isotopes, the $^{87}\text{Sr}/^{86}\text{Sr}$ in the successor phase reflects directly the proportion of Sr derived from the water and the precursor, respectively. As a rule, meteoric waters - relative to sea

water - are mostly ^{87}Sr enriched. Thus the overall shift in diagenetic product is toward higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Exceptions do exist in environments dominated by volcanic rocks or by young volcanoclastic sediments. In this case a decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ is possible. Regardless, for intermediate to high water/rock systems with high rates of recrystallization the entire microenvironment is usually swamped by Sr derived from precursor. This is because the partition coefficient $D_{\text{calcite}}^{\text{Sr}}$ is much less than unity and each recrystallization step therefore partitions more Sr into solution (cf, Veizer, 1983 a,b). In this case, the Sr isotopic composition of the precursor is sequestered into the successor phase with little isotopic shift.

The situation is more complex for C and O isotopes. Apart from recrystallization, the other important diagenetic process is the oxidation of organic matter. With burial, the sediment passes successively (Hesse, 1990) through the zones of (1) oxidation by dissolved O_2 , (2) nitrate reduction, (3) sulfate reduction, (4) carbonate reduction, (5) fermentation, and (6) thermocatalytic decarbonation. The processes in the first five zones are mediated by assemblages of specific bacteria to temperatures of about 75°C . The abiogenic zone (6) extends to about 150°C , and at higher temperatures equilibria between graphite, CO_2 and CH_4 dominate. The processes (1) to (3) produce CO_2 and bicarbonate that are released to the pore space. The C in these species is thus derived from oxidation of C_{org} and is depleted in ^{13}C , with $\delta^{13}\text{C}$ usually around -25 per mil. The passage of sediment into the zone (4), particularly at the trailing edge of sulfate depletion, leads to production of methane. CH_4 is isotopically very light (-80 ± 20 per mil) and the residual C_{org} , that is subsequently oxidized to CO_2 , becomes thus exceptionally heavy ($\delta^{13}\text{C}$ in excess of +10 per mil). A return to ^{13}C depleted values again characterizes zone (6).

The meteoric diagenetic environment usually encompasses the zones (1), (2) and, in some instances, the early stages of zone (3). From the point of view of hydrology, this environment can be divided into the vadose zone (infiltration and percolation of water through air filled pores) and the phreatic zone below a permanent water table (see James and Choquette, 1990b). At depth, the phreatic zone changes into mixing zone and finally into the deep

phreatic or marine phreatic zone, the latter two usually containing dense waters with salinity in excess of 10 ppt. Some cementation and mineral neomorphism occurs in the vadose zone, but the bulk of diagenetic processes probably takes place in the phreatic zone. The usual isotopic signature of these processes will therefore be a light $\delta^{13}\text{C}$ in the products, the degree of ^{13}C depletion being proportional to the relative contribution of C from the precursor carbonate and from the oxidation of organic matter. The vadose zone in particular, because it includes the roots of vegetation, may be up to two orders of magnitude enriched in organically derived CO_2 .

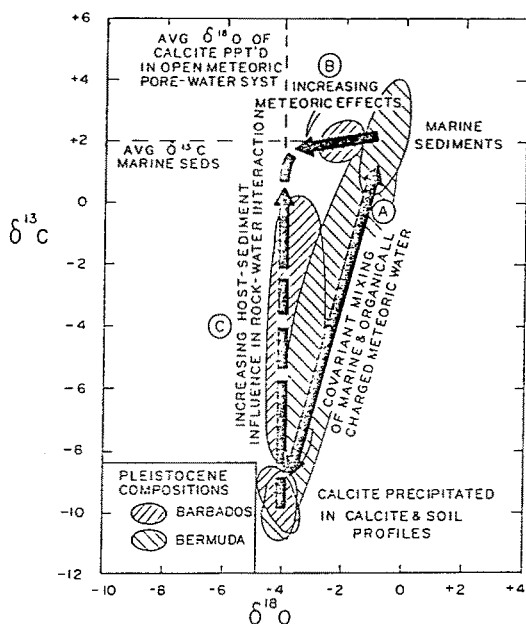


Figure 13: Diagram showing isotopic composition and trends in metastable carbonates where mineral-controlled alteration occurs in a meteoric system capped by a caliche-soil profile. The end members of trend (A) are sea water and ^{13}C depleted pore waters; diagenetic calcites precipitated in a marine-meteoric mixing zone might have compositions along that trend. If no caliche-soil profile existed, alteration of marine sediments might follow the trend shown by the top arrow (B). The long vertical trend (C) applies to a rock-water interaction beneath a caliche-soil profile in a shallow vadose zone, where $\delta^{13}\text{C}$ becomes heavier upward as "rock" CO_2 overpowers soil CO_2 while $\delta^{18}\text{O}$ remains the same. From James and Choquette (1990b)

The isotopic composition of O in meteoric water is, relative to sea water, also depleted in ^{18}O . This depletion is not very severe at low latitudes, with displacements mostly less than 5 per

mil. Recall that dissolution of carbonate precursors plays only a marginal role in O budget of coastal aquifers. The outcome results in trends in O/C isotope space that resemble mixing lines and/or the so called inverted "J" or "L" trajectories (Figs. 13 and 6c; Lohmann, 1988). The construction of these patterns is based on a suite of isotopic measurements of bulk rocks or, a much better practice, their constituent components. If bulk rocks are considered, the ^{13}C depletion patterns are ubiquitous in Quaternary sequences (e.g. Gross, 1964), but surprisingly rare in their ancient counterparts (Hudson, 1977). The patterns emerge only after the rocks are decomposed into their constituent grains and cement generations. This is somewhat an enigma. Brought to its logical conclusion, it would suggest that organically derived CO_2 played only a subordinate role in diagenetic transformation of ancient carbonate sediments into limestones. Perhaps, as pointed out by Land (1989), the answer lies in large Quaternary sea level fluctuations of about 100 m, due to glaciation. Sudden drops in sea level during that period exposed large tracts of carbonates to prolonged influence of vadose diagenesis. In contrast, the ancient counterparts reflect mostly the diagenetic inprint of the phreatic zone, with $\delta^{13}\text{C}$ buffered by the stabilizing carbonate phases.

Burial Pathway

This type of diagenetic stabilization is best documented in deep sea environments and in continually subsiding shallow water basins. The entrapped pore waters are of marine origin and in equilibrium with the assemblage of carbonate minerals. This is particularly the case for the predominantly low-Mg calcitic deep sea oozes. The conversion of sediment into limestone in this case is achieved not by a chemical gradient but through loading initiated by deposition of younger sediments. This results in pressure and temperature rise that, in turn, increases the solubility of the solid phases. Their dissolution-reprecipitation proceeds sequentially in a manner similar to that described for the meteoric pathway (Choquette and James, 1990).

In burial diagenesis, in contrast to the meteoric pathway,

the flow (advection) is confined to squeezing of pore waters upwards into the overlying water column. This is a slow process, particularly for sites with low sedimentation rate (loading). As a consequence, diffusion through the pore water column dominates the transport of solutes. It is therefore the rate of dissolution-precipitation of solid phases, relative to the rates of diffusion, that controls the magnitude of gradients in the pore water column. The recrystallization front, as it migrates upwards with continuous loading, causes dissolution of the original carbonate components and their reprecipitation as cements into the pore space, lithifying the sediment and reducing its porosity. Chemical species entering the solution at this front migrate downgradient in both directions, upwards toward the sediment/water interface and downward into the sediment. This may cause "smoothing" of the original isotope signal, as can be illustrated using Sr isotopes (Fig. 14). The $^{87}\text{Sr}/^{86}\text{Sr}$ of sea water evolved by about 0.0015 in the course of the Cenozoic. At present, the recrystallization front, or the ooze/chalk transition, is in about 20 million year-old sediments (Fig. 14). The Sr with isotopic composition of 0.7085 that is solubilized at this front is being incorporated into cements, thus lowering the bulk $^{87}\text{Sr}/^{86}\text{Sr}$ in the overlying younger sediments and increasing it in the underlying older sediments. This smoothing process diminishes the magnitude of the preserved temporal signal, particularly for higher order oscillations.

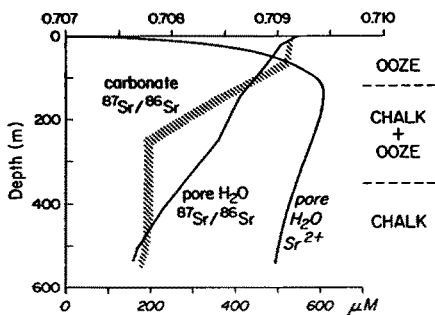


Figure 14: Dissolved Sr^{+2} and $^{87}\text{Sr}/^{86}\text{Sr}$ at DSDP site 528 as functions of depth. Note the intersection of pore water and carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ profiles at ooze/chalk transition that marks the recrystallization front. Reproduced from Veizer (1989) and based on the work of Gieskes et al. (1986)

A similar smoothing overprint operates also for C and O isoto-

pes, but here the overall picture is more complex. As for meteoric diagenesis, the ^{13}C depleted C may originate from oxidation of organic matter but, at greater depths, methane production can supply C enriched in ^{13}C . Such progression, from ^{13}C depleted to ^{13}C enriched processes is often observed in diagenetic carbonate concretions that may begin with marine $\delta^{13}\text{C}$ in the center, followed by ^{13}C depleted layers, and finally by an outer rim with ^{13}C -rich carbonate. This isotopic pattern thus records the passage of the sediment through oxidation zones (1) to (4) detailed earlier.

Theoretically, the ^{18}O , being of sea water origin, should not change appreciably with burial, whether in the solid phases or in the pore waters. Yet, with increasing depth the deep-sea sediments - and often also the water - show ^{18}O depletion by several per mil (Lawrence, 1989). It is believed that the major reason for this ^{18}O depletion is a low-temperature exchange of O either with volcani-clastic sediments in the underlying sedimentary pile or with the oceanic crust. Secular evolution of sea water (e.g. absence of polar caps) or other phenomena may have been contributory factors. The shift towards ^{18}O depletion in the solid phases is mostly due to increase in temperature. However, in contrast to pore waters, the bulk of this shift is achieved at the time of deep burial.

The carbonate sediment, regardless whether following the meteoric or the burial pathway, eventually reaches the deep burial environment. The boundaries can be set at cessation of most bacterial processes at about 75°C (or 2 km depth), but other authors would propose an earlier onset. The major process occurring at these depth is pressure-solution that results in dissolution of a portion of the already stabilized low-Mg calcitic limestone and reprecipitation of this material as late, mostly ferroan, blocky calcite cements that occlude the residual porosity (Bathurst, 1975). The deep phreatic waters that are involved in this process are mostly saline, with $\delta^{18}\text{O}$ heavier than sea water and with endowment of ^{87}Sr from interactions with silicate rocks in the sedimentary pile. Plagioclase, in particular, is subject to high dissolution rates. In terms of C isotopes, the system is mostly rock buffered, but introduction of light $\delta^{13}\text{C}$ from thermocatalytic decarboxylation may locally be important. The net result is forma-

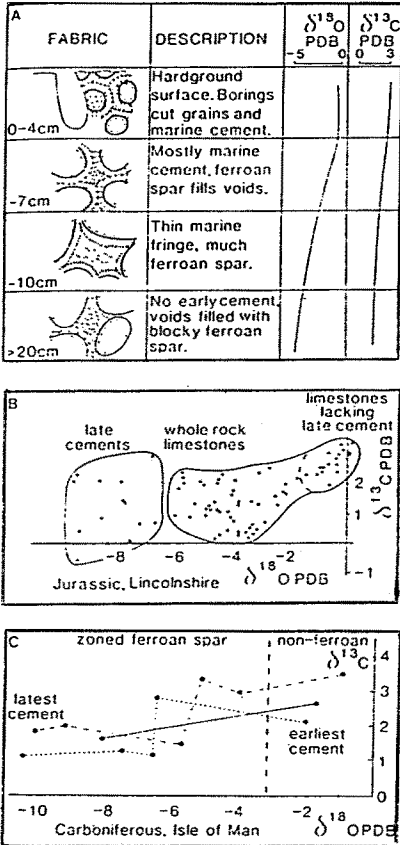


Figure 15: Stable isotopes, marine and burial cementation. (A) Diagram illustrating the changes in cement type and stable isotope signatures from a hardground surface with borings and abundant marine cements down to a grainstone with only burial calcite spar, 20 cm below. Middle Jurassic, Lincolnshire Limestone, England. (B) Isotopic data from the Jurassic Lincolnshire Limestone showing trend to more negative ^{18}O values with increasing content of late spar. (C) Isotopic signatures of early to late calcite cement phases in Carboniferous limestone from Isle of Man, UK. Later cements are more depleted in ^{18}O and more ferroan than early cements. Reproduced from Tucker and Wright (1990) and the sources listed therein.

tion of cements with a signal that is "marine" in $\delta^{13}\text{C}$, radiogenic in $^{87}\text{Sr}/^{86}\text{Sr}$ and depleted in ^{18}O (Fig. 15). The O isotope shift reflects mostly the increase in temperature that counteracts, and usually overrides, any shift toward ^{18}O -enrichment that may have been imprinted on deep phreatic waters during burial. It is essential to understand the fundamentals of these post-depositional

processes if we are to interpret the origin of an isotopic signal preserved in the ancient rock record.

CONCLUDING REMARKS

This description of the carbonate system, as it relates specifically to limestones, intentionally emphasizes principles rather than case histories. The reasons for such approach are twofold. Firstly, the allotted space would not have enabled a sufficiently representative review of the plethora of existing and potential applications. The reading list appended to this chapter may serve as an introduction into the subject. Secondly, the understanding of principles is a prerequisite for appreciation of case histories and for theoretical formulation of problems tractable by isotopic techniques. These techniques are unusually powerful if properly applied, but also relatively costly. Commercial rates for a combined O and C isotopic measurement are about 40\$ and for a high quality Sr isotopic measurement 250\$. They have to be applied therefore judiciously. As with every other technique, the isotopic approach has its advantages and weaknesses and it should be applied only with the former in mind.

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