10 Influence of Geochemical Processes on Stable Isotope Distribution in Marine Sediments

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10.1 Introduction

Stable isotope geochemistry has become an essential part of marine geochemistry and has contributed considerably to the understanding of the ocean's changing environment and the processes therein. In some fields, such as biogeochemistry and paleoceanography, the application of stable isotopes is still growing due to new microanalytical techniques, permitting a relatively precise analysis of very small samples or single compounds, which allows the investigation of a new generation of problems. Stable isotopes are useful tracers for reconstructing past temperatures, salinities, productivity, pCO_2, nutrients, etc. However, limitations exist on the application of these tracers because of diagenetic processes which may considerably alter the primary signals, due to preferential preservation, decomposition or relocation of particular tracers. On the other hand, stable isotope geochemistry offers the chance to iden-tify and better understand such diagenetic processes, which is essential for the interpreta-tion of isotope variability in marine sediments of the past.

Within this chapter, we focus on four elements (C, O, N, S), which participate in most marine geochemical reactions and which are important elements in the biological system. Some recent developments in the use of B isotopes are added to this chapter. We summarize the influence of geochemical processes on the stable isotope distribution of those elements in ocean water and marine sediments. After a short review on the fundamentals of stable isotope fractionation and mass spectrometry, the most important fractionation mechanisms for each element within the marine environment are described, followed by the identification of geochemical processes responsible for syn- or post-sedimentary changes in isotope signals.

10.2 Fundamentals

Excellent summaries of the use of stable isotopes in the study of sediments and the environment in which they are deposited are given by Hoefs (2004), and by Faure and Mensing (2005). The fundamentals of stable isotope fractionation for selected elements (esp. H, C, O, S) are also presented in a special volume edited by Valley and Cole (2001).

10.2.1 Principles of Isotopic Fractionation

The stable isotopic compositions of elements having low atomic numbers (e. g. H, C, N, O, S) vary considerably in nature as a consequence of the fact that certain thermodynamic properties of molecules depend on the masses of the atoms of which they are composed. The partitioning of isotopes between two substances or two phases of the same substance with different isotope ratios is called isotopic fractionation. In general, isotopic fractionation occurs during several kinds of physical processes and chemical reactions:

- Isotope exchange reactions involving the redistribution of isotopes of an element among different molecules containing that element.

- Kinetic effects, which are associated with unidirectional and incomplete processes such as condensation or evaporation, crystallization or

melting, adsorption or desorption, biologically mediated reactions, and diffusion.

In general, light isotopes are more mobile and more affected by such processes than heavy isotopes. The isotope fractionation that occurs during these processes is indicated by the fractionation factor α which is defined as the ratio R_A of the heavy to the light isotopes in one compound or phase A divided by the corresponding isotope ratio R_B for the compound or phase B:

$$\alpha_{A\text{-}B} = R_A / R_B \qquad (10.1)$$

For example, the fractionation factor for the exchange of ^{18}O and ^{16}O between water and calcium carbonate is expressed as:

$$H_2{}^{18}O + 1/3\ CaC^{16}O_3 \Leftrightarrow H_2{}^{16}O + 1/3\ CaC^{18}O_3 \qquad (10.2)$$

with the fractionation factor $\alpha_{CaCO3\ -\ H2O}$ defined as:

$$\alpha_{CaCO3\ -\ H2O} = (^{18}O / {}^{16}O)_{CaCO3} / (^{18}O / {}^{16}O)_{H2O} = 1.031 \text{ at } 25°C \qquad (10.3)$$

Because isotopic fractionation factors are close to 1, they can be expressed in ‰ with the introduction of the ε-value defined as

$$\varepsilon_{A\text{-}B} = (\alpha_{A\text{-}B} - 1) \cdot 1000 \qquad (10.4)$$

For geochemical purposes, the dependence of isotope fractionation factors on temperature is the most important property. In principle, fractionation factors for isotope exchange reactions are also slightly pressure-dependent, but experimental studies have shown the pressure dependence to be of no importance within the outer earth environments (Hoefs 2004). Occasionally, the fractionation factors can be calculated by means of partition functions derivable from statistical mechanics. However, the interpretation of observed variations of the isotope distribution in nature is largely empirical and relies on observations in natural environments or experimental results obtained in laboratory studies. A brief summary of the theory of isotope exchange reactions is given by Hoefs (2004).

10.2.2 Analytical Procedures

Stable isotope measurements on light elements are made on gases, i.e. H_2 for hydrogen, CO_2 for carbon and oxygen, N_2 for nitrogen, and SO_2 or SF_6 for sulfur isotopes. A variety of techniques is used to convert samples to a compound suitable for analysis. The most important aspect of sample preparation is to avoid isotopic fractionation. Since molecules with different isotopic masses have different reaction rates, procedures with less than a quantitative (i.e. 100%) output may produce a reaction product that does not have the same isotopic composition as the original sample. Furthermore, a pure gas is necessary to avoid interference by contaminants in the mass spectrometer. Contamination may result from incomplete evacuation of the vacuum preparation system or degassing of the sample, as well as from unwanted side reactions in the preparation procedures. In general, the error attributable to sample preparation is greater than the instrumental analysis of the product gas.

Isotopic abundance measurements for geochemical research are determined using mass spectrometry. A mass spectrometer separates and detects ions based on their motions in magnetic or electrical fields. For detailed information on mass spectrometry and the according analytical techniques we refer the reader to the comprehensive review by Hoefs (2004). This volume also gives an introduction in new microanalytical techniques, such as laser-assisted ablation, which allows the on-line transfer of submilligram quantities of mineral into a standard gas-source spectrometer (Kyser 1995), and the gas chromatography combined with mass spectrometry, which allows the determination of the isotopic composition of single compounds previously separated by means of a gas chromatograph (Hayes et al. 1990; Merrit and Hayes 1994).

Boron isotope ratios are determined by positive or negative thermal ionization mass spectrometry (TIMS). Whereas the positive ionisation technique requires microgram quantities of boron producing $Na_2BO_2^+$ or $Cs_2BO_2^+$ ions (Spivack and Edmond 1986), the negative ionisation technique using BO_2^- ions allows for analyzing nanogram quantities of boron (Hemming and Hanson 1994). Recently, Lecuyer et al. (2002) described the use of multiple collector ICP-MS technique for boron isotopic measurements of waters, carbonates,

Table 10.1 Absolute isotope ratios of international standards and laboratory standards (after Hoefs 2004)

Standard	Ratio	Accepted value ·10⁶ within 95% confid. interval	Lab standard	δ-value [‰]
SMOW	D/H	155.8 ± 0.1	VSMOW	0.00
Standard Mean Ocean Water			SLAP	-428.00
	$^{18}O/^{16}O$	2005.2 ± 0.4	VSMOW	0.00
			SLAP	-55.50
PDB	$^{13}C/^{12}C$	11237.2 ± 2.9	NBS 19 (calcite)	+1.95
Pee Dee Belemnite	$^{18}O/^{16}O$	2067.1 ± 2.1	NBS 19 (calcite)	-2.20
			NBS 19 (carbonatite)	-23.01
N_2 (atm.)	$^{15}N/^{14}N$	3676.5 ± 8.1	Air nitrogen	0.00
Air nitrogen				
CDT	$^{34}S/^{32}S$	45004.5 ± 9.3	CDT (FeS)	0.04
Canyon Diablo Troilite				
NIST 951	$^{11}B/^{10}B$	4.04558 ± 0.00033	NIST 951 (boric acid)	0.25
Searles Lake Borax				

phosphates, and silicates with an external reproducibility of ±0.3‰.

In Earth sciences, the relative differences in isotopic ratios between a sample and a standard are mostly used for reporting stable isotope abundances and variations. The reason is that the absolute value of an isotopic ratio is difficult to determine with sufficient accuracy for geochemical applications. The reporting notation employed is the δ-value, defined as

$$\delta \text{ in } ‰ = (R_{sample} - R_{standard}) / R_{standard} \cdot 1000 \qquad (10.5)$$

where R_{sample} is the isotopic ratio of the sample ($^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{15}N/^{14}N$, $^{34}S/^{32}S$, etc.) and $R_{standard}$ is the corresponding rate in a standard. Nevertheless, the determination of absolute isotope ratios (Table 10.1) is essential, since these numbers form the basis for the calculation of the relative differences.

Isotope laboratories use different reference gases or working standards for the measurement of relative isotope ratios by mass spectrometry. However, all results are reported relative to an internationally accepted standard (Table 10.1). The selection of standards is an important procedure in isotope geochemistry because their definition and availability controls the extent to which results from different laboratories can be compared. Since the supply of PDB, the working standard introduced by H. C. Urey's laboratory at the University of Chicago, as well as of SMOW, a water sample prepared by H. Craig for distribution by the IAEA, have been exhausted for years, some confusion and irregularities occurred in the past regarding standards, particularly oxygen isotope standards. These problems may be resolved following the recommendations of the Commission on Atomic weights and isotopic abundances of the International Union of Pure and Applied Chemistry, published in 1995 (see Appendix in Coplen 1996). Isotope reference materials may be obtained from the National Institute of Standards and Technology (NIST), Gaithersburg, MD, or the International Atomic Energy Agency (IAEA), Vienna, Austria.

10.3 Geochemical Influences on $^{18}O / ^{16}O$ Ratios

10.3.1 $\delta^{18}O$ of Seawater

Principles of Fractionation

The oxygen isotopic composition of seawater ($\delta^{18}O_w$) is controlled by fractionation effects due to evaporation and precipitation at the sea surface, freezing of ice in polar regions, the admixing

of water masses containing different $^{18}O/^{16}O$ ratios such as melt water, river runoff, etc., and the global isotope content of the oceans (Craig and Gordon 1965; Broecker 1974). Since the salinity of seawater is similarly affected by these processes, Craig and Gordon (1965) and later Fairbanks et al. (1992) defined a set of regression relationships between salinity and $\delta^{18}O_w$ with different slopes for several modern water masses, varying between 0.1 for humid tropical and 1.0 for arid polar surface water masses with a global mean of 0.49 (Fig. 10.1). Higher slopes represent areas where evaporation exceeds precipitation, and vice versa. However, the extent of oxygen isotope enrichments due to evaporation is limited due to the recycling of atmospheric moisture by the different pathways of precipitation. The slope of the global trend extrapolates to a $\delta^{18}O$-value of –17‰ at zero salinity, reflecting the influx of high-latitude precipitation and glacial meltwater. For the Antarctic continental ice, even $\delta^{18}O$-values as low as –54‰ have been determined (Weiss et al. 1979; Jacobs et al. 1985). However, the slope of the $\delta^{18}O_w$-salinity relationship may have changed through geological time (see discussion below).

For water masses deeper than 2000 m, Zahn and Mix (1991) obtained a slope as high as 1.53. This gradient is explained with the formation of sea-ice in the source areas especially for southern component water masses. Since the freezing of polar surface waters raises the salinity, but does not fractionate oxygen isotopes, southern source deep water masses, like the Antarctic Bottom Water, exhibit relatively low $\delta^{18}O_w$ values, and so do other water masses, which are derived from the admixture of south polar water masses (Mackensen 2001).

Modern Range of Values and Historical Variability

The modern $\delta^{18}O_w$ values of seawater are close to 0‰ (V-SMOW) and vary only within narrow limits. From the GEOSECS $\delta^{18}O$ sections for the today's world oceans, compiled by Birchfield

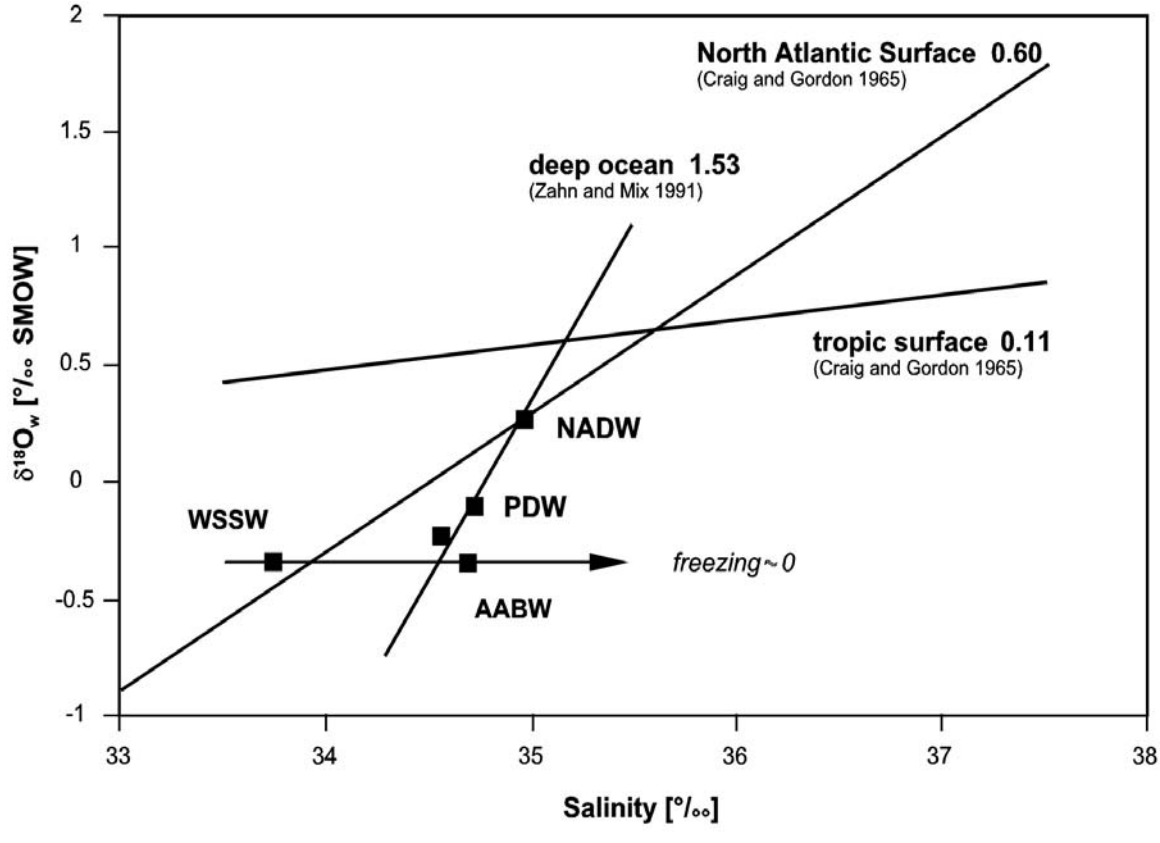

Fig. 10.1 Relationship between salinity and $\delta^{18}O_w$ of major water masses (after Craig and Gordon 1965; deep water line according to Zahn and Mix 1991).

(1987), a range of +1.0‰ in the mid-latitude surface Atlantic to –0.6‰ in the northern surface Pacific is present. Deep water mass $\delta^{18}O_w$ ranges from +0.3‰ in the core of North Atlantic Deep Water to –0.1‰ in the Circumpolar Deep Water (for a recent compilation search the Global Seawater Oxygen-18 Database, Schmidt et al. 1999). Since $\delta^{18}O_w$ exhibits only a narrow range within open ocean conditions, this proxy is an excellent tracer for indicating the influence of freshwater input to ocean water masses, since river discharge or meltwater release is always depleted in ^{18}O (Craig and Gordon 1965). For example, Mackensen et al. (1996, 2001) showed isotopically light meltwaters of the Antarctic Peninsula shelves to cascade down slopes the Weddell Sea Basin and thereby contributing to bottom water formation.

In geologic history, the $\delta^{18}O_W$ has been shown to vary considerably. For the sea-level low stand of -120 m during the last glacial maximum, Fairbanks (1989) showed Barbados coral oxygen isotopic composition to be enriched by 1.2‰, which coincides with an isotopic change of 0.10‰ corresponding to a 10 m sea-level change earlier estimated by Shackleton and Opdyke (1973). A slightly lower glacial interglacial range of 0.7 to 1.1‰ has been reported from porewater analyses of different drill holes in the Atlantic (Adkins et al. 2002). In an ice-free world, like in the Cretaceous, the global mean should have been depleted by another -0.8‰. On longer time scales, additional processes affecting the $\delta^{18}O_W$ have to be considered. A compilation of Phanerozoic $\delta^{18}O_W$ values showed an 5‰ increase in $\delta^{18}O_W$ since the Cambrian (Veizer et al. 1999 with a recent update of the database in 2004). By mass balance calculations, Wallmann (2001) demonstrated that this increase in $\delta^{18}O_W$ is in agreement with the ocean's 6-10% loss of seawater over the last 600 mio years because the subduction of water structurally bound in altered oceanic crust exceeds the water emission by mantle degassing. However, the large isotopic shifts observed episodically in the Paleozoic, as recorded in fossils (Veizer et al. 1999) and abiotic marine calcites (Lohmann and Walker 1989; Carpenter et al. 1991), exceed by far the variability in isotopes observed in Neogene and Quaternary times and are too fast to be explained with ocean crust-seawater interactions. Those changes must be attributed to changes in earth climate systems, like ice volume and ocean circulation (e.g. Railsback 1990; Bickert et al. 1997).

10.3.2 $\delta^{18}O$ in Marine Carbonates

Principles of Fractionation

The oxygen isotope ratios in carbonates are a function of both temperature and the $\delta^{18}O_w$ of the surrounding seawater. Since the early equation given by Epstein et al. (1953), many equations have been published, which substantiated the potential of oxygen isotope paleothermometry for biogenically precipitated calcite. The first equation based on laboratory experiments with planktonic foraminifera was generated by Erez and Luz (1983). Their measurements on the cultured symbiotic species *G. sacculifer* were approximated by the second order polynom

$$T = 17.0 - 4.52 \cdot (\delta^{18}O_c - \delta^{18}O_w) + 0.03 \cdot (\delta^{18}O_c - \delta^{18}O_w)^2 \quad (10.6)$$

with T standing for the *in-situ* temperature during calcite precipitation (°C), $\delta^{18}O_c$ representing the oxygen isotopic composition of the calcite (as ‰ PDB), and $\delta^{18}O_w$ representing the $\delta^{18}O$ value (‰ PDB) of the seawater from which the calcite has been precipitated. Since oxygen isotope analyses of waters are commonly reported relative to SMOW, the conversion of $\delta^{18}O_w$ to the PDB scale can be calculated according to Hoefs (2004)

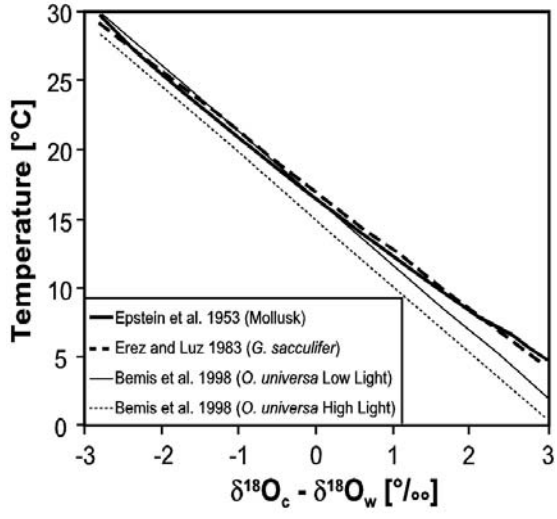

Fig. 10.2 Comparison of the results of different paleotemperature equations (see Bemis et al. 1998 for review).

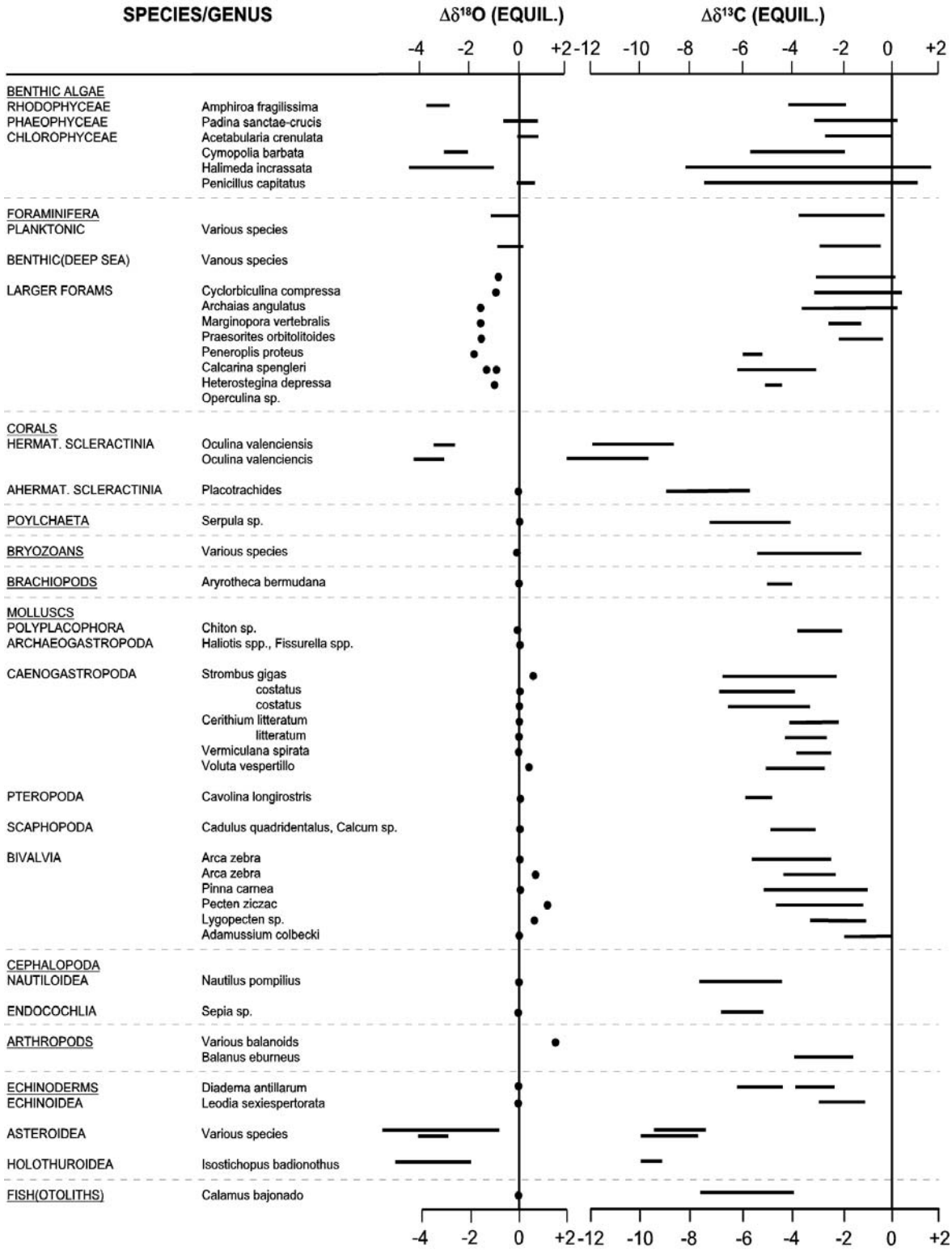

Fig. 10.3 $\delta^{18}O$ and $\delta^{13}C$ deviations from equilibrium isotope composition of selected calcareous species (adopted from Wefer and Berger 1991).

$$\delta^{18}O_{PDB} = 0.97002 \cdot \delta^{18}O_{SMOW} - 29.98 \qquad (10.7)$$

A $\delta^{18}O_w$ correction of –0.27‰ is therefore necessary to compare $\delta^{18}O$ values measured in CO_2 produced by the reaction of calcite with H_3PO_4 with those measured in CO_2 equilibrated with water.

Most of the paleotemperature equations appear to be similar to the one stated above (Eq. 10.6), but temperature reconstructions can differ as much as 2°C when ambient temperature varies between 5°C and 25°C (Fig. 10.2; Bemis et al. 1998; for a recent review see Mulitza et al. 2003). The reason is that, in addition to *in-situ* temperature and water isotopic composition, the shell $\delta^{18}O$ may be affected by the photosynthetic activity of algal symbionts and by the carbonate ion concentration in seawater. Wefer and Berger (1991) summarized the importance of such effects, previously called 'vital effects', on a broad spectrum of organisms (Fig. 10.3). For oxygen isotopes, most organisms are shown to precipitate $CaCO_3$ close to equilibrium with the water in which they live. However, some organisms, such as planktonic foraminifera and hermatypic corals, exhibit significant differences from isotopic equilibrium (see Waelbroek et al. 2005 for a review). Laboratory experiments with live planktonic foraminifera demonstrated that an increase in the symbiont photosynthetic activity results in a decrease in shell $\delta^{18}O$ values (Spero 1992; Spero and Lea 1993). The mechanisms driving the effects of symbiont photosynthesis on shell $\delta^{18}O$ are not well understood, but appear to be linked to the carbonate ion concentration. During photosynthetic activity, CO_2 uptake by the symbionts increases the pH in the microenvironment around the shell (Jørgensen et al. 1985; Rink 1998; Zeebe 1999). Consequently, more alkaline conditions correspond to locally elevated $[CO_3^{2-}]$. The ^{18}O depletion of shells due to higher symbiont photosynthetic activity is consistent with the effect of higher ambient $[CO_3^{2-}]$. Spero et al. (1997) obtained a $\delta^{18}O/[CO_3^{2-}]$ slope of –0.002‰ $\mu mol^{-1}kg^{-1}$ from experiments with symbiotic (*O. universa*) and non-symbiotic (*G. bulloides)* foraminifer species. This previously undocumented carbonate isotope effect may help to solve inconsistencies in temperature reconstructions by applying oxygen isotope paleothermometry relative to other marine or terrestrial temperature proxies (see discussions in Spero et al. 1997; Zeebe 1999).

Diagenesis

The isotopic composition of a carbonatic shell will remain unchanged until the shell material dissolves and recrystallizes during diagenesis. Diagenetic modification, however, could begin immediately after deposition or even in the water column due to corrosive deep ocean or pore waters. Such waters are generally enriched in CO_2 due to the respiration of organic matter mediated by specific bacteria. In shells of the planktonic foraminifera *P. obliquiloculata* sampled in a depth profile in the western equatorial Pacific Wu and Berger (1989) showed that below the depth of the modern lysocline the $\delta^{18}O$ of this species increased with water depth due to increasing calcite dissolution. Close to the modern depth of calcium carbonate compensation, the observed deviation reached a maximum value of +0.9‰. This effect of differential dissolution, i.e. the preferential removal of the light isotope ^{16}O, has recently helped to unravel the so-called cool tropics paradox. Using exceptionally well preserved planktonic foraminifer shells extracted from clay-rich late Cretaceous to Eocene sediments, Pearson et al. (2001) could show that the previously reported cooler tropical sea surface temperatures are the result of up to 3 ‰ increased $\delta^{18}O$ values caused by a subtle diagenetic recrystallization on a micrometer scale, without obliterating surface ornaments or internal layering features. Pearson et al. (2001) emphasized that this kind of diagenesis is hard to detect compared to more obvious modes of alteration like the precipitation of euhedral inorganic calcite resulting in substantial infillings or overgrowth.

The conversion of sediment into limestone within deep-sea sediments results from pressure and temperature rises which both increase with burial depth. Within carbonate sediments, diagenesis generally transforms the less stable aragonite and Mg-calcite into a low-Mg calcitic cement by means of a dissolution-reprecipitation process. Theoretically, the oxygen isotope composition of carbonates should not change significantly with burial, since the ^{18}O in pore waters originates from seawater. However, in many cores recovered during DSDP/ODP drilling, deep-sea carbonates and often pore waters as well, exhibit ^{18}O depletions by several permil (e.g. Lawrence 1989). Mass balance calculations by Matsumoto (1992) indicated that the ^{18}O shift in pore water towards lower values in sediments of the Japan Sea

is controlled by a low-temperature alteration of basement basalts (see also discussion in Sect. 10.3.1), which is slightly compensated by the transformation of biogenic opal to quartz. Furthermore, detailed measurements on different generations of carbonate cements suggest that late cements exhibit lower $\delta^{18}O$ values compared to early precipitates. This $\delta^{18}O$ trend may be due to the increasing temperatures with increasing burial depth or to the isotopic evolution of pore waters during precipitation (Hoefs 2004).

10.4 Geochemical Influences on ^{13}C / ^{12}C Ratios

10.4.1 $\delta^{13}C_{\Sigma CO2}$ of Seawater

Principles of Fractionation

The carbon isotopic composition of ΣCO_2 in seawater is mainly controlled by two processes, the biochemical fractionation due to the formation and decay of organic matter, and the physical fractionation during gas exchange at the air-sea boundary (Broecker and Maier-Reimer 1992). Surface water is enriched in ^{13}C, because photosynthesis preferentially removes ^{12}C from the CO_2. Deeper water masses have lower $\delta^{13}C$ values, since nearly all of the organic matter that is produced by photosynthesis is subsequently remineralized in the water column. Broecker and Maier-Reimer (1992) showed that if there were no air-sea gas exchange, the relationship between $\delta^{13}C$ and PO_4 in the ocean would be

$$\delta^{13}C - \delta^{13}C_{m.o.} = \varepsilon_p / \Sigma CO_{2\,m.o.} \cdot C / P_{org} \cdot (PO_4 - PO_{4\,m.o.}) \quad (10.8)$$

where ε_p (‰) is the isotopic effect associated with the photosynthetic fixation of carbon, C/P_{org} is the Redfield Ratio, and the subscript m.o. stands for mean ocean values. When reasonable values are substituted ($\delta^{13}C_{m.o.}$ = 0.3‰, ε_p = –19‰, $\Sigma CO_{2\,m.o.}$ = 2200 µmol kg^{-1}, C/P_{org} = 128, $PO_{4\,m.o.}$ = 2.2 µmol kg^{-1}), the predicted relationship closely matches the relationship for waters in the deep Indian and Pacific Oceans ($\delta^{13}C = 2.7 - 1.1 \cdot PO_4$). This is to be expected, as the effect of air-sea exchange should be constant for these deep water masses due to the homogeneity of source waters for the deep Indian and Pacific Oceans.

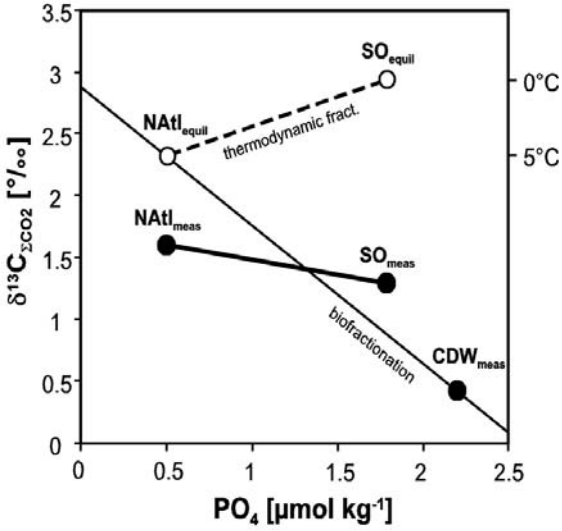

Fig. 10.4 Schematic diagram showing the effect of biofractionation and thermodynamic effects on the carbon isotopic composition of total dissolved inorganic carbon (according to Zahn and Keir 1994).

On the other hand, carbon isotope fractionation during air-sea gas exchange is also an important factor in determining the isotopic composition of carbon in surface water (Charles and Fairbanks 1990; Broecker and Peng 1992; Lynch-Stieglitz et al. 1995). If the CO_2 in the atmosphere were in isotopic equilibrium with the dissolved inorganic carbon in the ocean, the dissolved inorganic carbon would be enriched in ^{13}C by about 8‰ at 20°C relative to the atmosphere CO_2 (Zhang et al. 1995). This thermodynamic fractionation depends on the temperature of equilibration, with ΣCO_2 becoming more enriched relative to the atmospheric value by about 1‰ per 10°C cooling (Fig. 10.4; Mook et al. 1974). If the surface ocean were in complete isotopic equilibrium with atmospheric CO_2, one expects a 3‰ range in oceanic $\delta^{13}C$ for the 30°C range in ocean temperatures, similar to the magnitude of $\delta^{13}C$ change induced by biological processes. In fact, CO_2 exchange rates between the ocean and the atmosphere are slow enough (relative to mass transport of ΣCO_2 within the ocean) that the range of $\delta^{13}C_{\Sigma CO2}$ in surface waters is less than 3‰. Moreover, Zahn and Keir (1994) showed in their ocean-atmosphere box-model that even in the absence of the temperature effect, the air-sea gas exchange modifies the $\delta^{13}C$ distribution of the upper

ocean and the Atlantic deep water. The observed deviations occur because net biological production in the Southern Ocean is low relative to the upwelling fluxes of nutrients and dissolved carbon, allowing low $^{13}C/^{12}C$ ratios in the dissolved carbon to outcrop and exchange with the atmosphere. As a consequence, a dynamic balance is achieved where CO_2 evading from Antarctic waters to the atmosphere has a lower $\delta^{13}C$ than the invading CO_2, while the isotope ratio of the evading CO_2 from the warm ocean is greater than that of the return flux of CO_2.

Modern Range of Values and Historical Variability

The modern $\delta^{13}C_{\Sigma CO2}$ values of seawater are close to 0‰ (PDB) and vary only within a small range. From the GEOSECS $\delta^{13}C_{\Sigma CO2}$ sections for today's world oceans, compiled by Kroopnick (1985), a range of +2.5‰ in the mid-latitude surface Atlantic to +0.7‰ in the northern surface Pacific has been determined. Deep water mass $\delta^{13}C_{\Sigma CO2}$ ranges from +1.2‰ in the core of North Atlantic Deep Water and +0.4‰ in the Circumpolar Deep Water to –1.0‰ in the northern Pacific Deep Water. As stated above, $\delta^{13}C_{\Sigma CO2}$ of a deep water mass behaves like a conservative tracer for phosphate, since the water mass left its sea surface source area. On the other hand, paired $\delta^{13}C_{\Sigma CO2}$ and PO_4 measurements on two sections in the Southern Ocean clearly support the thermodynamic imprint during Weddell Sea Bottom Water formation by a significant deviation from the Redfield $\delta^{13}C_{\Sigma CO2}/PO_4$ relationship (Mackensen et al. 1996; Mackensen 2001). A recent matter of concern is the so-called oceanic Suess effect, which describes the uptake of ^{13}C-depleted anthropogenic CO_2 by the oceans and the consequent decrease in the oceanic $\delta^{13}C$. Comparisons between modern sediment trap and core top foraminiferal $\delta^{13}C$ reveal a modern depletion in $\delta^{13}C$ of the upper water column of up to 0.65‰ in the Subantarctic Zone and up to 0.9‰ in the Arctic realm (e.g., King and Howard 2004). This effect has to be considered before using surface sediment values for carbon cycle proxy calibrations.

The $\delta^{13}C_{\Sigma CO2}$ varied considerably in geologic history. Generally, three explanations are given for changes of $\delta^{13}C_{\Sigma CO2}$ distribution in the ocean: (1) changes in the surface-ocean productivity which cause variable fractionation between surface and deep water carbon isotopic composition, (2) changes in the gas exchange rates between ocean and atmosphere due to changes in surface temperatures and ocean circulation, and (3) changes in the marine carbon budget by variations in the reservoirs of the atmosphere, the ocean, or the lithosphere. Of course, these different processes act on different time scales. Variations on a scale of 10^1 to 10^5 years might be attributed to changes in the effectivity of the biologic pump (Berger and Vincent 1986), to rapid changes between land and ocean reservoirs (Shackleton 1977; Broecker 1982), or to changes in ocean circulation responding to climate variability (e.g. Sarnthein et al. 1994; Bickert and Mackensen 2003).

On scales of 10^5 years and longer, changes in the influx and in the burial of sedimentary inorganic and organic carbon exert a primary control on the $\delta^{13}C$ of the ocean and the atmosphere (Holser 1997). Main sources for carbon comprise the erosional flux of sedimentary carbon (as C_{org} and carbonate) and the degassing of volcanic CO_2; main sinks are the burial of organic matter and the deposition of carbonate. Changes in the oceanic $\delta^{13}C$ are assumed to be the result of variations in the ratio of inorganic to organic carbon contributed to sediments (e.g. Derry and France-Lanord 1996). An increase in the burial of organic carbon would preferentially remove ^{12}C from seawater, so that the ocean reservoir would become isotopically heavier, and vice versa.

10.4.2 $\delta^{13}C$ in Marine Organic Matter

Principles of Fractionation

The carbon isotopic composition of marine organic matter produced in the photic zone depends on the isotope ratio of the total dissolved inorganic carbon and the degree to which this inorganic pool is utilized (Degens et al. 1968). Although more than 90% of the inorganic carbon pool is in the form of HCO_3^-, phytoplankton utilizes mostly carbon of the very small reservoir (1%) of dissolved $CO_{2(aq)}$. While the equilibrium exchange fractionation is only small between atmospheric CO_2 and dissolved $CO_{2(aq)}$ (about 1‰), and moderate between $CO_{2(aq)}$ and HCO_3^- (with a range of 10‰ to 8‰ between 5°C and 25°C; Mook et al. 1974), a large kinetic fractionation accompanies the biological carbon fixation during photosynthesis. The main isotope-discriminating steps are (1) the uptake and intracellular diffusion of CO_2, and (2) the enzymatic carbon fixation (Park

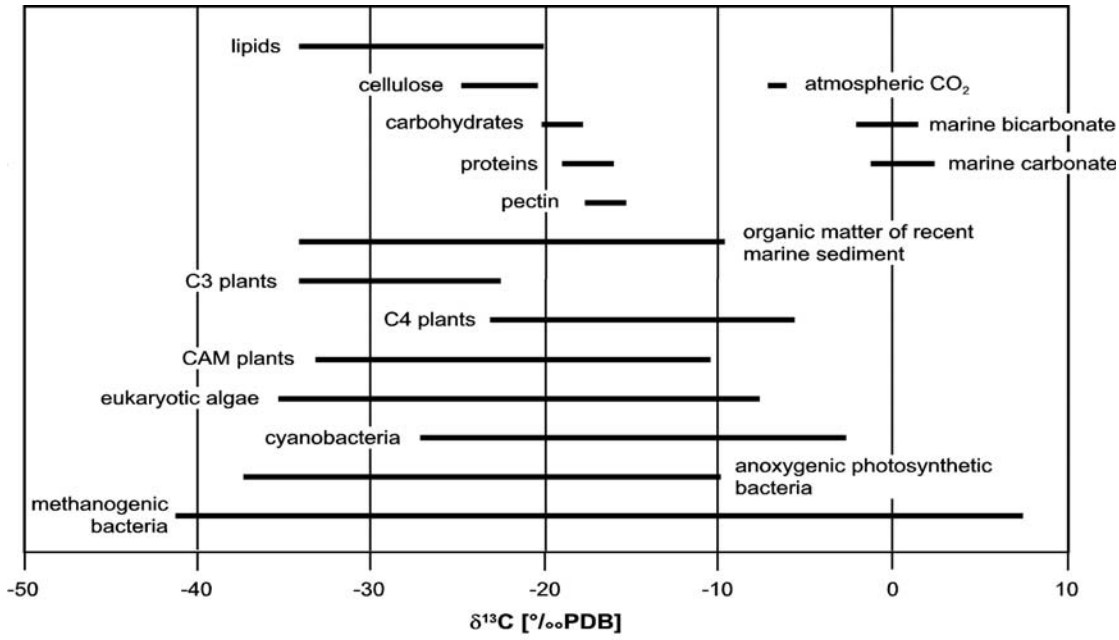

Fig. 10.5 Carbon isotopic composition of autotrophic marine and terrestrial organisms in comparison to the range observed in anorganic compounds (after Schidlowski 1988) and organic constituents (after Degens 1969).

and Epstein 1960). The first, reversible step is associated with a moderate fractionation of about –4‰, the second, irreversible step causes a kinetic fractionation of up to –40‰ (O'Leary 1981).

The $\delta^{13}C_{org}$ values of marine phytoplankton range between –10‰ and –31‰, but most of the warm-water plankton exhibits values between –17‰ to –22‰ (Fig. 10.5; Degens et al. 1968, 1969). The two-step model of carbon fixation clearly suggests that isotope fractionation depends on the concentration of $CO_{2(aq)}$. The fractionation decreases with decreasing CO_2 availability, such that in warm marine surface waters one would expect higher $\delta^{13}C_{org}$ values than in colder waters, since the solubility of CO_2 increases with decreasing temperature. However, other factors, such as species composition, light intensity, growth rate and cell geometry may also influence organic $\delta^{13}C$ values of particulate organic matter (e.g. Hayes 1993; Bidigare et al. 1997; Rau et al. 1997; Popp et al. 1998).

An important application of carbon stable isotope ratios lies in the reconstruction of the carbon dioxide concentration in surface waters and subsequently in the atmosphere at the time the organic matter was produced. Experimental and field studies have shown that the fractionation of stable carbon isotopes during photosynthesis by plankton depends on the concentration of ambient dissolved molecular carbon dioxide ($CO_{2(aq)}$), which led to the suggestion that sedimentary $\delta^{13}C_{org}$ may serve as a proxy for surface water $CO_{2(aq)}$ (Popp et al. 1989; Rau et al. 1991). The applicability of this tool in paleoceanographic studies has been shown repeatedly (e.g. Jasper and Hayes 1990, 1994; Fontugne and Calvert 1992; Müller et al. 1994), but the reconstruction of paleo-pCO_2 has become more and more complex due to the growing knowledge of factors influencing carbon isotopic fractionation during organic matter construction. Recent laboratory and field experiments as well as theoretical considerations indicate that the isotopic fractionation of carbon during photosynthesis (ε_p), and consequently also the sedimentary $\delta^{13}C$ of organic matter, could be influenced by physiological processes and environmental factors such as growth rates, temperature, nutrient supply, irradiance (Laws et al. 1995; Bidigare et al. 1997; Burkhardt et al. 1999; Rost et al. 2002), cell geometries and membrane permeability (Popp et al. 1998; Burkhardt et al. 1999), and active carbon uptake (for a review see Schulte et al. 2003). To better follow the discussion of this complex matter, the consecuting paragraphs introduce the use of δ^{13}Corg in pCO_2 recon-

struction, knowing the fact that there is an ongoing debate on the applicability of this proxy.

For algae where CO_2 is thought to reach the photosynthetic site only by passive diffusion, ε_p can be calculated by the following equation (Bidigare et al. 1997):

$$\varepsilon_p = \varepsilon_f - b / [CO_{2(aq)}] \quad (10.9)$$

where ε_f (‰) is the maximum isotopic effect associated with the photosynthetic fixation of carbon mediated by the enzyms Rubisco and β-carboxylase (≈25 ‰; Bidigare et al. 1997), and the variable b reflects the intracellular carbon demand. Because the b-value combines a suite of factors, like growth rate, membrane permeability, cell geometry, and boundary layer thickness, significant variations in b (–109 ‰μM to –164 ‰μM) have been observed in empirical fits to field and experimental data (Laws et al. 1995). For example, higher growth rates lead to higher b-values (Bidigare et al. 1997; Rau et al. 1997). Based on chemostat experiments with the coccolithophorid *E. huxleyi*, Bidigare et al. (1997) found a close correlation between ε_p and the growth rate μ:

$$\varepsilon_p = 24.6 - 137.9 \cdot \mu / [CO_{2(aq)}] \quad (10.10)$$

To obtain $CO_{2(aq)}$, Equation 10.9 has to be rearranged, and values for ε_p are determined from the carbon isotopic compositions of the primary photosynthate $\delta^{13}C_p$ (‰) and of the ambient dissolved molecular carbon dioxide $\delta^{13}C_d$ (‰) (Fig. 10.6):

$$\varepsilon_p = ((\delta^{13}C_p + 1000) / (\delta^{13}C_d + 1000) - 1) \cdot 1000 \quad (10.11)$$

Assuming that diagenetic isotopic alterations can be neglected (see below), $\delta^{13}C_p$ may be directly substituted by the measured $\delta^{13}C_{org}$ value.

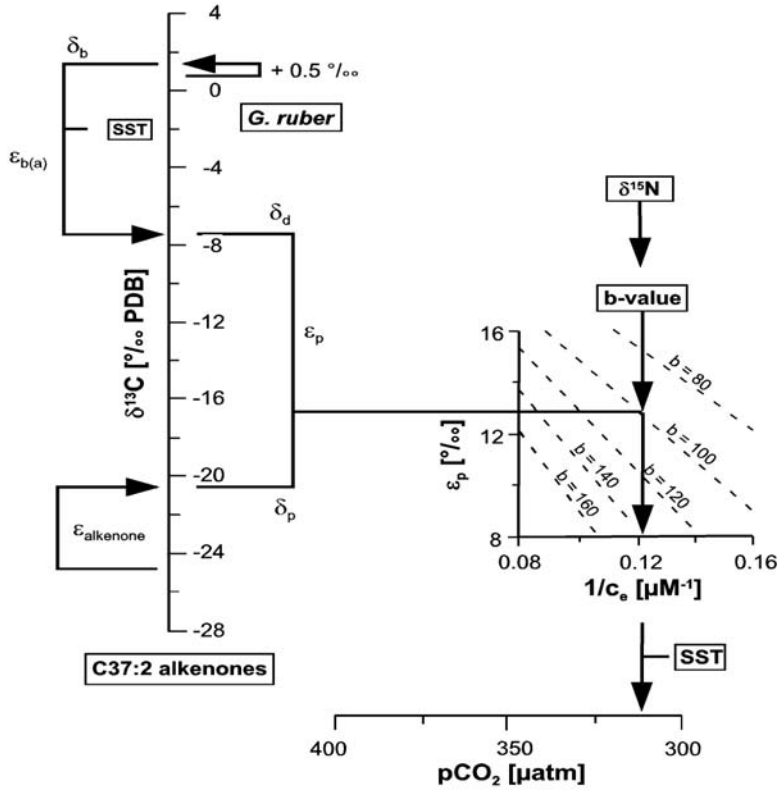

Fig. 10.6 Diagram outlining the estimation of surface ocean $CO_{2(aq)}$ and pCO_2, when $\delta^{13}C_{alkenones}$, $\delta^{13}C_{calcite}$, $\delta^{15}N$ as a proxy for carbon demand b, and surface ocean temperature are provided (Andersen et al. 1998; modified from Jasper and Hayes 1994).

Values for $\delta^{13}C_d$ are estimated on the basis of the $\delta^{13}C$ of calcite tests assuming that the calcite was precipitated in equilibrium with the ΣCO_2, correcting for the temperature-dependent fractionation $\varepsilon_{b(a)}$ between $CO_{2(aq)}$ and dissolved bicarbonate according to Mook et al. (1974):

$$\delta^{13}C_d = \delta^{13}C_{\Sigma CO2} - \varepsilon_{b(a)}$$
$$= \delta^{13}C_{\Sigma CO2} - 24.12 - 9866 / T \qquad (10.12)$$

T is the temperature of surface waters measured in K. The $CO_{2(aq)}$ concentrations are then converted to CO_2 partial pressure values (pCO_2 in µatm) using Henry's Law:

$$pCO_2 = CO_{2(aq)} / \alpha \qquad (10.13)$$

where the solubility coefficient α is mainly a function of temperature and, to a minor extent, of salinity (Rau et al. 1991). α may be calculated according to Weiss (1974). The success of the equations in determining surface $CO_{2(aq)}$ is dependent on the estimation of the sea-surface temperatures and on the determination of the complex variable b for the past. While several proxies exist for reconstructing past SST, the determination of ancient b-values is difficult. A promising approach is the use of bulk sediment $\delta^{15}N$ as proxy for b (Andersen et al. 1999). However, the use of $\delta^{15}N$ as a proxy for carbon demand introduces a number of potential problems associated with the complex fractionation mechanisms of nitrogen isotopes (see Sect. 10.5).

A topic of much concern regarding the use of bulk $\delta^{13}C_{org}$ in paleoceanographic investigations is the masking of the marine $\delta^{13}C_{org}$ signal by terrestrially-derived organic matter. Since terrigenous material is usually substantially depleted in ^{13}C (estimated mean value of –27‰, since 90% of land plants are C_3 plants) compared to marine-derived matter (mean value of –19‰), the carbon isotopic composition of ocean sediments have been used to trace the origin of sedimentary organic carbon (Newman et al. 1973; Rühlemann et al. 1996). However, the underlying assumption regarding the mixing of a marine and a terrestrial $\delta^{13}C_{org}$ end member is not always supported because of the possible variability of $\delta^{13}C_{org}$ values produced in terrestrial systems (e.g. change in the relative contribution of C_3 and C_4 plants). Also, marine values may change by processes occurring in the water column (e.g. changing phytoplankton growth conditions, see above).

To circumvent the problem of influencing carbon isotope signals by terrigenous organic matter contamination or by marine photosynthesizers with varying carbon fixation pathways and cell geometries, recent studies concentrated on certain organic molecules (biomarker) from known marine sources unique to a particular class of organism. In this context, C_{37} alkenones have been shown to serve as excellent biomarkers (e.g., Andersen et al. 1999), because they derive exclusively from some haptophyte algae, which have a narrow range of cell geometries and diameters (Bidigare et al. 1997; Popp et al. 1998), thereby minimizing these variables as a significant control on isotopic compositions. As an application, Pagani et al. (1999) concluded on the basis of $\varepsilon_{p37:2}$ records that early to late Miocene (25-9 Ma) pCO_2 levels were similar to those recorded for Pleistocene glacial-interglacial intervals. This pattern of low pCO_2 levels throughout the Neogene has been confirmed independently by Pearson and Palmer (2000) using boron isotopes (see chapter 10.7)

Diagenesis

Early diagenesis begins in the photic zone of the oceans, continues during the sinking of particles, and is intense in the bioturbated surface layer of sediments. Therefore, only a few percent of the initially produced organic matter becomes buried in the sediments (Berger et al. 1989). However, despite the extensive loss of organic matter due to remineralization, the carbon isotopic composition of particulate organic matter appears to undergo only little change (see review in Popp et al. 1997). On the other hand, large and nonsystematic differences have been observed between the isotopic composition of total organic carbon and single organic compounds, e.g. phytoplankton biomarkers, in the same deposit (Fig. 10.5; Degens et al. 1969). Therefore, the assumption that the carbon isotopic composition of marine sedimentary organic matter directly or indirectly reflects the carbon isotopic composition of phytoplanktonic matter must be taken cautiously (Popp et al. 1997). Furthermore, since marine organic matter is easily digestible, whereas terrestrial organic matter is rather resistant, such preferential decomposition of organic matter has great impact on the estimation of the average marine and terrestrial $\delta^{13}C_{org}$ component (de Lange et al. 1994).

The carbon isotopic composition of pore waters reflects both the decomposition of organic matter, which releases ^{13}C-depleted CO_2 to the

pore water, and the dissolution of $CaCO_3$, which adds CO_2 relatively enriched in ^{13}C. Since the depletion of organic matter $\delta^{13}C$ exceeds by far the range of $\delta^{13}C$ exhibited in sedimentary carbonate, the net result of these two processes is to make dissolved CO_2 in pore water isotopically lighter compared to the overlying bottom water. Below the sediment/water interface, where pore water has a $\delta^{13}C$-value near that of seawater, a $\delta^{13}C$-gradient exists in the uppermost few centimeters. McCorkle et al. (1985) and McCorkle and Emerson (1988) showed that the gradient of $\delta^{13}C$-profiles observed in several box cores vary systematically with the rain of organic matter to the seafloor. In slowly deposited oxic sediments containing little amounts of organic carbon, only a small decrease in $\delta^{13}C$ relative to seawater $\delta^{13}C$ occurs. In organic-carbon rich sediments, the rates of organic matter decomposition and the production of reduced nitrogen compounds would rapidly decrease the pore water $\delta^{13}C$. In these anoxic sediments, the situation is even more complex due to bacterial methanogenesis, which follows the sulfate reduction during early diagenesis. Since methane-producing bacteria metabolize methane highly enriched in ^{12}C (–50‰ to –100‰; Deines 1981), the pore water becomes significantly enriched in ^{13}C. Such trends in $\delta^{13}C$ of total dissolved CO_2 from pore waters within anoxic sediments have been recovered in various Deep Sea Drilling sites (Arthur et al. 1983). However, because pore waters are not truly closed systems, other factors like carbon loss due to upward diffusion of methane and other dissolved carbon species as well as precipitation of authigenic carbonates may also affect pore water $\delta^{13}C$. For example, if significant amounts of methane are utilized in sulfate reduction, the rate of $\delta^{13}C$ decrease associated with the ΣCO_2 increase would be anomalously high (Arthur et al. 1983).

10.4.3 $\delta^{13}C$ in Marine Carbonates

Principles of Fractionation

Precipitation of carbonate, largely from total dissolved carbon which is present primarily as HCO_3^-, involves a much smaller fractionation of carbon isotopes compared to the photosynthetic fixation of carbon. In fact, the $\delta^{13}C$ of calcite is relatively insensitive to changes in temperature (e.g. ≈0.035‰ $°C^{-1}$; Emrich et al. 1970) such that carbonate minerals can be used generally to monitor changes in the $\delta^{13}C_{\Sigma CO2}$ in the waters from which they precipitate. However, the possible effects of biologically mediated carbonate precipitation have been considered already for oxygen isotopes (see Sect. 10.3.2). Observations summarized by Wefer and Berger (1991) reveal that most organisms exhibit $\delta^{13}C$-values which are in disequilibrium with the $\delta^{13}C_{\Sigma CO2}$ of the waters, from which shell carbonate is precipitated (Fig. 10.3). As discussed for the influences on oxygen isotopic composition in carbonate, there may be several reasons for these deviations. McConnaughy et al. (1997) distinguish metabolic and kinetic effects on the carbon isotopic disequilibria. Kinetic isotope effects result from the discrimination against ^{13}C during hydration and hydroxylation of CO_2. Such effects appear to be associated with rapid calcification, as observed in corals. Metabolic effects apparently result from changes in the $\delta^{13}C_{\Sigma CO2}$ of the microenvironment due to photosynthesis and respiration. For example, infaunal benthic foraminifera precipitate their calcite in equilibrium with ambient pore water $\delta^{13}C_{\Sigma CO2}$, and therefore monitor the vertical carbon isotope gradient due to organic matter remineralization rather than bottom water $\delta^{13}C_{\Sigma CO2}$ (Fig. 10.7; McCorkle et al. 1990, 1997). Mackensen et al. (1993) discuss several ways, how the $\delta^{13}C$ of even epibenthic living foraminifer species could be influenced by the decay of organic matter. An example for the consequences of such a 'Mackensen' effect is discussed by Bickert and Wefer (1999) for the late Quaternary reconstruction of South Atlantic deep water circulation. An extreme depletion in $\delta^{13}C$ is recorded in endobenthic foraminifers sampled from ODP Site 680. Wefer et al. (1994) attributed these excursions to the release of methane in the continental margin off Peru sediments, which lowers substantially the carbon isotopic composition of CO_2 in the porewater. Furthermore, the laboratory experiments with live planktonic foraminifera which demonstrated symbiont photosynthetic effect on shell $\delta^{18}O$ values (Spero 1992; Spero and Lea 1993) revealed a similar effect on shell $\delta^{13}C$ values. Spero et al. (1997) obtained from experiments with symbiotic (*O. universa*) and non-symbiotic (*G. bulloides)* foraminifer species a $\delta^{13}C/[CO_3^{2-}]$ slope of –0.007‰ $\mu mol^{-1}kg^{-1}$. Furthermore, Bemis et al. (2000) showed a clear disequilibrium effect related to the calcification temperature, which has recently been approved in a field study by King and Howard (2004). These effects might partly be responsible for the shifts observed in foraminiferal

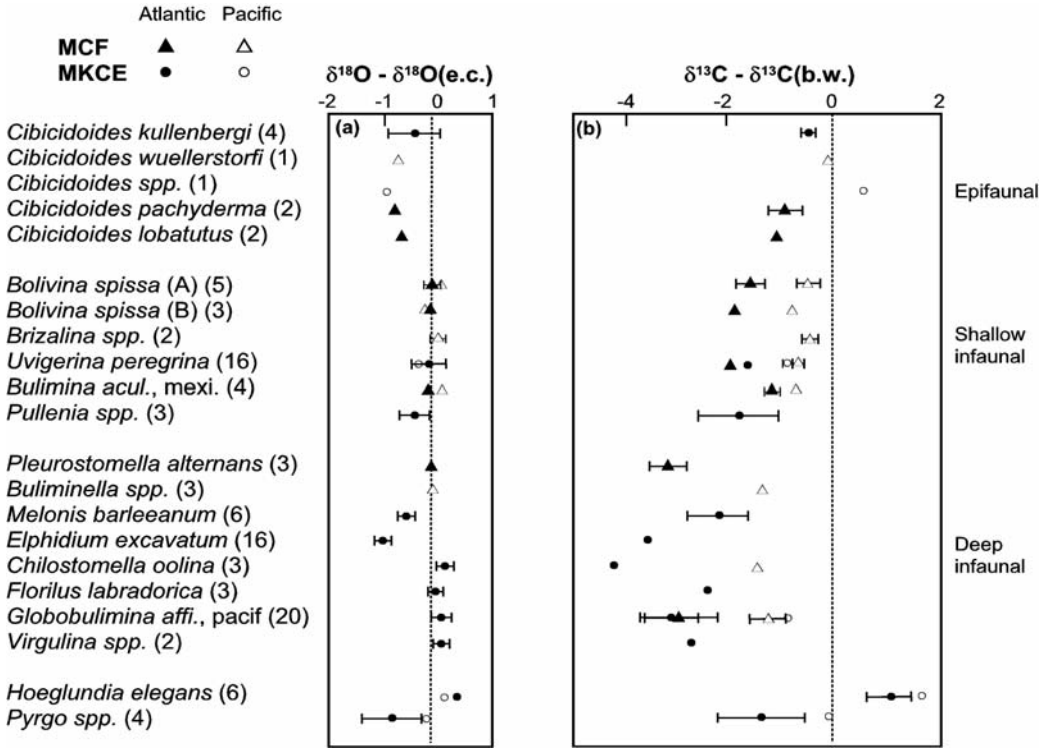

Fig. 10.7 $\delta^{18}O$ and $\delta^{13}C$ values of benthic foraminifera species in comparison to equilibrium calcite $\delta^{18}O$ values and to the pore water $\delta^{13}C_{\Sigma CO2}$ gradient, respectively (McCorkle et al. 1990).

calcite previously attributed to global changes in $\delta^{13}C_{\Sigma CO2}$ of the ocean (see discussion in Spero et al. 1997).

Carbonate Dissolution and Precipitation

Some aspects of the influence of diagenesis on the isotopic composition of carbonate have already been discussed for oxygen isotopes (see Sect. 10.3.2). The isotopic composition of a carbonatic shell will remain unchanged until the shell material dissolves and recrystallizes during diagenesis. As stated above, diagenetic modification could begin immediately after deposition or even in the water column due to corrosive deep ocean or pore waters. McCorkle et al. (1995) showed in shells of the benthic foraminifera *C. wuellerstorfi* sampled in a depth profile in the western equatorial Pacific that below the depth of the modern lysocline the $\delta^{13}C$ of this species decrease with water depth. Close to the modern depth of calcium carbonate compensation, the observed deviation reached a minimum value of –0.35‰. Since the effect of differential dissolution would cause a preferential removal of the light isotope ^{12}C, an increase would be expected to occur with increasing dissolution. The opposite is observed and requires therefore other explanations, beside the effect of carbonate ion concentration (Spero et al. 1997).

Under oxic porewater conditions, no further change in the carbon isotopic composition of shell material is expected, until dissolution occurs under deep burial. But while a temperature-effect is negligible (Emrich et al. 1970), an alteration of the primary $\delta^{13}C$ value may arise during mineral transformations (aragonite → low Mg-calcite), depending on the amount of carbon present in the postdepositional solutions. Under suboxic conditions in sediments with high organic carbon contents, the carbon isotope signal may be affected by early diagenesis (Nissenbaum et al. 1972; Irwin et al. 1977). The degradation of organic matter will cause an intense degree of carbonate dissolution and the reprecipitation of authigenic calcite standing in equilibrium with porewater $\delta^{13}C_{\Sigma CO2}$. Schneider et al. (1992) estimated for continental slope sediments off Angola that a precipitation of 5% authigenic calcite on foraminiferal tests would produce a decrease of –1‰ in the

$\delta^{13}C$ of these tests. Again, the fractionation of $\delta^{13}C$ during precipitation has only a minor effect on the carbon isotope composition of the solid phase, the major effect is determined by the $\delta^{13}C_{\Sigma CO2}$ of the pore water which itself is controlled by the degradation of organic matter.

10.5 Geochemical Influences on ^{15}N / ^{14}N Ratios

10.5.1 $\delta^{15}N$ in Marine Ecosystems

Principles of Fractionation

The use of nitrogen isotopes in marine sediments is a relatively new tool in the field of paleoceanography. The usefulness of this proxy lies in its recording changes of nutrient dynamics in the water column. Major biological transformations of nitrogen in marine systems include the utilization of the dissolved forms of inorganic nitrogen (NO_2^-, NO_3^-, NH_4^+) by phytoplankton, the consumption of phytoplankton by grazers, and the remineralization of organic nitrogen by animals and bacteria. In addition, various marine prokaryotes are able to carry out a suite of reactions that move nitrogen in and out of the major inorganic pools. These include nitrogen fixation and dissimilatory transformations of nitrogen, such as nitrification, denitrification, and anaerobic ammonium oxidation (anammox) which has recently been recognized as a major sink for fixed inorganic nitrogen in oxygen minimum zones (e.g. Kuypers et al. 2003, 2005). The marine nitrogen cycle involves multiple inorganic and organic pools which are coupled by rapid biological transformations of nitrogen (cf. Chap. 6).

Since most marine autotrophs require combined nitrogen as a substrate for growth, the isotopic composition of dissolved inorganic nitrogen acts as a sort of master variable in setting the baseline isotopic composition of marine plankton. A number of biological processes may alter the isotopic composition of the marine pool of inorganic nitrogen. The most important are nitrogen fixation, nitrification, denitrification, and anaerobic ammonium oxidation, all of which may lead to a net transfer between the oceanic pool of combined nitrogen and the atmosphere. The basic biochemical reactions are the following:

Nitrogen fixation:

$$N_2 \text{ atm.} \Rightarrow \text{organic N} \qquad (10.14)$$

It is well known that symbiontic bacteria in the roots of plants, but also bacteria and algae in the ocean can fix nitrogen. The high energy needed to break the triple bond of the nitrogen gas molecule makes natural nitrogen fixation a process feasable by only few organisms.

Ammonification:

$$N_{org} \Rightarrow NH_4^+ \qquad (10.15)$$

Nitrification:

$$NH_4^+ + 3/2\ O_2 \Rightarrow NO_2^- + H_2O + 2\ H^+ \qquad (10.16)$$

$$NO_2^- + 1/2\ O_2 \Rightarrow NO_3^- \qquad (10.17)$$

Although ammonium is the direct product of decomposition of nitrogenous organic compounds (deamination), most inorganic nitrogen in the ocean occurs in the form of nitrate. Conversion of ammonia into nitrate is carried out by nitrifying organism.

Denitrification:

$$5\ (CH_2O) + 4\ NO_3^- + 4\ H^+ \Rightarrow 5\ CO_2 + 7\ H_2O + 2\ N_2 \qquad (10.18)$$

or Anammox:

$$NH_4^+ + NO_2^- \Rightarrow N_2 + 2\ H_2O \qquad (10.19)$$

After oxygen is exhausted, nitrate can serve as electron acceptor in the degradation of organic matter. Denitrification results in the conversion of nitrate to nitrogen gas and therefore balances the biological fixation of nitrogen. If there were no denitrification or anammox, atmospheric nitrogen would be exhausted in less than 100 million years. Denitrification and anaerobic ammonium oxidation occur in stratified or stagnant water masses of the ocean (e.g. within oxygen minimum layers) and in the sea bed.

The main processes involved in the biological utilization of nitrogen are all associated with kinetic fractionation effects, nevertheless they exhibit different fractionation factors. The isotope effect of nitrogen fixation (α = 1.000 to 1.004) is small relative to the effects of bacterial nitrification, denitrification, or anammox (α = 1.02 to 1.04) (see Montoya et al. 1994: Table 1). The results by Miyake and Wada (1971) indicate that little overall isotope fractionation occurs in the

bacterial mineralization of organic nitrogen. Equilibrium isotope exchange reactions, which commonly occur in nature, are the ammonia volatilization and the solution of nitrogen gas. The former process has a significant isotopic effect (α= 1.034), whereas the latter process induces only a small fractionation (α = 1.0008).

Modern Range of Values and Historical Variability

The isotopic composition of some important nitrogen compounds is summarized in Fig. 10.8. NO_3^- dominates the oceanic pool of dissolved inorganic nitrogen, and the available data indicate that the $\delta^{15}N$ of NO_3^- from oxygenated deep waters ranges between 3‰ and 7‰ with a mean value around 6‰ (Liu and Kaplan 1989). The $\delta^{15}N$ of NO_3^- is significantly higher than this mean in and around anoxic water masses where denitrification occurs (Liu and Kaplan 1989). For the eastern tropical North Pacific Ocean values as high as 18.8‰, for the western Caribbean Sea values up to 12‰ have been reported to occur within the active denitrification zone (Cline and Kaplan 1975).

On geological time-scales, the entire nitrogen cycle has to be considered to describe the factors controlling the nitrogen isotopic balance in the ocean. The major input of nitrogen compounds into the ocean results from precipitation, river discharge and the fixation of molecular nitrogen. Nitrogen is removed from the ocean mainly by burial in the sediment and denitrification. Although it is generally assumed that the nitrogen balance in the ocean is in a steady state, it is diffcult to estimate the budget for mass balance as well as for isotopic balance (for a review of estimates see Gruber and Sarmiento 1997). However, denitrification in the water column and in the sediment is the dominant process maintaining mass balance. It is also the only process that can produce a large fractionation. All other processes add or remove nitrogen compounds with $\delta^{15}N$ values mostly in the range between –2‰ and +8‰. Changes in the global rate of denitrification could therefore lead to significant changes in the $\delta^{15}N$ of marine NO_3^- , which in turn would affect the $\delta^{15}N$ of marine plankton, since the isotopic composition of the phytoplankton at the base of the food web depends at least in part on the $\delta^{15}N$ of the dissolved inorganic nitrogen available (Altabet and Curry 1989). Today, it appears that denitrification (and maybe also anammox; Kuypers et al. 2005) is the principal mechanism that keeps the marine nitrogen compounds at a higher $\delta^{15}N$ value than atmospheric nitrogen.

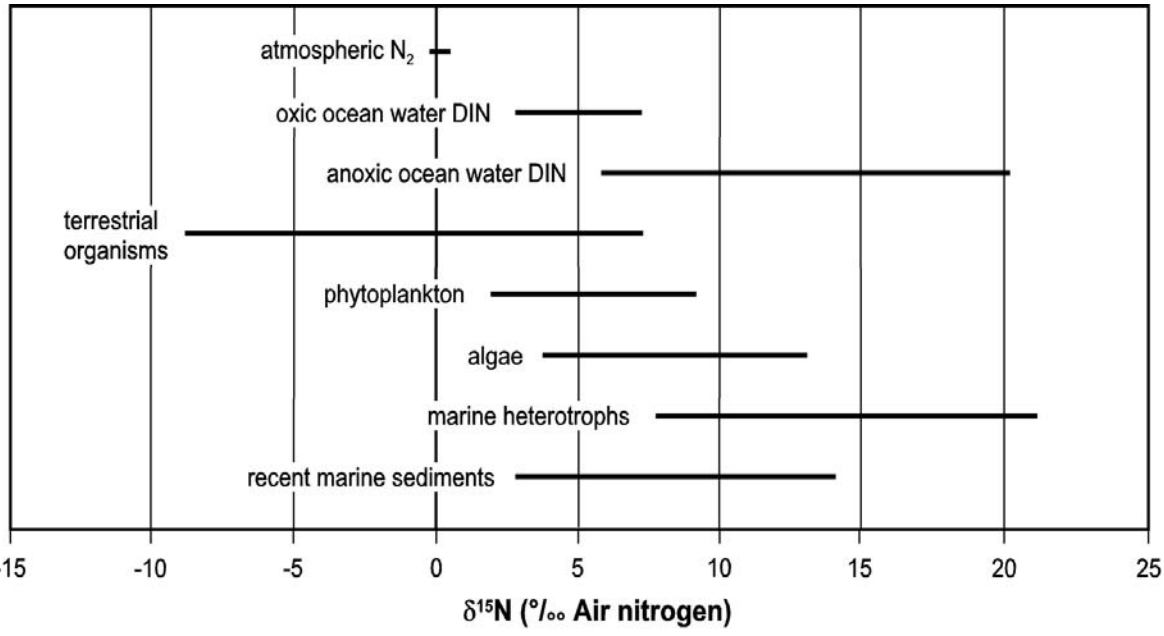

Fig. 10.8 $\delta^{15}N$ ranges of some important nitrogen compounds (according to Arthur et al. 1983).

10.5.2 $\delta^{15}N$ in Marine Organic Matter

Principles of Fractionation

The nitrogen isotopic composition of marine organic matter produced in the photic zone depends on the isotope ratio of nitrate and the degree to which this inorganic pool is utilized (Wada 1980; Altabet et al. 1991; Voss et al. 1996). The preferential uptake of $^{14}NO_3^-$ leads to a depletion of ^{15}N in organic matter relative to the dissolved inorganic nitrogen used as a substrate for growth (Montoya 1994). Subsequently, the remaining nitrogen pool becomes progressively enriched in ^{15}N according to Rayleigh fractionation kinetics (Cifuentes et al. 1988). The degree of isotopic fractionation associated with primary productivity varies between taxa and with growth conditions. Culture experiments suggest that diatoms may discriminate more strongly than flagellates (Wada and Hattori 1978). The ensuing transfer of nitrogen through trophic levels is associated with a systematic increase in $\delta^{15}N$, with each trophic step resulting in an enrichment of 3.5‰ (Montoya 1994). This effect, however, should not affect the bulk sedimentary $\delta^{15}N$ values because of mass balance considerations.

An important use of nitrogen stable isotope ratios is the reconstruction of the degree of nitrate utilization in surface waters at the time the organic matter was produced. The applicability of this tool in paleoceanographic studies has been shown repeatedly (e.g. Altabet and Francois 1994; Holmes et al. 1997; Freudenthal et al. 2001). To determine changes in the fraction of unutilized nitrate in surface waters, Altabet and Francois (1994) defined the following equations:

$$\delta^{15}NO_{3(f)}^- = \delta^{15}NO_{3(f=1)}^- - \varepsilon_u \cdot \ln(f) \quad (10.20)$$

$$\delta^{15}N\text{-}PN_{(f)} = \delta^{15}NO_{3(f)}^- - \varepsilon_u \quad \text{(instantaneous product)} \quad (10.21)$$

$$\delta^{15}N\text{-}PN_{(f)} = \delta^{15}NO_{3(f=1)}^- + f/(1-f) \cdot \varepsilon_u \cdot \ln(f) \quad \text{(accumulated product)} \quad (10.22)$$

where f is the fraction of unutilized NO_3^- remaining (i.e. $[NO_3^-]/[NO_3^-]_{initial}$), ε_u is the fractionation factor associated with the NO_3^- uptake, and $\delta^{15}N$-PN and $\delta^{15}NO_3^-$ refers to the measured $\delta^{15}N$ of the particulate nitrogen and of NO_3^-, respectively. The success of these equations in determining surface nitrate utilization depends on the estimation of the fractionation factor ε_u exhibited by phytoplankton during photosynthesis. The magnitude of ε_u sets an upper limit to the amplitude in $\delta^{15}N$ observed. ε_u may be obtained from the slope of the regression line between the photosynthate $\delta^{15}N$ (routinely, sedimentary $\delta^{15}N$ is used) and $\ln[NO_3^-]_{surface}$. A limited number of culture experiments with marine phytoplankton have shown significant variations in ε_u between phylogenetic groups (1‰ to 9‰) and growth conditions (0‰ to 16‰; Montoya 1994). Field estimates of ε_u in regions of moderate to high nitrate concentrations in the open ocean have fallen within a narrower range of 5‰ to 9‰ (Altabet and Francois 1994). At 90% utilization of NO_3^-, this latter range in ε_u corresponds to an increase of 12‰ to 21‰ in $\delta^{15}N$.

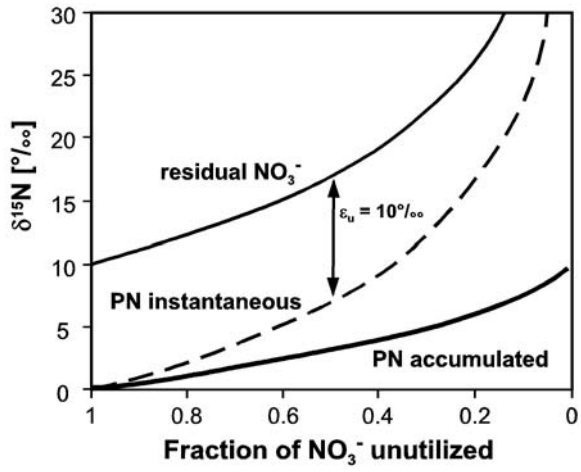

Fig. 10.9 Effects of nitrate utilization (assuming an ε_u of 10 ‰) on the $\delta^{15}N$ of the residual nitrate (solide line; Eq. 10.19), the instantaneous product (broken line; Eq. 10.20) and the accumulated product (heavy line; Eq. 10.21) of a reaction (according to Altabet and Francois 1994).

$[NO_3^-]_{initial}$ is the nitrate concentration of newly upwelled water or surface waters before the onset of springtime productivity. Equation 10.20 underscores that changes in $\delta^{15}N$ are in reality a function of nitrate utilization and not simply concentration per se. Equation 10.21 refers to particulate nitrogen produced at any one point in the course of reaction (instantaneous product) (Fig.10.9). Observations would fit Equation 10.21, only if particulate nitrogen is rapidly removed from the system. On the other hand, if there is no

removal of particulate nitrogen from the system, the change of $\delta^{15}N$ within this accumulating pool is described by Equation 10.22, the integral of Equations 10.20 and 10.21. However, this latter case almost never occurs (Altabet and Francois 1994).

A topic of much concern regarding the application of bulk $\delta^{15}N$ in paleoceanographic investigations is the effect of terrestrially derived organic matter on the marine $\delta^{15}N$ signal. Since terrigenous material is mostly substantially depleted in ^{15}N relative to marine-derived matter, the nitrogen isotopic composition of ocean sediments have been used to trace the origin of sedimentary nitrogen (Sweeny and Kaplan 1980; Wada et al. 1987). However, the underlying assumption regarding the mixing of a marine and terrestrial $\delta^{15}N$ end members is not always conclusive because of the wide range of $\delta^{15}N$ values produced in terrestrial systems (Sweeney et al. 1978). Furthermore, marine values may be subject to changes produced by processes in the water column (as discussed above).

Diagenesis

Reconstructing past variations of nutrient conditions in surface waters requires the preservation of the nitrogen isotope surface-water signal in the sedimentary organic matter. Diagenesis, however, may significantly alter the nitrogen isotopic composition of particles even before they are buried at the seafloor. Altabet and McCarthy (1985) suggested that bacterial remineralization of sinking particles resulted in a ^{15}N enrichment in the residual organic matter. Francois et al. (1992) reported a ^{15}N enrichment of 5‰ to 7‰ in core top values of Southern Ocean sediments compared to measurements of organic matter in the photic zone. However, Altabet and Francois (1994) demonstrated that there was only little offset between sinking particles at 150 m water depth in the equatorial Pacific and the respective core tops. Sigman et al. (1999) suggested that the difference in preservation of the isotopic signal existent in the two regions may be explained with the high opal content in the Southern Ocean sediments, in which organic matrices with high $\delta^{15}N$ may be captured. In any case, the findings of these authors suggest that where differences between the surface-generated signal and sediments exist, the offset appears to be relatively constant within geographic regions.

Further decomposition of organic matter occurs at the sediment/water interface and in the upper sections of the sediment. However, observations from equatorial Pacific sediments indicate that the loss of organic carbon as well as of nitrogen in the uppermost few millimeters is not accompanied by a corresponding shift in $\delta^{15}N$ over this depth interval (Altabet and Francois 1994). Freudenthal et al. (2001) found that early diagenesis in sediments of the eastern tropical Atlantic led to variability in $\delta^{15}N$ of even less than 1‰. With further diagenesis of organic matter, nitrogen may occur as ammonium incorporated in the lattice of clay minerals, where it replaces potassium. But even this complex substitution is not associated with an isotopic effect, since this nitrogen exhibits an isotopic composition very similar to the organic matter from which it is derived (Williams 1995). Therefore, beside the possible fractionation mechanisms, which may alter the nitrogen isotopic composition of organic matter in the water column, there seems to be no significant diagenetic alteration of the isotope signal within the sediments. The nitrogen isotopic composition of sediments is primarily determined by the source organic matter.

10.6 Geochemical Influences on ^{34}S / ^{32}S Ratios

10.6.1 $\delta^{34}S$ of Seawater and Pore Waters

Principles of Fractionation

In the marine environment, sulfur occurs most commonly in its oxidized form as dissolved sulfate in seawater or as precipitated sulfate in evaporites and in its reduced form as sedimentary pyrite. The ratio of $^{34}S/^{32}S$ is a sensitive indicator for the

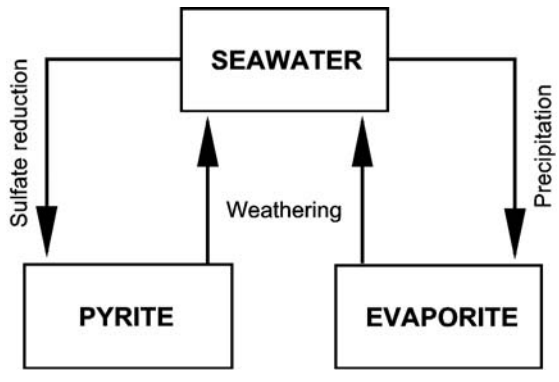

Fig. 10.10 Main reservoirs of the sedimentary sulfur cycle (adopted from Strauss 1997).

transfer of sulfur between the different reservoirs, which is often associated with a change in the oxidation state of the element. The main processes to be considered in the sulfur cycle are the riverine input of sulfate as a weathering product of sulfur-bearing rocks, the precipitation of evaporites from seawater and the biological reduction of seawater sulfate and subsequent formation of sedimentary pyrite (Fig. 10.10). The associated fractionation mechanisms are therefore:

- isotope exchange reactions between sulfate and sulfides
- kinetic isotope effects in the bacterial reduction of sulfate or in the oxidation of sulfides

Only a small fractionation is associated with the precipitation of sulfates in seawater. Theoretical considerations as well as sulfur-isotope measurements in natural environments revealed an isotopic difference between seawater sulfate and crystallized gypsum of 0 to +2.4‰ (Raab and Spiro 1991). Therefore, within the generally observed variability in an evaporitic deposit, calcium sulfate is assumed to record the isotopic composition of seawater sulfate at the time of deposition (Claypool et al. 1980; Strauss 1997).

By far the largest fractionation is associated with the bacterial sulfate reduction (see a recent review by Canfield 2001). Due to the activity of sulfate-reducing bacteria, such as *Desulfovibrio desulfuricans*, organic matter is oxidized according to the following equation:

$$2\,(CH_2O) + SO_4^{2-} \Rightarrow H_2S + 2\,(HCO_3^-) \qquad (10.23)$$

The resulting hydrogen sulfide reacts with sedimentary iron, which is available in the reactive non-silicate bond form (oxy-hydroxydes), and is fixed as iron sulfide (e.g. pyrite). In general, a substantial depletion of $\delta^{34}S$ occurs due to preferential utilization of the ^{32}S-isotope by the sulfate reducing bacteria. Whereas the fractionation

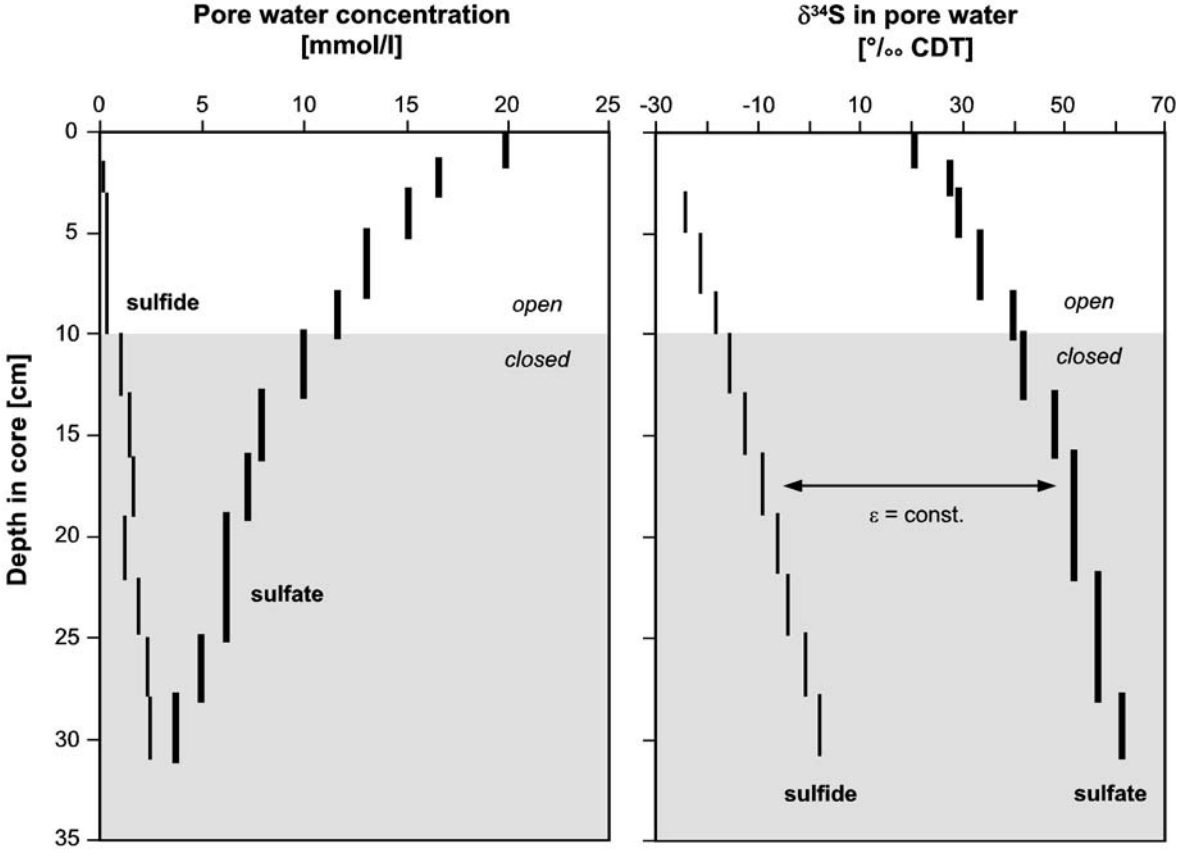

Fig. 10.11 Variation of sulfate and sulfide concentration and $\delta^{34}S$ values of pore water in core 2092 from the western Baltic Sea (Hartmann and Nielsen 1969).

is small during the entrance of sulfate into the cell (-3 to 0‰), the subsequent breaking of the S-O bonds is causing a large change in the isotope composition of the reactants (SO_4^{2-} => SO_3^{2-} : 22‰, SO_3^{2-} => H_2S: up to 18‰; see Canfield 2001). As a result, sedimentary sulfide is depleted in ^{34}S relative to ocean water sulfate (Kaplan and Rittenberg 1964). The depletion is usually in the order of 20‰ to 70‰ (Hartmann and Nielsen 1969; Ohmoto 1990), although cultural experiments yielded only depletions between 10‰ and 30‰, with a maximum reported value of 49‰ (Kaplan and Rittenberg 1964; Bolliger 2001). The much larger fractionation ocurring under natural conditions may be generated by a concurrent recycling of H_2S via an intermediate oxidation to elemental sulfur or thiosulfate by buried Fe(III) and a disproportionation of these intermediates to SO_4^{2-} and H_2S (Jørgensen 1990; Habicht and Canfield 1997). The disproportionation shunts produce ^{34}S-enriched SO_4^{2-} and ^{34}S-depleted H_2S and thereby increase the resulting isotopic difference between SO_4^{2-} and H_2S in the sediment pore water (for a recent discussion see Canfield 2001).

The extent of depletion during bacterial sulfate reduction is affected by the magnitude of reduction rates and by the availability of sulfate. Generally, an increasing rate of sulfate reduction leads to a decrease in fractionation. Furthermore, if the availability of sulfate is reduced, e.g. through limited diffusion in non-bioturbated or impermeable sediments, the isotopic composition of both reactant and product shifts towards higher values. Such a Rayleigh fractionation process has been shown by Hartmann and Nielsen (1969) for dissolved sulfate and sulfide in the pore water of a core retrieved from the western Baltic Sea (Fig. 10.11). The $\delta^{34}S$-values of both reactant and product increase with depth, because the two isotopes in sulfate or in sulfide do not diffuse in the same proportion as they occur in the pore water (Jørgensen 1979).

Fractionation also occurs during processes in the oxidative part of the sulfur cycle. Sulfide oxidation, which is pervasive in marine environments (for example, 90% or more of the sulfide produced during sulfate reduction in coastal sediments are reoxidized) includes various processes, which are all associated with inverse isotope fractionation effects. These processes include the phototrophic oxidation by a variety of anoxygenic bacteria (-2 to 0‰), the non-phototrophic oxydation (up to -18‰), and the already mentioned disproportionation of sulfur compounds with intermediate oxidation states as elemental sulfur or thiosulfate (up to -33 ‰) (Canfield 2001).

Modern Range of Values and Historical Variability

The isotopic composition of sulfur in modern ocean sulfate is constant within very narrow limits and is represented by a $\delta^{34}S$-value of +20‰ with a standard deviation of ±0.12‰ (Longinelli 1989). The small isotopic range over a great variety of localities and at various depths is explained with the residence time of sulfate in the ocean which is well in excess of the ocean mixing time (Holland 1978). This sulfate homogeneity should be considered for the evaluation of isotope data analyzed in ancient deposits.

The sulfur isotopic composition in oceanic sulfate through Phanerozoic time shows a Cambrian maximum of about +30‰, a decrease to a Permian minimum of about +10‰ and an increase towards the modern ocean value of +20‰ (Claypool 1980; Strauss 1997). Superimposed over this long-term secular variation is a pronounced short-term variability exhibiting about the same isotopic range as documented for the entire Phanerozoic. The observed variations are assumed to reflect changes in the sulfur redox cycle within the ocean. Since bacterial sulfate reduction and the subsequent formation of sedimentary pyrite is associated with a substantial fractionation, any changes in the isotopic mass balance are generally interpreted as changes in the burial of reduced sulfur. Furthermore, both the rate of sulfur input and its isotopic composition may vary as a function of time depending on the weathering rates of different sedimentary rocks, or on the intensity of volcanic activity. For example, increased erosion of black shales containing ^{34}S-depleted sulfides may lower the $\delta^{34}S$ value of oceanic sulfate. On the other hand, the increased reduction of sulfate by bacteria and removal of ^{34}S-depleted sulfide from the ocean may increase its $\delta^{34}S$ value. However, the fact that the deposition of evaporites in the Phanerozoic history occurred in rather short episodes raises the question about the validity of the sulfate isotope curve with respect to representativeness and homogeneity. The specific causes for the variation of $\delta^{34}S$ of marine sulfate at a particular geologic time interval are still largely speculative (for further discussion see Strauss 1997).

A special case in the modern ocean sulfur isotope distribution is the isotopic composition of hydrogen sulfide in anoxic basins. Fry et al. (1991) compared depth profiles of the Black Sea and the

Cariaco Basin. Sulfide isotopic compositions in deep waters of the Black Sea were roughly constant near –41.5‰, while those of the Cariaco Trench averaged –31‰. In contrast, in the uppermost 50 m of the Black Sea's sulfidic waters (that is in water depths between 100 and 150m) the sulfide isotopic compositions change significantly in a region of sulfide consumption, increasing up to 5‰ vs. the deep-water background. These increases may be due to sulfide oxidation mediated by MnO_2 or oxygen, but are not consistent with sulfide oxidation by photosynthetic bacteria (Fry et al. 1991). Growth experiments with sulfate-reducing bacteria suggested that part of the increase in sulfide isotopic compositions could be attributed to rapid rates of sulfate reduction in the oxic/anoxic interface region.

10.6.2 $\delta^{34}S$ in Marine Sediments

Evaporitic Sulfate

The general aspects of isotopic fractionation during the evaporation of sulfates have been addressed in the previous section. Due to a minor fractionation during precipitation, marine evaporitic sulfates are assumed to reflect the original seawater signature. However, exceptions might occur in sulfates precipitated during late stages of evaporation. Sulfur isotope measurements from the Permian Zechstein in Germany (e.g. Nielsen and Ricke 1964) and experiments by Raab and Spiro (1991) indicate that sulfate deposited within the halite or even the potash-magnesia facies is depleted in ^{34}S in comparison to sulfate precipitated within the calcium sulfate facies. Progressive crystallization of ^{34}S-enriched sulfate minerals results in a residual brine depleted in ^{34}S, by possibly as much as 4‰. Therefore, to obtain a true record of seawater sulfate isotopic composition in the past no late-stage sulfates should be included.

Sedimentary Pyrite

Modern sedimentary pyrites are generally depleted in ^{34}S relative to ocean water sulfate with average $\delta^{34}S$-values around –20‰ and a range between +20‰ and –50‰. The majority of isotopic compositions of pyrites in modern sediments indicate the sedimentary sulfides having formed through bacterial sulfate reduction under open system conditions with respect to sulfate availability. These measurements agree well with experimental data as discussed above. However, higher values have been reported for pyrites formed under anoxic bottom-water conditions like in the Black Sea (Vinograd et al. 1962; Lyons and Berner 1992). They are interpreted to result from an open-system diagenesis combined with the effect of differential diffusion (Jørgensen et al. 2004).

During Earth history, the isotope fractionation between contemporaneous seawater sulfate and sedimentary reduced sulfur compounds like pyrite increases (Shen et al. 2001). With a few exceptions, sulfur isotope fractionations seem to have been negligible during the Archean but increased during the Proteozoic, presumably as a consequence of increased oceanic sulfate concentrations (Habicht et al. 2002). In sediment deposits younger than about 800 Myr, as in modern anoxic systems like the Black Sea, sulfur fractionations often exceed what appears to be the maximum reached during sulfate reduction in surface sediments as well as in cultures of sulfate reducers, as has been mentioned above. The isotope record for sedimentary sulfides of Phanerozoic age shows a much higher variability than observed for marine sulfates (Strauss 1997). Beside a long-term trend with a Cambrium maximum of about +2 ‰, a Permian to Cretaceous minimum around –30 ‰ and an increase to about –10 ‰ to –20 ‰ in the modern ocean sediments, there is a considerable variation as high as 80 ‰ within a single sedimentary unit. The observed range clearly reflects that in addition to the factors which control the sulfate isotopic composition in ancient seawater, changes in the geochemical conditions during sulfate reduction and pyrite formation may affect the $d^{34}S$ of sulfides. For example, changing bottom-water conditions (oxic to anoxic and vice versa) during the time of deposition may alter the conditions for pyrite formation. The amount of pyrite formed in sediments is known to be limited by (1) the amount of metabolizable organic matter (2) the amount of sulfate and (3) the amount of reactive iron. Under normal marine conditions, the amount of organic matter limits the reduction process (Raiswell and Berner 1986). This is documented in a positive correlation of organic carbon and pyrite sulfur through geologic history (Berner and Raiswell 1983). In anoxic environments, reactive iron appears to be the limiting factor for pyrite formation, since the amount of H_2S exceeds its removal by the reaction with iron (Raiswell and Berner 1985).

In that case, some H_2S diffuses back to the sediment surface, where it is reoxidized, whereas some H_2S undergoes further reactions. All these processes are associated with different fractionation effects on the sulfur isotopic composition of sulfides.

In addition to these primary, syngenetic effects, the isotope variability may reflect the diagenetic history of the sediments with a progressive evolution from early to late diagenetic sulfides (i.e. framboids to concretions or overgrowth). In summary, due to the large number of processes that might affect the isotopic composition of sulfides, their potential for interpreting features of the Phanerozoic sulfur cycle appears to be rather limited (Strauss 1997).

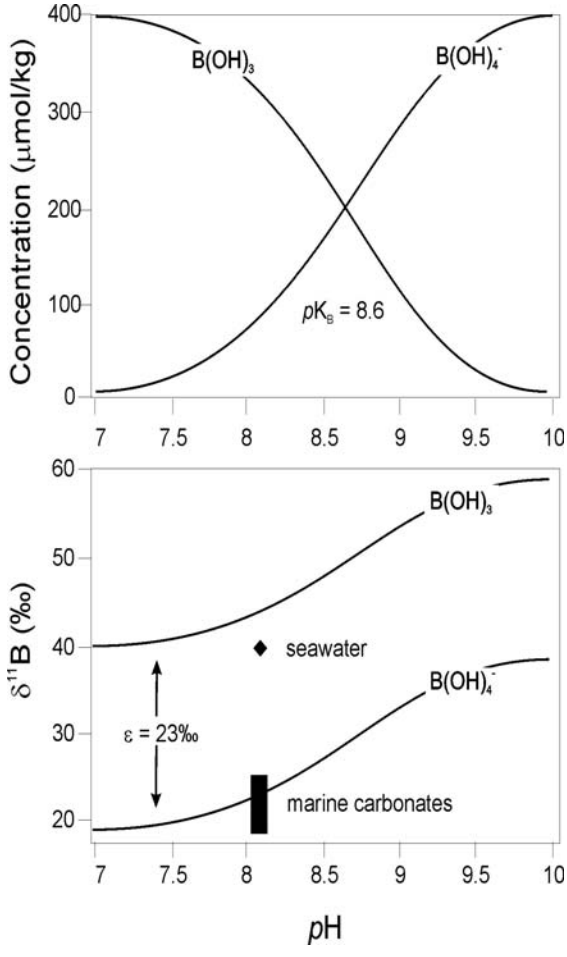

Fig. 10.12 Relative abundance of boron acid and borate in seawater, and their isotopic composition versus pH (according to Hemming and Hanson 1992).

10.7 Geochemical Influences on ^{11}B / ^{10}B Ratios

10.7.1 $\delta^{11}B$ of Seawater and Pore Waters

Principles of Fractionation

In ocean water, boron occurs in two dominant species, boric acid $B(OH)_3$ and borate $B(OH)_4^-$. The relative concentration of these two species is pH dependent such that the boric acid $B(OH)_3$ is dominant at pH < 9.0, whereas the tetrahedral complex of $B(OH)_4^-$ dominates at pH >9.0 (Fig.10.12; Hemming and Hanson 1992). The principal process that causes fractionation of boron isotopes in aqueous solutions is the following exchange reaction:

$$^{10}B(OH)_3 + {}^{11}B(OH)_4^- \Leftrightarrow {}^{11}B(OH)_3 + {}^{10}B(OH)_4^- \qquad (10.24)$$

In seawater, $B(OH)_3$ is enriched in ^{11}B compared to $B(OH)_4^-$ by 23‰ at 25°C (Kakihana et al. 1977). Consequently, as the relative concentration of the dissolved species changes with pH, also their isotopic composition changes, but with a constant offset (Fig. 10.12).

Modern Range of Values and Historical Variability

The $\delta^{11}B$ value of modern ocean water is constant at about 40‰, relative to average continental material like the borax at Searles Lake, California, which serves as a standard reference material for boron isotope analyses (see Tab. 10.1).The ^{11}B enrichment of seawater is explained with the preferential absorption of $^{10}B(OH)_4^-$ by hydrothermally altered basalts of the oceanic crust, by clay-rich marine sediments, and by the precipitation of carbonate minerals (e.g., Hemming and Hanson 1992). Typical values for geologically important reservoirs summarized by Hoefs (2004) range between -2 to +10‰ for (altered) oceanic basalts, -18 to +20‰ for clay-rich sediments, and +18 to +35‰ for marine evaporites. Varying $\delta^{11}B$ values in geologic history might reflect changes in the relative contribution of boron from different reservoirs, especially due to selective erosion of rocks or enhanced production and alteration of fresh marine basalts, or by changes in the oceanic pH value in the past (see separate paragraph below).

10.7.2 $\delta^{11}B$ in Marine Carbonates

Principles of Fractionation

Diverse biogenic and inorganic marine carbonates record boron isotopic compositions close to the boron isotopic composition of $B(OH)_4^-$ at modern seawater pH. Therefore, Hemming and Hanson (1992) suggested that it is the charged borate species that is preferably incorporated into marine carbonates. This interpretation has been confirmed by a number of empirical calibration studies on inorganic calcium carbonates (Hemming et al. 1995; Sanyal et al. 2000), corals (Hönisch et al. 2004; Reynaud et al. 2004), and planktonic foraminifers (Sanyal et al. 1996; Sanyal et al. 2001) over a wide range of culture water pH. Although biogenic carbonates and even inorganic-precipitated calcite show $\delta^{11}B$ offsets of up to 4‰ relative to the theoretical borate curve, all empirical calibration curves follow the shape of the theoretical curve and therefore support the validity of the calculated isotope fractionation factor by Kakihana et al. (1977) (cf. Fig. 10.13).

However, the causes for these offsets are yet not completely understood. Culture experiments using living planktonic foraminifers (Hönisch et al. 2003) and numerical modeling experiments (Zeebe et al. 2003) identified physiological processes, such as symbiont photosynthetic activity, respiration and calcification, to be important. These processes influence the pH in the microenvironment of foraminifers and corals, and lead to specific offsets relative to seawater pH. Because the observed offsets between different carbonate producers are constant across the pH-range investigated, it is likely that the boron isotope fractionation related to these physiological processes is not influenced by the varying pH itself. Nevertheless, an important consequence resulting from these observations is the effect on shell precipitation during the life cycle of foraminifers. $\delta^{11}B$ data measured in different shell size classes of the symbiont-bearing planktonic foraminifer species *Globigerinoides sacculifer* showed a significant increase of $\delta^{11}B$ with increasing shell size (Hönisch and Hemming 2004), which could only be explained by a deeper growth habitat of smaller shells, where symbiont photosynthetic activity is reduced because of lower light levels. In addition to the original shell size effect, Hönisch and Hemming (2004) discovered that partial shell dissolution significantly lowers $\delta^{11}B$. Because of the greater dissolution susceptibility of smaller shells the diagenetic effect on $\delta^{11}B$ was even more pronounced in shells of decreasing shell size (Fig. 10.14).

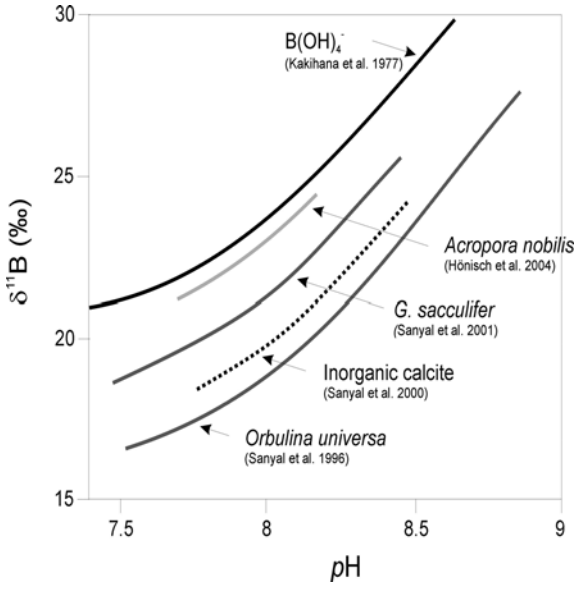

Fig. 10.13 Empirical $\delta^{11}B$ calibrations of laboratory precipitated inorganic calcite and cultured biogenic carbonates vs. pH.

Application as a paleo-pH proxy

One of the first studies that the boron isotopic composition in planktonic foraminifera shells reflects climate driven changes in marine carbonate chemistry was provided by Sanyal et al. (1995), who demonstrated an approximately 0.2 unit higher pH in the Last Glacial Maximum surface water compared to today. Other surface ocean boron isotope studies estimated the strength of modern and past upwelling areas in the Holocene and late Pleistocene. In a comparative study of the northwest African and eastern equatorial Pacific upwelling zones Sanyal and Bijma (1999) proposed that the eastern equatorial Pacific upwelling system was a significantly larger source of CO_2 to the atmosphere during the last glacial period compared to the eastern Atlantic upwelling zone. Similarly, Palmer and Pearson (2003) reconstructed surface water pH and aqueous pCO_2 in the western equatorial Pacific over the past 23 ky and suggested that this area was a strong source of CO_2 to the atmosphere during the last deglaciation.

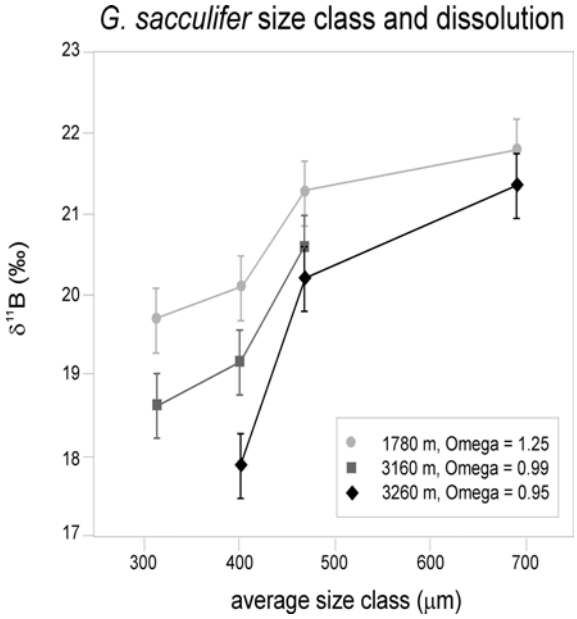

Fig. 10.14 $\delta^{11}B$ of symbiont-bearing planktonic foraminifer species from core-top samples at the different water depth on the Ontong Java Plateau, western equatorial Pacific (Hoenisch and Hemming 2004). Ω values indicate the carbonate saturation with respect to calcite at different sites.

Although still limited in their spatial coverage, the studies cited above provide strong support for using the boron isotope pH proxy to evaluate the role of different ocean parts to estimate past sources and sinks of CO_2 to the atmosphere. However, the application of the boron isotope proxy in mixed benthic foraminifera species for deep ocean pH reconstruction led to some doubt, because it suggested a 0.3 units higher glacial pH (i.e., +2.5‰ in $\delta^{11}B$) compared to modern deep water pH (Sanyal et al. 1995), which is not corroborated by sedimentary records of glacial calcite preservation suggesting no significant change in deep ocean carbonate ion concentration and pH. But this too large increase in pH was most probably due to the use of mixed benthic species instead of a single species, only (B. Hoenisch, pers. comm.).

Pearson and Palmer (2000) extended the $\delta^{11}B$ application to the Paleogene and estimated a pH of 7.4 and corresponding pCO_2 values higher than 2000 ppmv for the early Eocene time period. However, several uncertainties may limit the confidence in their interpretation, because of the residence time of boron in the ocean of only 3-5 million years (Lemarchand et al. 2000) and the use of extinct foraminifer species without a significant crosscalibration against modern species. So far, such records need to be interpreted with caution, and considerable efforts will have to be made to improve confidence in pre-Quaternary reconstructions.

Acknowledgements

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10.8 Problems

Problem 1

Antarctic and Greenland ice sheets store today about 2 % of the ocean water mass with an average $\delta^{18}O$ value of -45‰. What would be the $\delta^{18}O_w$ value of an ice-free world?

Problem 2

A number of authors have proposed that the 0.3‰ lower $\delta^{13}C$ mean ocean value during the last glacial maximum (about 21000 years ago) resulted from an increased erosion of organic carbon from terrigenous soils and shelf sediments during a drop in sea-level as a result of continental glaciation. Assuming an oceanic carbon mass of 38,000 Gt and an average $\delta^{13}C$ value of terrestrial organic carbon of -25‰, calculate the transfer of organic carbon from the terrestrial to the oceanic reservoir necessary to explain the carbon isotope shift. Is the result realistic? What other explanations would be reasonable?

Problem 3

Given the range of b-values (equation 10.9) between 80 and 160 ‰µM as derived from South Atlantic core tops (Schulte et al. 2003), what would be its effect on atmospheric pCO_2 assuming an ε_p of 12‰, an enzymatic fractionation ε_f of 25‰, and a solubility coefficent $\alpha = 0.032$ at 20°C?

Problem 4

Seasonal $\delta^{15}N$ values of particulate organic matter collected in a sediment trap off Namibia varied between 3‰ at the end of spring and 8‰ during mid fall. Applying the principles of Rayleigh fractionation to the nitrate utilization in ocean surface water (eq. 10.22), what is the range of nitrate utilization assuming an initial $\delta^{15}NO_3$ value of 10‰ and an ε_u of 10‰? How to interpret those data in terms of seasonal changes in productivity?

Problem 5

Last glacial boron isotope composition of planktonic foraminifers has been shown to be 2‰ higher compared to the modern value of 23‰. What is the result for surface ocean pH during the last glacial? What happened to the carbonate ion concentration and consequently to atmospheric pCO_2 assuming the ΣCO_2 to be the same as today (see chapter 9)?

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