

# Stable Isotopes in Foraminiferal Carbonate

Steve Cooke and Eelco J. Rohling

School of Ocean and Earth Science, University of Southampton,  
Southampton Oceanography Centre, Southampton SO14 3ZH, UK.  
(S.Cooke@soc.soton.ac.uk)

## Abstract

Analyses of stable oxygen and carbon isotopes from foraminiferal shells have played a pivotal role in palaeoceanography since Emiliani (1955) interpreted the isotopic record from deep-sea cores as a series of Pleistocene climate/temperature cycles.

Oxygen isotope stratigraphy has become a global correlation tool, and an established dating tool. The primary ice-volume control on (benthic) oxygen isotope records has led to their use in the approximation of past sea level variations after calibration with studies of other sea level indicators.

Downcore  $\delta^{13}\text{C}$  variations are used in studying water mass movement and palaeoproductivity, and connections between climatically induced changes in the terrestrial biosphere with observed carbonate dissolution cycles and the flux of dissolved  $\text{CO}_2$  in the oceans.

We review and summarise the fundamental controls on  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in foraminiferal carbonate. Several have only recently been discovered, and we aim to offer a state-of-the-art overview with pointers to relevant specialist literature, to facilitate evaluation of the palaeoceanographic value of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ .

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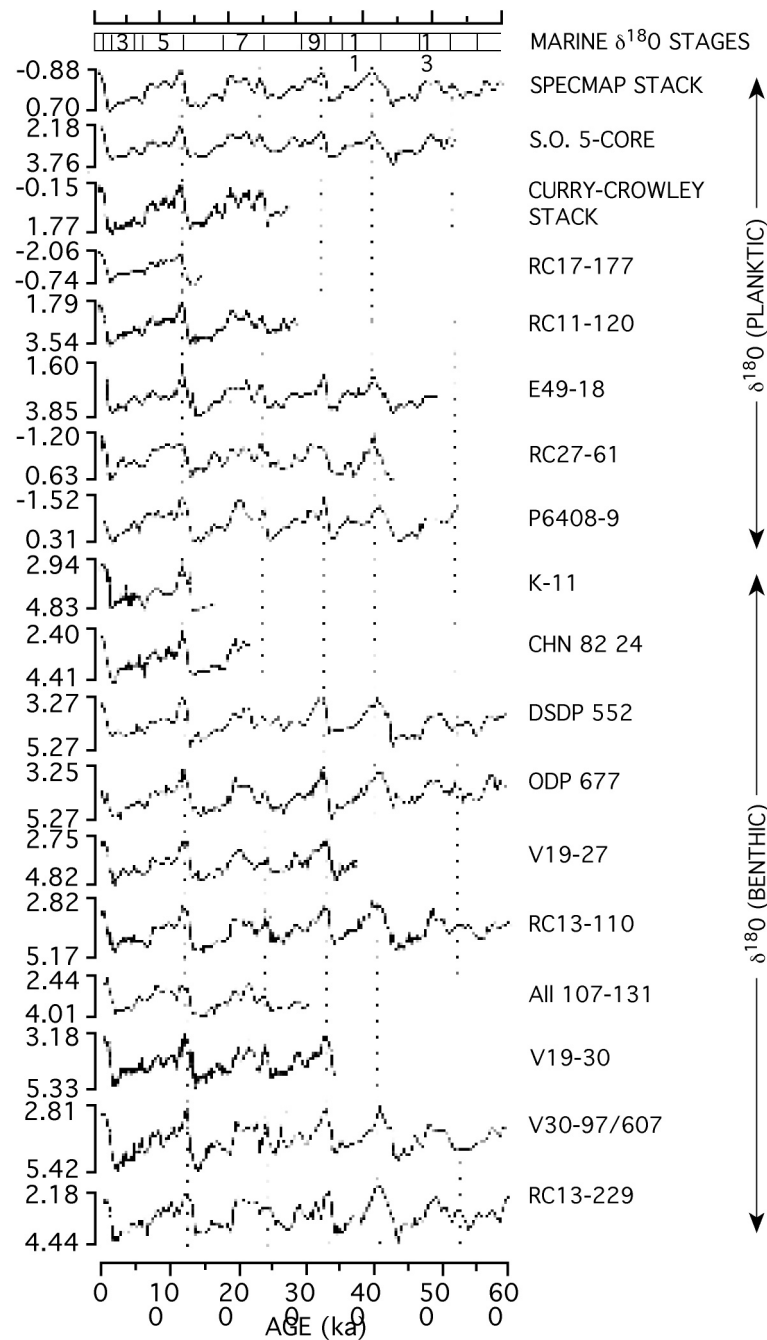
#### 1. Introduction

Analyses of stable oxygen and carbon isotopes from foraminiferal shells have played a pivotal role in palaeoceanography since the pioneering efforts of Emiliani (1955) who - building on work of Urey (1947), McCrea (1950) and Epstein *et al.* (1953) - interpreted the isotopic record from deep-sea cores as a series of Pleistocene climate/temperature cycles. Cores from various locations in the Atlantic, Pacific and Indian Oceans provided isotopic records showing similar trends. Shackleton and Opdyke (1973) correlated the isotope stratigraphy with magnetic stratigraphy, dating 22 recognisable isotopic stages. Analysing not only records for planktonic Foraminifera, but also for deep-sea benthic Foraminifera - which avoid the noise imposed by short-term temperature and salinity fluctuations - Shackleton and Opdyke (1973) demonstrated that the  $\delta^{18}\text{O}$  signal predominantly reflects fluctuations in global ice volume, while temperature plays a secondary role. This discovery started widespread use of  $\delta^{18}\text{O}$  records in global stratigraphic correlations (*e.g.*, Imbrie *et al.*, 1984; 1992). Turning attention to downcore  $\delta^{13}\text{C}$  variations, Shackleton (1977a) showed their potential significance in studying water mass movement and palaeoproductivity, and postulated a connection between climatically induced changes in the terrestrial biosphere with observed carbonate dissolution cycles and the flux of dissolved  $\text{CO}_2$  in the oceans.

Detailed age control for  $\delta^{18}\text{O}$  records around the world has been established by stacking a great number of records in various ways to form a global curve for comparison with models of astronomically forced ice volume fluctuations (*cf.* Imbrie *et al.*, 1984; Pisias *et al.*, 1984; Prell

*et al.*, 1986; Martinson *et al.*, 1987; Imbrie *et al.*, 1992). Consequently, oxygen isotope stratigraphy has become not only a global correlation tool, but also an established dating tool (Figure 1). In addition, the primary ice-volume control on (benthic) oxygen isotope records has led to their use in the approximation of past sea level variations after calibration with studies of other sea level indicators (*e.g.*, Chappell and Shackleton, 1986; Shackleton, 1987; Bard *et al.*, 1996; Linsley, 1996; Rohling *et al.*, 1998).

**Figure 1.** Overview of oxygen isotope records from various locations world-wide, illustrating the global correlation potential and dating through recognition of Marine Isotope Stages and correlation of these and specific events to a standard chronology (modified after Imbrie *et al.*, 1992). For location map and further details about the cores, see Imbrie *et al.* (1992).



### **1.1. Natural abundance and physico-chemical behaviour**

Oxygen and carbon exist in nature in various stable isotopic species. There are three stable isotopes of oxygen:  $^{16}\text{O}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$ , with relative natural abundances of 99.76%, 0.04% and 0.20%, respectively. Because of the higher abundances and the greater mass difference between  $^{16}\text{O}$  and  $^{18}\text{O}$ , research on oxygen isotopic ratios normally concerns  $^{18}\text{O}/^{16}\text{O}$  ratios. Carbon occurs as two stable isotopes:  $^{12}\text{C}$  and  $^{13}\text{C}$ , with relative natural abundances of 98.89% and 1.11%, respectively.

Comprehensive introductions on stable isotopes and their physico-chemical behaviour are given in Craig and Gordon (1965), Garlick (1974), Gonfiantini (1986), and Hoefs (1997). Here, we summarise aspects relevant to the subsequent discussion of mechanisms of change in stable O and C ratios in the marine environment, as recorded in foraminiferal carbonate.

The word isotope (Greek, meaning ‘equal places’) implies that the various isotopes occupy the same position in the Periodic Table. The difference between the atomic masses of the isotopic species for each element consists of a different amount of neutrons in the nucleus. The carbon isotope  $^{12}_6\text{C}$  for example contains 6 protons and 6 neutrons, giving it an atomic mass of 12 (NB, the mass of this carbon isotope serves as a reference standard for all atomic weights). The isotope  $^{13}_6\text{C}$  contains 6 protons and 7 neutrons.

All isotopes of a given element contain the same number and arrangement of electrons, and so broadly display similarity in their chemical behaviour, were it not that the mass differences of different isotopes impose differences in their physico-chemical properties. The mass differences are particularly important in light elements (low numbers in the Periodic Table). Molecules vibrate with a fundamental frequency which depends on the mass of the isotopes from which it is composed. The resultant differences in dissociation energy of the light and heavy isotopes imply that bonds formed by light isotopes are weaker than those formed by heavy isotopes. Hence, as a rule-of-thumb, molecules comprised of the light isotopes react somewhat more easily than those comprised of the heavy isotopes.

Partitioning of isotopes between substances with different isotopic compositions has been named ‘fractionation’. The fractionation factor ( $\alpha$ ) quantifying isotopic fractionation between two substances A and B is defined as  $\alpha = R_A/R_B$ . Here,  $R_A$  and  $R_B$  are the heavy/light ratios between the abundances of any two isotopes (e.g.  $^{18}\text{O}/^{16}\text{O}$ ) in the exchanging chemical compounds A and B, respectively. Fractionation mainly results from: (1) isotopic exchange reactions; and (2) kinetic effects. Isotopic exchange reactions concern partitioning of isotopes between phases that are in equilibrium, and are therefore also known as ‘equilibrium isotope fractionation’ processes. Processes of equilibrium fractionation are essentially temperature dependent. Kinetic effects cause deviations from the simple equilibrium processes due to different rates of reaction for the various isotopic species (due directly to vibration differences, or indirectly through differences in bonding energies). Important kinetic effects are associated with diffusion. Detailed accounts on equilibrium and kinetic fractionation may be obtained from Craig *et al.* (1963), Craig and Gordon (1965), Ehhalt and Knott (1965), Merlivat (1978), Merlivat and Jouzel (1979), Garlick (1974), Stewart (1975), Gonfiantini (1986), Knox *et al.* (1992), Hoefs (1997), and references therein.

### **1.2. Analysis of stable O and C isotopes**

The stable isotopes of oxygen and carbon in carbonates are analysed by mass spectrometric determination of the mass ratios of carbon dioxide ( $\text{CO}_2$ ) obtained from the sample, with reference to a standard carbon dioxide of known composition. The  $\text{CO}_2$  is produced by reaction of the carbonate with phosphoric acid:  $\text{CaCO}_3 + \text{H}_3\text{PO}_4 \rightleftharpoons \text{CaHPO}_4 + \text{CO}_2 + \text{H}_2\text{O}$ , usually using a process approximating the technique of McCrea (1950).

A mass spectrometer separates a charged molecular mixture according to mass, using the motions of the molecules in a magnetic or electric field. Most isotope geology mass spectrometers have evolved from the original design by A.O. Nier, and for carbonate analysis, a dual inlet magnetic sector mass spectrometer (or isotope ratio mass spectrometer, IRMS) is most commonly used. The major components of the IRMS are: (1) the analyser consisting of ion source, flight tube and collector system; (2) a differential pumping system to maintain a vacuum within the analyser; (3) the dual inlet; (4) a carbonate preparation apparatus to generate CO<sub>2</sub> for analysis.

*The Analyser:* The ‘heart’ of the IRMS consists of an ion source which produces a ‘beam’ of mono-energetic ions from the sample gas, a flight path which passes through a permanent magnetic field, and a collector system which collects spatially separated components of the beam. The ion source is designed to be at a pressure some 100 times higher than the analyser and its function is to impart energy to the maximum number of incoming neutral gas molecules. Individual molecules are first given an electric charge by stripping them of single electron, a process known as ionisation. The charged molecules are then given a precise amount of energy (in the form of momentum) by an electric field, and ‘shot’ into a magnetic field, where they follow curved paths dependent on their mass. For efficient separation, there must be efficient transmission of ionised species through the source, while the collectors must experience the beams as if they had originated from a point source, to ensure they enter the collectors effectively. This object point must be at the object plane of the mass spectrometer. These factors effect the sensitivity and peak shape respectively. Assuming perfect focusing by the IRMS, whatever is at the object plane will be reproduced at the collector split into m/z units. In reality, no mass spectrometer is capable of perfect focusing owing to effects such as energy spread, magnetic fringe fields and pole face shape. Parameters therefore have to be adjusted to yield the best possible performance. The position of the ion source is fixed in relationship to the flight tube, and so the object plane is fixed. The only means of shifting the object plane is by use of the magnet.

After passing through the magnetic field, the separated ‘beams’ of molecules are collected in Faraday ‘bucket’ collectors. The beams are, in effect, a flow of current (an electrical current is defined as a flow of charge, usually electrons). This is of the order of 10<sup>-9</sup> Ampere for a common isotope, and a head amplifier converts this into a low impedance voltage output. By collecting two or three ion beams of the isotopes (for CO<sub>2</sub>, the isotopes collected are of masses 44, 45, and 46 amu) simultaneously, the ratio of the currents can be measured directly, thus obtaining greater precision. The ratios are calculated by the software controlling the IRMS.

*Differential Pumping System:* In order for molecules to travel anywhere at all, the probability of them colliding with other molecules must be low; *i.e.* the ‘mean free path’ between collisions must be high. If measurable separation is to be achieved, then the molecules must be enclosed in a system operating at pressures no higher than 10<sup>-6</sup> mbar, *i.e.* a vacuum (mean distances between molecules increase as pressure is reduced). Two stages of pumping are needed to achieve this level of vacuum: a turbo-molecular pump (high-speed turbine) provides the ultimate vacuum at the analyser, but the outlet of this must be held below 10<sup>-3</sup> mbar. A multi-stage rotary vane pump provides this ‘roughing vacuum’. In order to monitor the operation of the pumping system, a vacuum gauge is normally mounted close to the throat of the high vacuum pump. Penning or Pirani gauges, which work on the basis that the electrical conductance of a gas varies with pressure, are commonly used.

*The Dual Inlet:* The dual inlet was devised as a means of ensuring that both sample and reference gases are presented to the analyser at the same pressure, and handled in the same way. While one is flowing into the ion source, the same amount of the other is being pumped to waste, ensuring that flow conditions remain the same for both sample and reference. This allows the continuing alternating measurement of sample and reference necessary to attain precise and reproducible ratios. The ion currents of sample and standard are balanced by varying the size of

the gas reservoirs using stepper motors. Very small samples may be isolated outside the variable volume reservoir and the beam currents balanced using only the reference reservoir.

*Carbonate Preparation System:* There are two main approaches to generating CO<sub>2</sub> from carbonates automatically and on-line (*i.e.* attached to the IRMS), the common acid bath, and the individual acid bath. In the common acid bath method, samples are dropped into an aliquot of phosphoric acid, and the products are continuously removed during the reaction. After the completion of one reaction, the same acid is used to react the next sample. To decrease reaction times and reduce ‘memory’ between samples, temperatures as high as 90°C are used, accompanied by stirring to reduce the amount of CO<sub>2</sub> retained in the acid.

In the individual acid dosing or ‘drip’ method, a small amount of acid is allowed to drip onto the sample, and the product is frozen out. The samples are loaded into individual reaction vessels, which in turn are placed in a carousel. Each sample is analysed sequentially. The vessel is evacuated and a predetermined dose of phosphoric acid is dispensed. While the sample is reacting the evolved CO<sub>2</sub> is frozen onto a dedicated cold finger, positioned close to the mass spectrometer inlet, to minimise sample transfer time. Water is removed during the reaction by passing the CO<sub>2</sub> through a loop that is maintained at –80°C.

### 1.3. Conventional notation: delta values and per mille deviations

While the absolute abundances of minor isotopes (such as <sup>18</sup>O and <sup>13</sup>C) cannot be determined accurately, it is still possible to get quantitative results by comparing the result given for a known external standard with that for the unknown sample. These differences in isotope ratios, known as δ-values, are defined as:

$$\delta_{sam} = \frac{R_{sam} - R_{std}}{R_{std}} \times 1000$$

where *sam* is the sample value and *std* is the standard or reference value. These variations in composition are given in delta (δ) notation, and are reported in parts per thousand (per mille, ‰). So, for example, δ<sup>13</sup>C ‰ = (<sup>13</sup>C/<sup>12</sup>C<sub>sample</sub>) - (<sup>13</sup>C/<sup>12</sup>C<sub>std</sub>) / (<sup>13</sup>C/<sup>12</sup>C<sub>std</sub>) × 1000. A positive δ value indicates enrichment in the heavy isotope, relative to the standard, and conversely, depletion is shown by a negative δ value.

### 1.4. Standards

The standard commonly used for both oxygen and carbon in carbonates is referred to as PDB (Pee Dee Belemnite), having δ<sup>18</sup>O = 0, and δ<sup>13</sup>C = 0 by definition (Epstein *et al.*, 1953). The PDB standard (not now available) is a guard from *Belemnitella americana*, a Cretaceous belemnite from the Pee Dee Formation in North Carolina, U.S.A., and not, as is variously reported, the acid-liberated CO<sub>2</sub> (Friedman and O’Neil, 1977).

Various international standards have been run against PDB for comparative purposes. Two are commonly used and distributed by National Institute of Standards and Technology (NIST) in the U.S.A., and the International Atomic Energy Agency (IAEA) in Vienna. They are: NBS-18 (carbonatite), for the analysis of carbonates with δ<sup>13</sup>C and δ<sup>18</sup>O isotope ratios stated in per mille difference from Vienna Pee Dee Belemnite (VPDB) or Vienna Standard Mean Ocean Water (VSMOW), respectively; and NBS-19 (limestone), for the δ<sup>13</sup>C and δ<sup>18</sup>O isotope ratio analysis of carbonates, and is used to define the VPDB scale (Coplen, 1988; 1994). The isotopic compositions of these reference materials, as given by NIST (1992) are listed in Table 1.

To convert VPDB to VSMOW, use δ<sup>18</sup>O<sub>VSMOW</sub> = 1.03092 δ<sup>18</sup>O<sub>VPDB</sub> + 30.92 (Coplen *et al.* 1983; NIST, 1992).

**Table 1.** Isotopic compositions (in ‰) of reference materials (National Institute of Standards and Technology, 1992).

	$\delta^{13}\text{C}_{\text{VPDB}}$	$\delta^{18}\text{O}_{\text{VPDB}}$	$\delta^{18}\text{O}_{\text{VSMOW}}$
NBS-18	-5.04	-23.05	17.16
NBS-19	1.95	-2.20	28.65

Some further corrections are needed. The IRMS measures two ratios: the mass 45/44 ratio ( $\delta 45$ ), and the mass 46/44 ratio ( $\delta 46$ ), these being the three isotopic masses collected and measured in the analyser. However, the final results required are the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  ratios relative to the VPDB standard, and a correction for  $^{17}\text{O}/^{18}\text{O}$  must also be applied. The corrections used in these equations below, after Craig (1957), do almost the final calculation:

$$\delta^{13}\text{C}_{\text{VPDB}} = (1.067544 \times \delta 45) - (0.03600782 \times \delta 46)$$

$$\delta^{18}\text{O}_{\text{VPDB}} = (1.000966 \times \delta 46) - (0.00206322 \times \delta^{13}\text{C}_{\text{VPDB}})$$

Thus, the enrichment or depletion of the sample, relative to VPDB may be determined. These equations are valid only when differences between the sample and standard are small (<10‰) as it is only in this range that some correction factors can be ignored.

A further complication is that there is a fractionation effect between the  $\delta^{18}\text{O}$  in calcite and in the  $\text{CO}_2$  produced by reaction with phosphoric acid, which is a function of the temperature at which that reaction takes place, and to an extent on the dissolution technique. Hence, there needs to be a correction applied to the  $\delta^{18}\text{O}$  ratio obtained to allow for this temperature effect. The fractionation factor for O ( $\alpha$ ) is defined as  $\alpha = (\delta^{18}\text{O})_{\text{carbonate}} / (\delta^{18}\text{O})_{\text{CO}_2}$  and can be determined by experiment to suit the technique being used to generate the  $\text{CO}_2$ . There does not appear to be a similar fractionation effect on carbon (Swart *et al.*, 1991).

### 1.5. This paper

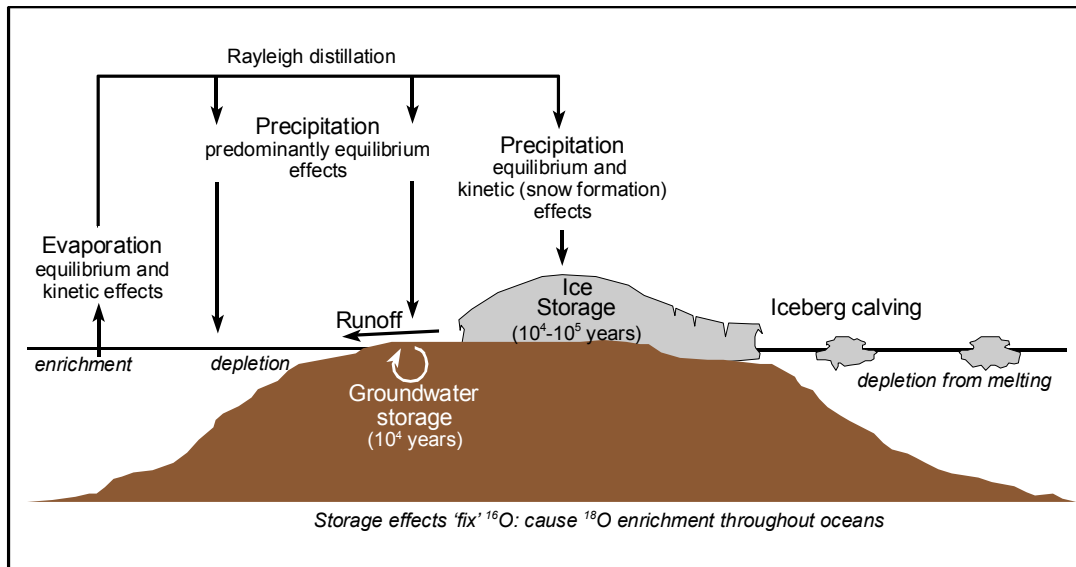
Major contributions of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  to palaeoceanography in the applied sense are captured in Emiliani (1955), Shackleton and Opdyke (1973), Shackleton and Kennett (1975), Savin *et al.* (1975), Shackleton (1977a,b), Keigwin (1979), Savin *et al.* (1981), Duplessy *et al.* (1984), Imbrie *et al.* (1984), Vergnaud-Grazzini (1985), Chappell and Shackleton (1986), Kennett (1986), Berger and Labeyrie (1987), Shackleton (1987), Woodruff and Savin (1989), Savin and Woodruff (1990), Imbrie *et al.* (1992), Zachos *et al.* (1994), Sarnthein *et al.* (1995), and are reviewed in, for example, Haq (1984), Kennett (1985), Crowley and North (1991), Frakes *et al.* (1992), and Broecker (1995). We, instead, review the fundamental controls on  $\delta^{18}\text{O}$  (*section 2*) and  $\delta^{13}\text{C}$  (*section 3*) in foraminiferal carbonate. Several have only recently been discovered, and we aim to offer a state-of-the-art overview with pointers to the relevant specialist literature. Since isotope ratios in carbonates to a great extent reflect those in the ambient water, each section first evaluates the processes governing  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in seawater and then those causing fractionation during carbonate formation. To facilitate evaluation of the palaeoceanographic value of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , *section 4* summarises the various controls and highlights analytical strategies to minimise complications.

## 2. Oxygen Isotopes

### 2.1. Oxygen isotope ratios in sea water

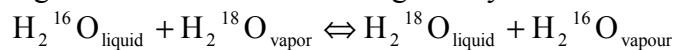
The oxygen isotope ratio of sea water is intimately linked with fractionation-processes within the hydrological cycle. Schematically, this cycle comprises of evaporation, atmospheric vapour transport, precipitation and subsequent return of freshwater to the ocean (directly via precipitation and via runoff/iceberg melting). Long-term storage of freshwater in aquifers and especially ice-sheets is important for sea water isotope ratios as well (**Figure 2**). Formation and melting of seasonal sea ice imposes strong local variability. Finally, the spatial distribution of oxygen isotopes in the world ocean depends on processes of advection and mixing of water masses from different source regions with different isotopic signatures.

**Figure 2.** Schematic presentation of the hydrological cycle influences on oxygen isotope ratios. Effects on seawater are described in italics.



#### 2.1.1. Evaporation

The isotopic exchange at the sea-air interface is given by:



Molecules composed of lighter isotopes have higher vapour pressures and the lighter molecular species are therefore preferentially enriched in the vapour phase. The fractionation factor for the equilibrium exchange is  $\alpha_{l-v} = [^{18}\text{O}/^{16}\text{O}]_l / [^{18}\text{O}/^{16}\text{O}]_v$ . The most commonly used relationship between  $\alpha_{l-v}$  and temperature during evaporation is that given by Majoube (1971):

$$\alpha_{l-v} = \exp. \{ (1.137 \text{ T}^{-2}) \times 10^3 - (0.4156 \text{ T}^{-1}) - 2.0667 \times 10^{-3} \}$$

where T is in Kelvin. This relationship illustrates a decrease in fractionation with increasing temperature. The fractionation causes a difference between  $\delta^{18}\text{O}$  of sea water and  $\delta^{18}\text{O}$  of vapour evaporated from that sea water equal to  $\delta^{18}\text{O}_l - \delta^{18}\text{O}_v = 10^3 \ln(\alpha) \text{ ‰}$ . At a temperature of  $20^\circ\text{C}$  this difference amounts to about 9.8 ‰. The equilibrium enrichment factor  $\epsilon$  is defined as  $\epsilon = \alpha - 1$ , and is often reported as a ‰ value. For  $\alpha = 1.010$ ,  $\epsilon = 10 \text{ ‰}$ .

Craig and Gordon (1965) argued that after the primary equilibrium fractionation, further fractionation should have occurred to explain their observations of stronger depletions in vapour than expected from equilibrium fractionation only. Gonfiantini (1986) summarised the arguments



of Craig and Gordon (1965), ascribing the further depletion to kinetic effects during molecular diffusion within the boundary layer between the water-air interface and the fully turbulent region (where no further fractionation occurs). Within that boundary layer, diffusion predominates because of slow atmospheric transport (Ehhalt and Knott, 1965; Stewart, 1975). Gonfiantini (1986) elaborated how the kinetic enrichment factor ( $\Delta\epsilon$ ) for oxygen isotopes depends on the relative air humidity ( $h$ ) in the turbulent region outside the boundary layer, giving a relationship for most natural circumstances of  $\Delta\epsilon = 14.2(1-h)\text{‰}$ , where  $h$  is presented as a fraction (*i.e.* 0.7 means 70% relative humidity). Since diffusion rates depend on property-gradients, the final isotopic composition of newly evaporated water also depends on the isotopic composition ( $\delta^{18}\text{O}_{\text{atm}}$ ) of vapour already present in the turbulent region of the atmosphere, and on  $\delta^{18}\text{O}$  of the surface water (Gonfiantini, 1986):

$$\delta^{18}\text{O}_E = \frac{1}{1-h+\Delta\epsilon} \left( \frac{\delta^{18}\text{O}_{\text{SeaSurface}} - \epsilon}{\alpha} - h\delta^{18}\text{O}_{\text{atm}} - \Delta\epsilon \right)$$

Note that  $\delta^{18}\text{O}$ ,  $\Delta\epsilon$ , and  $\epsilon$  values, normally reported in‰, are to be used in true form, *i.e.* value  $\times 10^{-3}$ .

Merlivat and Jouzel (1979), in addition, argue that there may be a step-wise factor two decrease in the kinetic fractionation factor related to a change from a ‘smooth’ to a ‘rough’ water-atmosphere interface. As this transition would occur around near-surface mean wind-speeds of  $7\text{ m s}^{-1}$ , most areas in the world ocean would, on the long term, be in the ‘smooth’ domain. The potential impact of this ‘roughness’ effect should however be borne in mind in settings where the threshold wind speed may have been persistently exceeded (*e.g.* Rohling, 1994).

The preferential uptake of the lighter isotope during evaporation causes  $\delta^{18}\text{O}$  enrichment in the remaining surface waters. The effect may be underestimated when only equilibrium fractionation is taken into account. However, the influences of kinetic fractionation are predominantly related to relative air humidity and surface roughness, both of which are extremely hard to assess for past (even relatively recent) geological periods. In the bulk of geological studies, it may therefore be best to consider only equilibrium fractionation, and use considerations of possible changes in kinetic fractionation to determine confidence-intervals.

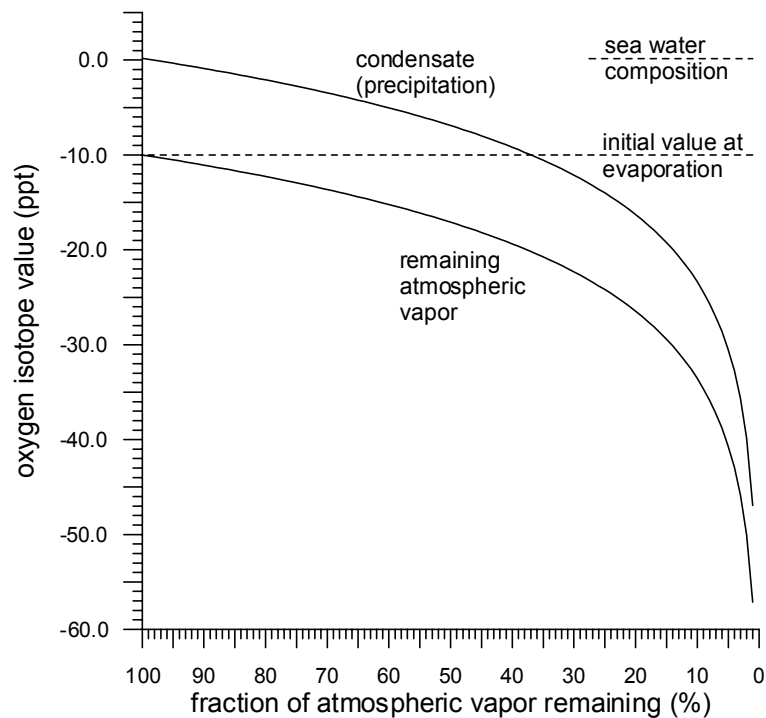
### 2.1.2. Precipitation and Atmospheric Vapour transport

Fractionation processes during the formation of droplets are basically the same as during evaporation, but work in the opposite sense. Stewart (1975) argued that, during condensation of droplets, kinetic fractionation could play a role, but concludes that it is usually negligible so that droplets normally are near equilibrium with atmospheric vapour. A main cause for the absence of significant kinetic fractionation during condensation is the fact that relative humidity is 100% (Ehhalt and Knott, 1965). The equilibrium fractionation factor for condensation is the same as that for evaporation and may therefore be determined with Majoube’s (1971) equation for the appropriate temperature, and then used in  $\delta^{18}\text{O}_l - \delta^{18}\text{O}_v = 10^3 \ln(\alpha)\text{‰}$  to determine the isotopic composition of the droplets for any given atmospheric vapour composition.

Since condensation preferentially removes the heavier isotope  $^{18}\text{O}$ , the  $\delta^{18}\text{O}$  of the remaining atmospheric vapour becomes progressively more depleted. Relative to an original atmospheric vapour composition that is given by the composition of evaporated water ( $\delta^{18}\text{O}_E$ ), the isotopic composition of the atmospheric vapour ( $AV$ ) is approximated by  $\delta^{18}\text{O}_{AV} = \delta^{18}\text{O}_E + 10^3(\alpha-1)\ln f$  (Dansgaard, 1964; Garlick, 1974), where  $\alpha$  is the fractionation factor at condensation temperature and  $f$  is the fraction of atmospheric vapour remaining after rain-out (*e.g.* 0.7 if 70% of the evaporated water remains as atmospheric vapour due to 30% rain-out). The isotopic composition of precipitation formed in equilibrium with the atmospheric vapour is found according to  $\delta^{18}\text{O}_P - \delta^{18}\text{O}_{AV} = 10^3 \ln \alpha$ . From these relationships, which represent a basic

Rayleigh distillation process, it is immediately obvious that the first precipitation will be of a similar isotopic composition as the original sea water, and that a longer pathway from the source region (and consequently more rain-out) causes atmospheric vapour to become more-and-more depleted. New precipitation from this vapour reflects this depletion (**Figure 3**). As a result, precipitation is significantly more depleted at high latitudes than in the tropics (reaching values as low as  $-57\text{‰}$  in Antarctica; Lorius, 1983; Rozanski *et al.*, 1993).

**Figure 3.** The relationships between isotopic composition of atmospheric vapour and precipitation relative to evaporation with an original composition of  $-10\text{‰}$  and fractionation at constant temperature of  $15^{\circ}\text{C}$ .



The magnitude of rain-out is strongly temperature dependent. As atmospheric vapour is transported towards colder regions, it experiences successive condensations. This effect - rather than temperature dependence of the fractionation factor - determines the basic quasi-linear relationship of  $0.69\text{‰ }^{\circ}\text{C}^{-1}$  between  $\delta^{18}\text{O}$  of precipitation and temperature, as has been observed for temperatures between  $-40$  and  $+15^{\circ}\text{C}$ . Above  $15^{\circ}\text{C}$ , this relationship with temperature breaks down. There, mainly in areas with strong convection in the atmosphere, the so-called 'amount effect' dominates. This effect approximately determines a  $1.5\text{‰}$  depletion in the  $\delta^{18}\text{O}$  of precipitation for every 100 mm increase in rainfall (Dansgaard, 1964; Rozanski *et al.*, 1993; Joussaume and Jouzel, 1993; Hoffmann and Heimann, 1997).

The above summarises only the main influences on the  $\delta^{18}\text{O}$  of precipitation and atmospheric vapour. For more complete accounts - including processes associated with snow-formation, re-evaporation of droplets below cloud-base, and isotopic variations within individual meteorological events as recorded in hailstones - the reader is referred to specialised sources, such as Dansgaard (1964), Craig and Gordon (1965), Jouzel *et al.* (1975), Stewart (1975), Merlivat and Jouzel (1979), Rozanski *et al.* (1982; 1993), Hoefs (1997), Hoffmann and Heimann (1997), and references therein.

The changes in oxygen isotope composition of atmospheric vapour and precipitation affect surface waters in the world ocean through addition of freshwater via precipitation directly on to the sea surface, or via run-off. Whereas arid, evaporative areas will demonstrate especially the

evaporative surface water  $\delta^{18}\text{O}$  enrichment, regions in reasonable proximity to a river mouth will be affected by the volumetrically weighted average isotopic composition of precipitation over the rivers catchment area. A high latitude river system imports freshwater with generally lower  $\delta^{18}\text{O}$  values than those of a low latitude river - for example, the average (pre-Aswan dam) Nile river  $\delta^{18}\text{O}$  composition was near  $-2\text{‰}$ , whereas the Arctic McKenzie river discharges waters with a composition around  $-20\text{‰}$  (see overview in Rohling and Bigg, 1998).

There are two main ‘delayed’ responses that need to be taken into account. Both result from long-term storage of precipitation. Besides run-off from rivers, icebergs calving from continental ice sheets also provide a source of ‘continental’ freshwater. Icebergs import into the ocean a ‘fossil’ isotopic signature depending on the age of the calving ice. Since ice cores in the Greenland and Antarctic Ice Sheets penetrate ice aged well over 100,000 years (Lorius *et al.*, 1985; Taylor *et al.*, 1993; Grootes *et al.*, 1993; Jouzel *et al.*, 1993) to even 400,000 years (Petit *et al.*, 1997), the isotopic signatures of bergs shed by those ice sheets should not be considered as a result of the present-day freshwater cycle. Similarly, but much less importantly, fossil waters may accumulate in aquifers and at a much later stage contribute to river discharge into the oceans, thus causing deviations from the isotopic compositions of rivers expected from precipitation in the catchment basin. Fossil ground waters may be as old as 35,000 years (*e.g.* Rozanski, 1985).

### 2.1.3. Long-term ‘storage’ – glacial ice-volume

Apart from delayed return of ‘fossil’ isotopic signals back into the ocean, long-term storage systems, such as glacial ice sheets and - to a much lesser extent - major aquifers, may also affect the global  $\delta^{18}\text{O}$  balance. Because the time-scales of storage (of order  $10^4$  to  $10^5$  years) exceed those of ocean ventilation (of order  $10^3$  years), the modification of ocean water  $\delta^{18}\text{O}$  due to these storage effects will be mixed throughout the ocean and, therefore, prevail both at the surface and at depth.

The main influence is related to the volume of glacial ice sheets. These are built up by high latitude precipitation (snow) at very low temperatures towards the end of the Rayleigh distillation process (**Figure 2**), and so record extremely depleted  $\delta^{18}\text{O}$  values (**Figure 3**). The resultant preferential sequestration of  $^{16}\text{O}$  in ice sheets leaves the oceans enriched in  $^{18}\text{O}$ . At the same time, build-up of ice volume lowers global sea level. Research on  $\delta^{18}\text{O}$  changes in fossil carbonate, with accurate constraint of sea level variations from fossil coral reef studies, illustrates that the relationship between sea level lowering and mean oceanic  $\delta^{18}\text{O}$  enrichment approximates  $0.012 \pm 0.001\text{‰ m}^{-1}$  (Aharon, 1983; Labeyrie *et al.*, 1987; Shackleton, 1987; Fairbanks, 1989).

The above relationship provides a sound working model for a well matured ice sheet, but it should be noted that the processes behind it may invoke a more non-linear relationship for growing or recently matured ice sheets. Ice sheets go through a cycle of growth (young), equilibrium (mature) and decay. Mature ice sheets are mass-balanced: ice accumulates at the surface, then flows from the surface to the bottom and out to the edges, where it is shed through iceberg calving. Precipitation reaching the summit of a recently ‘matured’ ice sheet may therefore be significantly more depleted in  $\delta^{18}\text{O}$  than that lost from the edges at the same time, which concerns ice deposited when the ice sheet was much ‘younger’ (smaller/lower with higher temperatures than over the mature ice sheet). Therefore, an ice sheet may be mass-balanced, but not yet isotopically balanced. After a significant lag ( $>10^4$  years), the ice reaching the edges will be that built up on a mature ice sheet, and the isotopic composition of accumulating and calving ice will be more-or-less the same; only then will the ice sheet have reached isotopic balance (Mix and Ruddiman, 1984).

#### 2.1.4. Sea ice freezing and melting

The  $\delta^{18}\text{O}$  of newly formed sea ice is  $2.57 \pm 0.10$  ‰ enriched relative to that of sea water (Macdonald *et al.*, 1995). Although this is a small offset compared with the massive salinity difference between sea water ( $S$  usually  $> 30$  ‰) and sea ice ( $S \approx 20$  ‰; Cox and Weeks, 1974), the isotopic difference still imposes a major seasonal fluctuation associated with ice formation and melting (cf. Strain and Tan, 1993). It is tempting to assume that such seasonal influences would cancel out in the long term, but Rohling and Bigg (1998) pointed out that increases in surface water salinity due to sea ice formation may lead to convection and transport of existing surface waters into the ocean interior. The removed surface waters would be replaced by surface waters that were not (as much) affected by freezing processes, and when the sea ice subsequently melts the isotopic effect would not cancel out. Rohling and Bigg (1998) illustrated the compounded effects with two simple examples, demonstrating that great errors may arise from overlooking the effects of freezing and melting when interpreting records of oxygen isotopic change near (present-day or past) sea-ice margins.

#### 2.1.5. Advection

Advection and mixing of water masses from different source areas is a very important factor in determining the basic  $\delta^{18}\text{O}$  composition observed at any site. Each ‘source area’ concerns a basin or region - which may be very remote from the study site - where surface waters are ‘imprinted’ with a certain  $\delta^{18}\text{O}$  composition, through action of the freshwater cycle, freezing/melting of sea ice, etc. This ‘pre-set’ isotopic composition may be considered as a virtually conservative property for the newly formed watermass, as long as this watermass does not come into contact with sinks or sources of  $\delta^{18}\text{O}$ , notably the freshwater cycle. In practice, therefore,  $\delta^{18}\text{O}$  may be used as a conservative tracer for transport (advection) and mixing of watermasses in the subsurface ocean (e.g. Weiss *et al.*, 1979; Fairbanks, 1982; Paren and Potter, 1984; Kipphut, 1990; Frew *et al.*, 1995).

A mixing endmember receives a  $\delta^{18}\text{O}$  composition resulting from the volumetrically weighted averaged  $\delta^{18}\text{O}$  compositions of its components:  $\delta^{18}\text{O}_{\text{endmember}} = (A \delta^{18}\text{O}_A + B \delta^{18}\text{O}_B + C \delta^{18}\text{O}_C)/(A + B + C)$  where  $A$ ,  $B$ , and  $C$  are the volumes of three mixing components and  $\delta^{18}\text{O}_A$ ,  $\delta^{18}\text{O}_B$ , and  $\delta^{18}\text{O}_C$  are their isotopic compositions, respectively. Any change in relative proportions or the individual ‘pre-set’ isotopic compositions of the various mixing components would, therefore, affect the basic isotopic composition of the mixing endmember. Any change in isotopic composition must therefore be viewed within the broader context of water mass formation and mixing on ocean-wide scales, instead of being purely ascribed to local changes in surface forcing (e.g. freshwater budget). Rohling and Bigg (1998) presented simple analytical arguments to illustrate the importance of these hitherto ‘ignored’ processes, and particularly emphasised that the impact of completely re-arranged ocean circulation during glacial periods on the global  $\delta^{18}\text{O}$  distribution should be assessed with realistic coupled ocean-atmosphere-isotope models. Schmidt (1998) performed such an exercise for the modern ocean, confirming the importance of advective processes. Both studies call for caution when interpreting past  $\delta^{18}\text{O}$  variations, since - after the necessary correction for ice volume effect - surface water forcing processes of both local (direct) and remote (through advection and mixing) origin need to be accounted for. This contrasts with the classical palaeoceanographic interpretation in terms of only local processes.

## 2.2. Oxygen isotope ratios in foraminiferal carbonate

There are several processes which determine the oxygen isotope composition of newly formed foraminiferal carbonate. First, equilibrium fractionations between water and the various carbonate species ( $\text{CaCO}_3$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ) determine an important temperature influence on the  $\delta^{18}\text{O}$  of foraminiferal carbonate. In addition, several processes cause deviations from simple equilibrium, both in planktonic Foraminifera (e.g. Shackleton *et al.*, 1973; Fairbanks and Wiebe, 1980; Duplessy *et al.*, 1981; Bouvier-Soumagnac and Duplessy, 1985) and in benthic Foraminifera (e.g. Duplessy *et al.*, 1970; Woodruff *et al.*, 1980; Vincent *et al.*, 1981; Wefer and Berger, 1991). McConnaughey (1989a) considered  $\delta^{13}\text{C}$  deviations from equilibrium to be due to both ‘metabolic’ (or ‘vital’) and kinetic effects (see *section 3*), while  $\delta^{18}\text{O}$  deviations from equilibrium would be due only to kinetic effects. Wefer and Berger (1991) reviewed data for a wide variety of calcareous organisms, and concluded that this likely was an oversimplification. Here, we first discuss equilibrium fractionation for  $\delta^{18}\text{O}$  and then the four main identified causes for deviations from equilibrium.

### 2.2.1. Equilibrium fractionation

The overall reaction involved in the precipitation of carbonate is:  $\text{Ca}^{2+} + 2\text{HCO}_3^- \rightleftharpoons \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ . For the range of 0 to 500°C, O’Neil *et al.* (1969) determined that the equilibrium fractionation factor  $\alpha_{\text{c-w}}$  between calcite and water ( $\alpha_{\text{c-w}}$ ) changes with temperature according to:  $\alpha_{\text{c-w}} = \exp\{(2.78T^{-2}) \times 10^3 - 3.39 \times 10^{-3}\}$  where  $T$  is in Kelvin. Harmon and Schwarcz (1981) use a slightly different equation with the last coefficient at  $2.89 \times 10^{-3}$  rather than  $3.39 \times 10^{-3}$ .

The overall effect of equilibrium fractionation is a roughly 0.2 ‰ depletion in carbonate  $\delta^{18}\text{O}$  for every 1°C temperature increase, although Kim and O’Neil (1997) presented a more detailed relationship where the  $\delta^{18}\text{O}$  change with temperature is more pronounced at low temperatures (up to 0.25 ‰ °C<sup>-1</sup>) than at higher temperatures (around 0.2 ‰ °C<sup>-1</sup>). This temperature dependence fueled initiatives to develop ‘isotopic palaeothermometers’, or ‘palaeotemperature equations’ (e.g. Urey, 1947; McCrea, 1950; Epstein *et al.*, 1953; O’Neil *et al.*, 1969; Shackleton, 1974; Erez and Luz, 1983). A comprehensive summary of the various proposed Temperature: $\delta^{18}\text{O}$  relationships was presented by Bemis *et al.* (1998), who proposed new calibrations based on data from cultured Foraminifera. Observations were made for Foraminifera with and without symbionts, for different levels of irradiance (photosynthetic activity) and concentrations of the carbonate ion,  $[\text{CO}_3^{2-}]$ , since photosynthetic activity and  $[\text{CO}_3^{2-}]$  had previously been found to cause deviations from equilibrium fractionation in Foraminifera (Spero and Lea, 1993; Spero *et al.*, 1997).

Equilibrium fractionation between calcite and water is a function of temperature. Regarding planktonic Foraminifera, therefore, it is important to emphasize that several species may inhabit different depths at different ontogenic stages. Since temperature decreases with increasing depth in the surface oceans, vertical migrations will influence equilibrium fractionation. Many species show an increase in  $\delta^{18}\text{O}$  values with growth that would appear to fit with calcification in progressively deeper, colder, waters (among others, Emiliani, 1954; Berger, 1971; Emiliani, 1971; Berger *et al.*, 1978; Fairbanks *et al.*, 1982; Bouvier-Soumagnac and Duplessy, 1985; Kroon and Darling, 1995). There are, however, also suggestions that a species like *Globigerina bulloides* may calcify as a juvenile at depth and migrate to shallower depths in later growth stages (Spero and Lea, 1996; Bemis *et al.*, 1998).

### 2.2.2. Deviations from equilibrium $\delta^{18}\text{O}$ in foraminiferal calcite

Research is beginning to link  $\delta^{18}\text{O}$  disequilibrium in foraminiferal shells to variations in sea water chemistry and depth-specific habitats, but the understanding remains largely descriptive.

Speculations regarding the processes involving kinetic fractionations and/or incorporation of metabolic products in shell formation are being formulated on the basis of the experimental results. Five main sources of deviation from equilibrium have been observed: the ontogenic effect; the symbiont photosynthesis effect; the respiration effect; the gametogenic calcite effect; and the effect of changes in  $[\text{CO}_3^{2-}]$ . The various effects may operate in opposite ways, masking one another. All of these influences are important for planktonic Foraminifera, but a great variety of deviations from equilibrium also exists in deep-sea benthic Foraminifera (e.g. Duplessy *et al.*, 1970; Woodruff *et al.*, 1980; Vincent *et al.*, 1981; Wefer and Berger, 1991). Since these benthics live in an environment with very stable low temperatures and in complete absence of photosynthetic activity, this suggests that microhabitat differentiation combined with pore water chemistry and food supply may cause important  $\delta^{18}\text{O}$  disequilibria. The various effects are not strictly separate, and there may be strong overlaps between their regulating processes.

#### 2.2.2.1. Ontogenic effect

In experiments with constant  $\delta^{18}\text{O}_{\text{water}}$  and temperature, Spero and Lea (1996) found a progressive  $\delta^{18}\text{O}$  increase of up to 0.8 ‰ with shell development from juvenile chambers to the final chamber in *Globigerina bulloides*. As a result, the juvenile chambers were found to be strongly (around 1.15 ‰) depleted, while the final chamber was found to be much less (around 0.30 ‰) depleted, relative to equilibrium. The mass-balanced average of the individual chambers as a result displays a systematic depletion of around 0.7 ‰ relative to equilibrium. Since a similar (but stronger) trend of increasing values through ontogeny was observed in  $\delta^{13}\text{C}$ , a tentative explanation was offered in terms of incorporation of metabolic (respired)  $\text{CO}_2$  during calcification. The higher metabolic rates in juvenile specimens would cause the strongest depletions, while the adults would gradually trend towards equilibrium values (see section 3.3.2.3.).

The  $\delta^{18}\text{O}$  trend is to some extent corroborated by other reports of a size-dependent  $\delta^{18}\text{O}$  trend in *G. bulloides* (e.g. Kroon and Darling, 1995), although the trend in those real-ocean results is a factor of 2 smaller than that observed under laboratory conditions. Spero and Lea (1996) also observed this difference when comparing the laboratory results with data from fossil *G. bulloides* from Chatham Rise, speculating that this reduced signal was caused by vertical migrations from deeper (cooler and more positive) waters during early stages to very shallow (warmer, less positive) water during later stages. Bemis *et al.* (1998) also argue that such migrations seem likely from their data, masking to some extent the ontogenic signal.

#### 2.2.2.2. Symbiont photosynthesis

In the photosynthetic symbiont bearing planktonic foraminiferal species *Globigerinoides sacculifer*, Spero and Lea (1993) observed no variations in shell  $\delta^{18}\text{O}$  with ontogeny within the size range 350–850  $\mu\text{m}$ . This corroborated earlier conclusions that growth alone do not cause disequilibrium in this species (Erez and Luz, 1982; 1983; Wefer and Berger, 1991). However, Spero and Lea (1993) noted a distinct average chamber  $\delta^{18}\text{O}$  decrease for increasing irradiance levels. A similar but weaker decrease with increasing irradiance levels occurs in another photosynthetic symbiont bearing species, *Orbulina universa* (Spero, 1992; Spero and Lea, 1993; Spero *et al.*, 1997). In addition, increased growth rates were observed with increasing light intensities, corroborating observations of light-enhanced calcification rates under elevated irradiance in photosynthetic symbiont-bearing corals (Chalker and Taylor, 1975) and larger Foraminifera (Ter Kuile and Erez, 1984). The  $\delta^{18}\text{O}$  decreases with increasing irradiance were considered to be due to a kinetic effect related to rates of skeletogenesis, where higher light intensities caused rapid skeletogenesis, favoring stronger kinetic fractionation effects and,

consequently, stronger depletions in shell  $\delta^{18}\text{O}$ . McConnaughey (1989a) and Wefer and Berger (1991) reported decreasing skeletal  $\delta^{18}\text{O}$  values with increasing growth rates. It has been suggested that the kinetic effects are a function of  $\text{CO}_2$  diffusion through the skeletal membrane with kinetic discrimination against the heavy isotopes, combined with rapid  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$  reaction cycles (McConnaughey, 1989b; Spero and Lea, 1993).

#### 2.2.2.3. Respiration

Reviewing studies on photosynthetic symbiont-bearing corals, Swart (1983) concluded that the process of photosynthesis *per se* would have no appreciable fractionation effects for  $\delta^{18}\text{O}$ . Respiration (the reverse of photosynthesis), on the contrary, does cause  $\delta^{18}\text{O}$  depletion (Lane and Doyle, 1956). Relative to ambient dissolved oxygen, the oxygen used in respiration is depleted by 21 ‰ in near-shore, shallow waters (Kroopnick, 1975), or 11 ‰ in the deep ocean (Grossman, 1987). The  $\delta^{18}\text{O}$  of ambient dissolved oxygen in surface waters commonly ranges around +24 to +26 ‰ (SMOW) (Kroopnick *et al.*, 1972; Kroopnick, 1975). For example, in North Atlantic station Geosecs II, preferential respiratory  $^{16}\text{O}$  utilisation causes a marked  $\delta^{18}\text{O}$  peak in dissolved oxygen (+31 ‰ SMOW) around 1000 m depth (Kroopnick *et al.*, 1972). Utilisation of the depleted respiratory products during calcification would result in depleted skeletal  $\delta^{18}\text{O}$  values. However, it is not yet certain whether Foraminifera use respiratory products during calcification, since Belanger *et al.* (1981) found that the carbon isotope depletions in respired  $\text{CO}_2$  were not systematically important for skeletal  $\delta^{13}\text{C}$ , while Grossman (1987) in contrast argued that his observations indicate a substantial role of respiratory products in calcification of many benthic foraminiferal species.

#### 2.2.2.4. Gametogenic calcite

Several planktonic foraminiferal species deposit a veneer of calcite on the surface of their shell at the end of the life-cycle (Bé, 1980; Duplessy *et al.*, 1981; Deuser, 1987; Spero and Lea, 1993; Bemis *et al.*, 1998). In laboratory cultures, Bé (1980) observed that *Globigerinoides sacculifer* secretes the additional calcite during gametogenesis for a period of up to 16 hours before gamete release. This gametogenic calcite layer comprises 18 to 28 % of the shell mass of *G. sacculifer* (Bé, 1980; Duplessy *et al.*, 1981), and around 26 % in the case of *Orbulina universa* (Bouvier-Soumagnac and Duplessy, 1985), which makes these layers very important for whole-shell isotopic analyses. Specimens covered by a layer of gametogenic calcite are often called thick-walled. Gametogenic calcite is usually strongly  $\delta^{18}\text{O}$  enriched relative to the earlier (thin-walled) stages of the shell.

Duplessy *et al.* (1981) speculated that the early stages of *G. sacculifer* are deposited at distinct disequilibrium in the warm shallow water layers (as observed from living Foraminifera in plankton tows, and in cultures), whereas the gametogenic layer is deposited in colder waters at depths of up to several hundreds of meters, possibly in near equilibrium. Bouvier-Soumagnac and Duplessy (1985) present a similar case for *O. universa*, and argue that their data indicate that also *Neogloboquadrina dutertrei* and *Globorotalia menardii* follow this pattern. Kroon and Darling (1995) apply such arguments to reconstruct changes between last glacial maximum and Holocene vertical temperature gradients in the Arabian Sea and Panama Basin. Spero and Lea (1993), on the contrary, consider that vertical distribution studies of most living planktonic Foraminifera would not support calcification at such great depths, so that another, unidentified, mechanism should be responsible for the  $\delta^{18}\text{O}$  enrichments in gametogenic calcite. In their cooperation to a subsequent study (Bemis *et al.*, 1998), however, the calcification-at-depth hypothesis was invoked again, without further discussion. Clearly, the nature of the  $\delta^{18}\text{O}$

enrichment in gametogenic calcite remains somewhat elusive, and further research is required before a definite solution may be offered.

#### 2.2.2.5. Carbonate ion concentrations

In laboratory experiments, Spero *et al.* (1997) subjected specimens of *Orbulina universa* to variations in  $[\text{CO}_3^{2-}]$  at constant alkalinity, both under high irradiance and under low irradiance conditions. They observed a constant  $\delta^{18}\text{O}$  offset between the high and low irradiance experiments, while the ratio of change in shell  $\delta^{18}\text{O}$  with change in  $[\text{CO}_3^{2-}]$  remained similar for both groups. A second experiment with manipulation of  $[\text{CO}_3^{2-}]$  by changes in alkalinity with constant  $\Sigma\text{CO}_2$  corroborated the results of the first experiment. A third experiment concerned *Globigerina bulloides*, which bears no symbionts, and again a change was observed in shell  $\delta^{18}\text{O}$  with  $[\text{CO}_3^{2-}]$  variations. Spero *et al.* (1997), therefore, concluded that  $\delta^{18}\text{O}$  in foraminiferal carbonate decreases with increasing  $[\text{CO}_3^{2-}]$ , that the magnitude of this response is strongly species-specific, and that the process is not related to symbiont photosynthesis.

Previously, McCrea (1950) had observed that the  $\delta^{18}\text{O}$  of rapidly precipitated inorganic  $\text{CaCO}_3$  also decreases with increasing  $[\text{CO}_3^{2-}]$ . Spero *et al.*'s (1997) findings for biological carbonates and McCrea's (1950) similar observations on inorganic precipitates point at a common, a-biological, kinetic fractionation effect. It was suggested that this effect is related to calcification rates and the pH dependent balance between  $\text{CO}_2$  hydration and hydroxylation reactions (for detailed discussions, see McCrea, 1950; McConnaughey, 1989b; Usdowski and Hoefs, 1993; Spero *et al.*, 1997; and references therein).

Bemis *et al.* (1998) re-evaluated existing data of the benthic Foraminifera *Uvigerina* and *Cibicidoides* and found that the epifaunal *Cibicidoides* appears to precipitate its shell close to oxygen isotopic equilibrium with ambient sea water, while *Uvigerina* shells show  $\delta^{18}\text{O}$  mild enrichment. They speculate that the deviation in *Uvigerina* may be caused by a more infaunal habitat, where it experiences low pore-water pH and decreased  $[\text{CO}_3^{2-}]$ . As indicated by Bemis *et al.* (1998), these speculations warrant targeted further research before any definite statements may be made.

### 2.3. Aragonite versus Calcite

Some benthic Foraminifera (e.g. *Hoeglundina elegans*) construct their test of aragonite rather than calcite. Grossman (1984a) observed that *H. elegans* is enriched relative to the equilibrium value for calcite by  $0.78 \pm 0.19$  ‰. This is in good agreement with experimental observations that, at room temperature, inorganically precipitated aragonite is enriched by about 0.6 ‰ relative to inorganically precipitated calcite, while theoretical evaluation would suggest an enrichment of 0.79 ‰ (Tarutani *et al.*, 1969). The offset from the calcite-water equilibrium was found to be virtually constant, giving a temperature dependence of the equilibrium fractionation between water and aragonite that is very similar to that for the calcite-water fractionation (Grossman and Ku, 1986).



### 3. Carbon Isotopes

#### 3.1. Carbon isotopes and the global carbon cycle

There are two main carbon reservoirs: organic matter; and the sedimentary carbonates. For comprehensive schematics of fluxes within the global carbon cycle, see Compton and Mallinson (1996), Mackenzie (1998), and references therein.

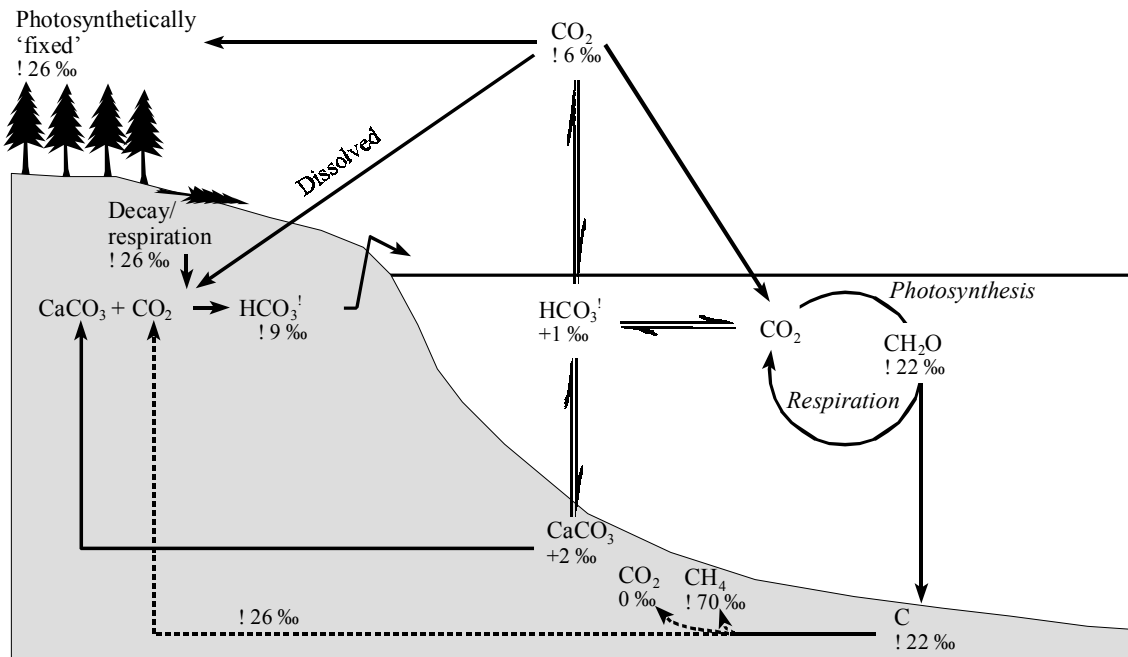
The organic carbon cycle revolves around CO<sub>2</sub> fixation into organic biomass through photosynthesis, which occurs in both the marine and the terrestrial biospheres. Simplified, the reaction describing photosynthesis is CO<sub>2</sub> + H<sub>2</sub>O + energy (sunlight) ⇒ CH<sub>2</sub>O + O<sub>2</sub>. Respiration under the presence of oxygen breaks down the organic biomass, and releases energy and CO<sub>2</sub> (reversal of the photosynthesis reaction). The organic carbon cycle acts on a great range of time scales, from the daytime photosynthesis - night-time respiration alternations within plants, to cycles of order 10<sup>8</sup> years where organic carbon is stored in sediments, only to become exposed and oxidised much later (NB also the burning of fossil fuels releases CO<sub>2</sub> that had been drawn down millions of years ago).

Weathering of most ordinary types of exposed/uplifted rocks (i.e. not only organic rich formations) also draws down CO<sub>2</sub> from the atmosphere. Schematically representing the rocks as calcisilicates (CaSiO<sub>3</sub>), the weathering reaction follows CaSiO<sub>3</sub> + CO<sub>2</sub> ⇒ CaCO<sub>3</sub> + SiO<sub>2</sub>. The CaCO<sub>3</sub> further dissociates in water (see below), utilising more CO<sub>2</sub>. Long-term cycles of orogeny and weathering (typically of order 10<sup>8</sup> years), therefore, cause fluctuations of atmospheric CO<sub>2</sub> concentrations, which in turn affect the oceans because the oceanic CO<sub>2</sub> content equilibrates through the air-sea interface with that in the atmosphere.

The inorganic carbon pool in the oceans is governed by the carbonate reactions. Most of the CO<sub>2</sub> in water is contained in HCO<sub>3</sub><sup>-</sup> (the bicarbonate ion), due to H<sub>2</sub>O + CO<sub>2</sub> ⇌ H<sup>+</sup> + HCO<sub>3</sub><sup>-</sup> while a further (weak) reaction may dissociate HCO<sub>3</sub><sup>-</sup> according to HCO<sub>3</sub><sup>-</sup> ⇌ H<sup>+</sup> + CO<sub>3</sub><sup>2-</sup>. At normal seawater pH of 7.8–8.3, sea water contains predominantly HCO<sub>3</sub><sup>-</sup> and only small amounts of CO<sub>3</sub><sup>2-</sup>. Total dissolved inorganic carbon (DIC) comprises HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and dissolved CO<sub>2</sub>. Calcium carbonate - biogenic and abiogenic - interacts with the inorganic carbon pool via the precipitation/dissolution equation 2HCO<sub>3</sub><sup>-</sup> + Ca<sup>2+</sup> ⇌ CaCO<sub>3</sub> + CO<sub>2</sub> + H<sub>2</sub>O.

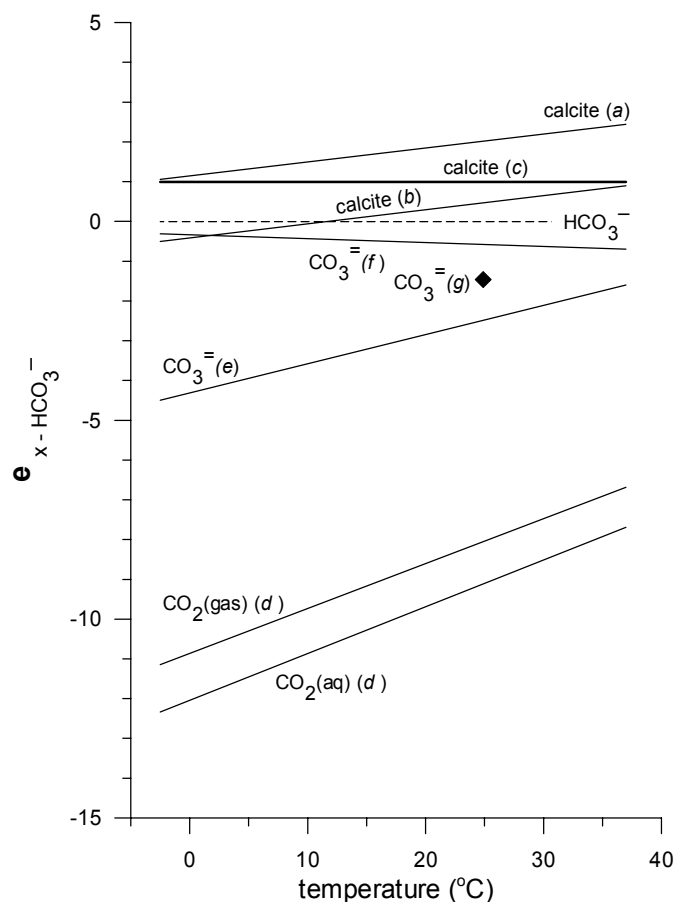
A summary of the main isotopic interactions within the organic and inorganic carbon cycles (**Figure 4**, modified after Garlick, 1974; also Hoefs, 1997) shows a clear distinction between the more depleted δ<sup>13</sup>C terrestrial organic matter (–26 ‰) and the less depleted marine organic matter (–22 ‰). According to Hoefs (1997), this difference is mainly due to the differences in the carbon isotopic composition of the carbon sources available, atmospheric CO<sub>2</sub> or oceanic HCO<sub>3</sub><sup>-</sup>, respectively. Swart (1983), however, reviewed δ<sup>13</sup>C fractionation during photosynthesis and concluded that dissolved CO<sub>2</sub> is the active carbon species involved in photosynthesis in the oceans, and that HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> can be utilized only at lower efficiencies. Since dissolved CO<sub>2</sub> is strongly depleted in δ<sup>13</sup>C relative to HCO<sub>3</sub><sup>-</sup> (**Figure 5**), and not much different from gaseous CO<sub>2</sub>, Hoefs' (1997) argument for the cause of the δ<sup>13</sup>C difference between terrestrial and marine organic matter may not be entirely valid. Swart (1983) proposed that the heavier δ<sup>13</sup>C signature of marine algae stems from differences in the CO<sub>2</sub> assimilation mechanisms between plants on land and in water, and from the absence of so-called translocation processes in the non-vascular algae. The ability to utilise HCO<sub>3</sub><sup>-</sup>, however, was later found to differ between phytoplankton taxa, compromising Swart's arguments (*e.g.*, Morel *et al.*, 1994; Riebesell and Wolf-Gladrow, 1995).

**Figure 4.** Main interactions between the terrestrial and marine organic and inorganic carbon cycles, with general mean carbon isotope values for the main phases (modified after Garlick, 1974). This diagram depicts only the main interactions in highly simplified form. There was no effort to incorporate a correct stoichiometry. Values are rough approximations only. Double arrows indicate isotopic equilibration.



**Figure 4** also illustrates the strong  $\delta^{13}\text{C}$  difference between the two main carbon reservoirs: the carbonate reservoir is characterized by values centered around 0 ‰, while the organic carbon reservoir shows average values centered around -25 ‰ (also, Hoefs, 1997). Extremely depleted values are known from methane in the form of gas-hydrates within the continental slope. Typical values are near -50 ‰, with variability between -35 ‰ and -80 ‰ and seepage of such gas-hydrates (clathrates) is thought to cause considerable  $\delta^{13}\text{C}$  depletions in infaunal benthic Foraminifera (Wefer *et al.*, 1994).

**Figure 5.** Temperature dependence of the carbon isotope enrichment factor (‰) relative to  $\text{HCO}_3^-$ . Sources: (a) Emrich et al, 1970; (b) Grossman, 1984b; (c) Romanek et al., 1992; (d) Mook et al., 1974; (e) Swart, 1983; (f) Freeman and Hayes, 1992; (g) Turner, 1982 (at PH >9).



### 3.2. Carbon isotopes in sea water

#### 3.2.1. Photosynthesis, respiration, export productivity, and surface-deep $\delta^{13}\text{C}$ gradients

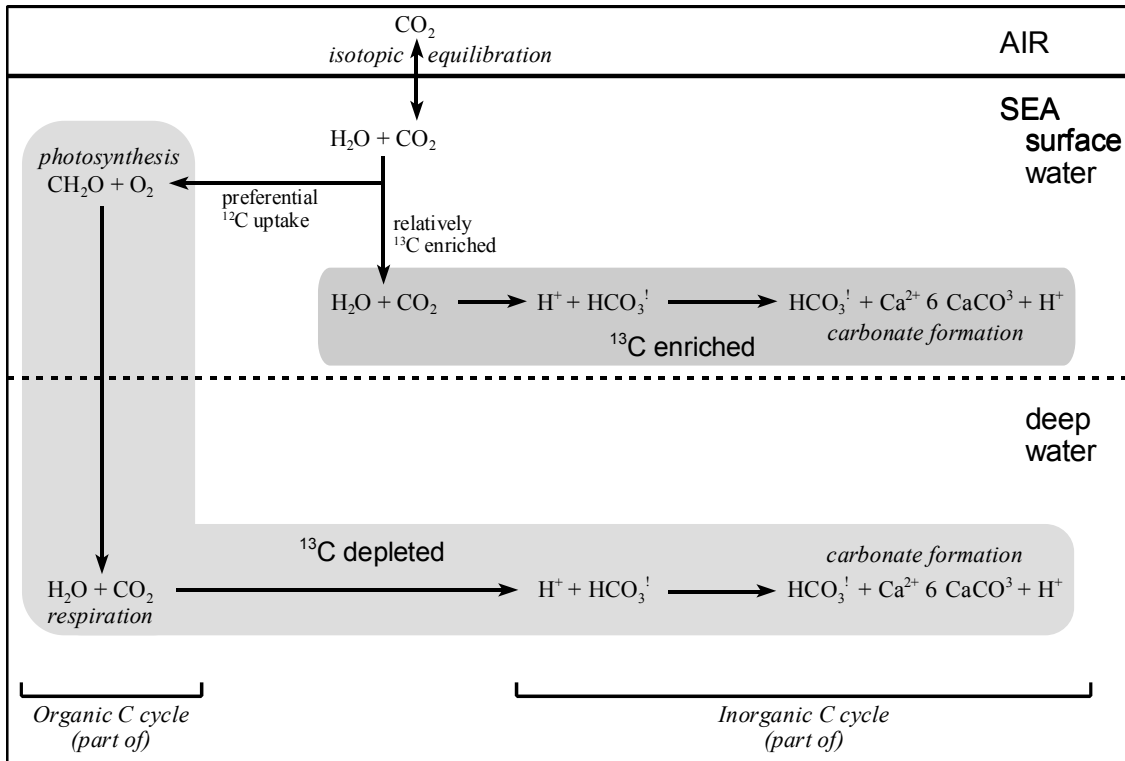
Formation of new marine organic matter occurs through photosynthesis. Photosynthesis is strongly discriminative in favor of  $^{12}\text{C}$ , and against  $^{13}\text{C}$ , through three main isotope-discriminating steps: (1) the uptake and intracellular diffusion of  $\text{CO}_2$ ; (2) the first  $\text{CO}_2$  fixing carboxylation reaction; and (3) translocation (Park and Epstein, 1960; Swart, 1983; Hoefs, 1997). In the aquatic environments, there may be additional fractionations, e.g. associated with hydration of  $\text{CO}_2$  (Swart, 1983; Hoefs, 1997). As mentioned before, the translocation step would appear to be unimportant in the non-vascular marine algae, while also step (1) may be of little relevance to  $\delta^{13}\text{C}$  fractionation in sub-aqueous environments (Swart, 1983).

The strong preferential uptake of  $^{12}\text{C}$  causes marine phytoplankton to form organic matter with  $\delta^{13}\text{C}$  values around  $-20$  to  $-23$  ‰ relative to ambient water. Photosynthesis naturally occurs only within the euphotic layer and due to the preferential uptake of  $^{12}\text{C}$  during photosynthesis, the dissolved carbon in surface waters becomes strongly enriched in  $\delta^{13}\text{C}$ . Through equilibrations, this enrichment also affects surface water  $\text{HCO}_3^-$ . Carbonates formed from that  $\text{HCO}_3^-$ , in turn, will also record the  $\delta^{13}\text{C}$  enrichment (**Figure 6**).

As organic matter is remineralised, the  $\delta^{13}\text{C}$  depletion is ‘released’ into the water column, again equilibrating with  $\text{HCO}_3^-$  and affecting the carbonate formed from it. Where remineralisation occurs within the mixed layer, this effect to some extent offsets the enrichment effect due to photosynthesis. However, any loss from the mixed layer through export productivity

will cause a ‘loss’ of the  $\delta^{13}\text{C}$  depleted marine organic matter from the mixed layer. When it remineralises at depth, an effective transfer of  $^{12}\text{C}$  has occurred from surface to deep water. Hence, increases in export productivity will cause increasing gradients between  $\delta^{13}\text{C}$  enrichment in surface waters and  $\delta^{13}\text{C}$  depletion in deep waters, which will be recorded in calcareous fossils (**Figure 6**).

**Figure 6.** Schematic presentation of the generation of a surface-deep carbon isotope gradient due to export production and interactions between the marine organic and inorganic carbon cycles. There was no effort to incorporate a correct stoichiometry.



### 3.2.2. Tracer for nutrient concentrations

The dependence of the surface-deep  $\delta^{13}\text{C}$  gradient on export production is corroborated by correlation with deep water nutrient concentrations. Remineralisation of organic matter at depth not only releases  $\delta^{13}\text{C}$  depleted  $\text{CO}_2$  into the deep water, but also nutrients. Hence, enhanced  $\delta^{13}\text{C}$  depletion in the present-day oceans correlates well with enhanced nutrient concentrations, where the expected relationship between  $\delta^{13}\text{C}$  (in ‰) and phosphate concentrations (in  $\mu\text{mol kg}^{-1}$ ) is  $-0.93 \text{ ‰ } \mu\text{mol kg}^{-1}$  (cf. Broecker, 1982; Broecker and Peng, 1982, pp. 308 and 309). Ortiz *et al.* (1996) present relationships between  $\delta^{13}\text{C}$  and nitrate concentrations, distinguishing between surface and deep water relationships. Provided sufficient validation is possible from independent evidence, this correlation of  $\delta^{13}\text{C}$  with nutrient concentrations has great potential in palaeoceanographic applications. For example, the application of paired  $\delta^{13}\text{C}$  and Cd/Ca - another proxy for phosphate concentrations - analyses by Boyle and Keigwin (1982; 1985/86; 1987) and Boyle (1986), who have reconstructed changes in nutrient concentrations associated with changes in deep and intermediate water production in the North Atlantic since the last glacial maximum.

### 3.2.3. Deep water ‘age’

The use of lateral gradients in deep water  $\delta^{13}\text{C}$  to determine the ‘age’ of deep water is based on exactly the same principles as the use in tracing nutrient concentrations. We emphasize that

the word ‘age’ should not be viewed within a strictly time-related context. Rather, the  $\delta^{13}\text{C}$  of deep waters reflects the amount of organic matter remineralisation sustained by the deep water, which varies as function of: (1) time of ‘exposure’ to organic matter decay (true age); (2) the amount of organic matter decaying (i.e. export production); and (3) the rapidity of organic matter decay, which is temperature dependent since - within the limits of normal oceanic temperatures - respiration-rates roughly double for each 10 °C temperature increase (cf. Swart, 1983). Even for constant temperature, deep water would ‘age’ rapidly when passing through an area of high export production, and slowly when crossing an area with low export production. At the extreme end of the scale, deep waters trapped in depressions or behind sills in high productivity basins (e.g. Gulf of California) will rapidly develop strong  $\delta^{13}\text{C}$  depletions and so appear very ‘old’ compared with freely flowing deep waters from the same source-region outside the obstruction. Obviously, the ‘age’ of deep water is a relative concept only.

Viewed within the proper, relative, context, the age of deep water provides a powerful tool for reconstruction of ocean circulation, identifying deep water flow pathways from their source areas. For example, the relatively high  $\delta^{13}\text{C}$  values in the present-day deep North Atlantic (around +1.0 ‰, relative to average surface waters at +1.6 ‰; Kroopnick *et al.*, 1972) correctly identify it as a basin with active deep water formation and consequently ‘young’ deep waters. Low North Pacific deep water  $\delta^{13}\text{C}$  values (around -0.2 ‰, relative to average surface waters around +1.5 to +2.0 ‰; Broecker and Peng, 1982; p.308) successfully identify these waters as ‘old’, derived from remote source-regions. Lynch-Stieglitz and Fairbanks (1994) used Cd/Ca ratios to separate  $\delta^{13}\text{C}$  signals into a part related to the age of deep water (hence nutrient enriched) and a part related to the air-sea exchange (which is defined in the deep water formation area, and does not change during deep water transport; cf. Broecker and Maier-Reimer, 1992). This subdivision allowed the authors to identify source areas for glacial deep water that differ greatly from those active today.

Note that the above implies that geographic shifts of deep water formation sites greatly affect the surface-deep  $\delta^{13}\text{C}$  gradients in the world ocean, being low in actively overturning basins, and high in non-overturning basins that receive ‘old’ deep waters from remote sources. It follows, therefore, that such major ocean-wide patterns should be determined before local/regional variability in surface (planktonic) to deep (benthic)  $\delta^{13}\text{C}$  gradients from past geological periods may be interpreted in terms of export productivity as discussed in *section 3.2.1*.

### *3.2.4. Influences of variability in $\delta^{13}\text{C}$ of atmospheric $\text{CO}_2$*

#### *3.2.4.1. Types of variability*

From **Figure 6**, it is obvious that major changes in the  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  will, via equilibration through the sea-air interface, be recorded in the marine cycles. There are two main influences to be taken into account: (1) spatial variability in the equilibration between atmospheric  $\text{CO}_2$  and the dissolved inorganic carbon in sea water; and (2) geographically widespread temporal variability in the  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$ . For atmospheric signals to be recorded in the marine reservoir, a signal of sufficient magnitude and duration is needed. Because the atmospheric  $\text{CO}_2$  reservoir is orders of magnitude smaller than the marine reservoir, a recordable signal transmitted by the atmosphere should involve the terrestrial biosphere and/or lithosphere.

#### *3.2.4.2. Spatial variability*

Spatial variability in the equilibration is caused by the temperature dependence of equilibrium exchange. The DIC in sea water is  $\delta^{13}\text{C}$  enriched relative to the atmosphere, but the

fractionation becomes weaker with increasing temperature (cf. **Figure 5** where surface water  $\delta^{13}\text{C}_{\text{DIC}}$  is a few tenths of a ‰ depleted relative to  $\delta^{13}\text{C}$  of  $\text{HCO}_3^-$ ). Allowing sufficient time for complete equilibration, therefore, warm low latitude sea water  $\delta^{13}\text{C}_{\text{DIC}}$  values will be less enriched than those in cold high latitude sea water (Kroopnick *et al.*, 1977; Broecker and Maier-Reimer, 1992; Lynch-Stieglitz and Fairbanks, 1994). If sufficiently long exposure to the atmosphere occurred for this relatively slow process to be completed, an equator to pole difference of order 2 ‰ would result in surface waters. In reality, however, things are much more complicated. For example, upwelling of deep,  $\delta^{13}\text{C}$  depleted water causes deviations from equilibrium in surface waters and affects the  $\delta^{13}\text{C}$  of the overlying atmospheric  $\text{CO}_2$ . Such deviations would be recorded in new deep water formed from surface waters which have just upwelled from great depth (e.g. Antarctic Bottom Water containing recently upwelled North Atlantic Deep Water) (cf. Kroopnick *et al.*, 1977). Even if total equilibration would take place at the surface, the surface values at a particular site would not necessarily (or even likely) be characteristic of deep waters formed at that site, because the properties of new deep water rely only to a limited extent on surface forcing and to a much greater extent on the properties of entrained subsurface waters. As with  $\delta^{18}\text{O}$  (section 2.1.5.), therefore, advection and mixing within the oceans also play a very important role in determining the spatial distribution pattern of  $\delta^{13}\text{C}$  through the world ocean.

#### 3.2.4.3. Temporal variability

Geographically widespread change through time in the  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  shows from Kroopnick *et al.*'s (1977) April-May 1970 data (their figure 6), with strong depletion in the Northern Hemisphere due to organically produced  $\text{CO}_2$ . A likely source for this  $\delta^{13}\text{C}$  depleted  $\text{CO}_2$  is the combustion of fossil fuel. Leavitt (1993) discussed  $\delta^{13}\text{C}$  records from trees and introduced a correction to eliminate the decline in values over the last century due to fossil-fuel inputs, using a model for atmospheric  $\delta^{13}\text{C}$  changes on the basis of  $^{14}\text{C}$  dilution (Peng *et al.*, 1983).

Another potential cause of widespread change with time in the  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  would be a major shift in terrestrial vegetation between domination of C3 plants, of which most trees are a subset, and C4 plants, which include many grasses (Leavitt, 1993). C3 plants and C4 plants photosynthesise in different ways: the former follow the Calvin-Benson cycle, and the latter the Hatch-Slack photosynthetic pathway. Consequently, C3 plants are much more  $\delta^{13}\text{C}$  depleted than C4 plants (Kelly *et al.*, 1993). The main difference lies in the absence of photorespiration and the associated isotopic fractionations in C4 plants, which are evolutionarily more advanced. This link with the process of photorespiration is borne out by the absence of change of  $\delta^{13}\text{C}$  fractionation with changing oxygen concentrations in C4 plants, whereas C3 plants show a (non-linear) fractionation of roughly 0.25 ‰ with every 1 ‰ increase in oxygen content (Swart, 1983). In aquatic plants, the degree of oxygenation seems also to be important for  $\delta^{13}\text{C}$  fractionation (Degens *et al.*, 1968), and  $\delta^{13}\text{C}$  values for algae are intermediate between those for C3 and C4 plants. Typical  $\delta^{13}\text{C}$  values for marine algae are around -22 ‰, for C3 plants around -28 ‰, and for C4 plants around -12 ‰.

With an increase in dominance of C4 plants relative to C3 plants, such as occurred during the late Miocene (Cerling *et al.*, 1993), the mean enrichment in atmospheric  $\delta^{13}\text{C}$  caused by terrestrial plants would have been reduced, which may explain the late Miocene shift to lower  $\delta^{13}\text{C}$  values in marine carbonates (Derry and France-Lanord, 1996). The long-term characteristic of this change would imply that the shift would be seen equally from surface waters to the greatest depths in the oceans. This uniform response differs from the results of fluctuations in export productivity and deep water 'age', which affect gradients between surface and deep waters.

### 3.2.5. Carbon burial and global isotope shifts

#### 3.2.5.1. Organic carbon

As argued above, marine organic matter shows strong  $\delta^{13}\text{C}$  depletion. Normally, the vast majority of the marine organic matter is remineralised, and the  $\delta^{13}\text{C}$  depletion then influences the deep sea. Upwelling and mixing eventually bring the depletion back to the surface. With time, therefore, there is little net effect. However, several periods in geological history have been characterized by higher than average organic matter preservation and ‘removal’ from the system by inclusion in sediments. Such a situation not only constitutes a ‘sink’ of carbon, so that eventually the atmospheric  $\text{CO}_2$  concentration should drop, but simultaneously causes a residual  $\delta^{13}\text{C}$  enrichment throughout the oceans and atmosphere. This line of reasoning was first developed as an explanation for the ‘carbon shift’ associated with the widely documented Middle Miocene cooling (Vincent and Berger, 1985). The organic carbon ‘sink’ for that event would have been the massive carbon deposition and burial that formed the Monterey Formation of California.

The inverse process, oxidation of fossil fuels, pumps out  $\text{CO}_2$  into the atmosphere and causes a noticeable depletion in atmospheric  $\delta^{13}\text{C}$  values (see *section 3.2.4.*), which will eventually equilibrate with the oceans and after a suitable ocean mixing period (of order  $10^3$  years) affect the surface and deep waters alike.

#### 3.2.5.2. Inorganic carbon

Weathering of the total sedimentary carbonate reservoir reflects the mean  $\delta^{13}\text{C}$  of that reservoir, which during the Neogene has been very stable around  $1.8 \pm 0.2$  ‰ (Derry and France-Lanord, 1996). The main reasons for the stability of this value lie in the enormous volume and very long (of order  $10^8$  years) residence time of sedimentary carbonate, which effectively smooth out even the strongest fluctuations in the input values. The stability of this value also means that relatively straightforward isotopic balance equations may be drawn up to estimate the fraction of organic carbon in the total eroded carbon ( $X_{\text{org}}^{\text{er}}$ ) and the fraction of organic carbon in the total carbon burial flux ( $X_{\text{org}}^{\text{bur}}$ ), as  $X_{\text{org}}^{\text{er}} = (\delta^{13}\text{C}_{\text{carb}}^{\text{mean}} - \delta^{13}\text{C}_{\text{TC}})/\Delta_{\text{E}}$ , and  $X_{\text{org}}^{\text{bur}} = (\delta^{13}\text{C}_{\text{carb}}^t - \delta^{13}\text{C}_{\text{rivers}})/\Delta_{\text{B}}$ , where  $\delta^{13}\text{C}_{\text{carb}}^{\text{mean}}$  is the average  $\delta^{13}\text{C}$  of sedimentary carbonate,  $\delta^{13}\text{C}_{\text{carb}}^t$  is that of the carbonates formed/removed from the oceans at time  $t$ ,  $\delta^{13}\text{C}_{\text{TC}}$  is the mean isotopic composition of total sedimentary carbon (about  $-5$  ‰),  $\delta^{13}\text{C}_{\text{rivers}}$  is the mean value for carbon inputs into the oceans that by first approximation is equal to  $\delta^{13}\text{C}_{\text{TC}}$ ,  $\Delta_{\text{E}}$  is the mean isotopic difference between the sedimentary carbonate and organic carbon being eroded, and  $\Delta_{\text{B}}$  is that between carbonates and organic carbon deposited at time  $t$  (Derry and France-Lanord, 1996).

By first approximation,  $\Delta_{\text{E}}$  and  $\Delta_{\text{B}}$  may be taken as equal to one another, although Derry and France-Lanord (1996) actually allow for change in  $\Delta_{\text{B}}$  with time to allow for such events as the Middle Miocene increase in C4 plant domination. The two relationships indicate that a main determinant in the ratio between the mean carbonate  $\delta^{13}\text{C}$  and the  $\delta^{13}\text{C}$  of carbonate formed at time  $t$  is the difference between the fractions of organic carbon eroded and buried at time  $t$ . This would suggest that variations in the organic carbon pool exert the dominant influence on global  $\delta^{13}\text{C}$  fluctuations, and that the inorganic carbon pool is not as important a driving factor, but instead ‘monitors/records’ the changes.

### 3.3. Carbon isotope ratios in foraminiferal carbonate

#### 3.3.1. Equilibrium fractionation

##### 3.3.1.1. Equilibrium between carbonate and dissolved inorganic carbon

Grossman (1984b) analyzed  $\delta^{13}\text{C}$  for both calcitic and aragonitic (*Hoeglundina elegans*) benthic foraminiferal species, and evaluated the results against inorganic precipitates. He presented new equations for the equilibrium isotopic enrichments of aragonite and calcite, relative

to bicarbonate. Here, we concentrate on calcite (*c*), and the isotopic enrichment factor for that carbonate species versus bicarbonate (*b*) was determined as  $\epsilon_{c-b} (\text{‰}) = 10.51 - 2980/T$ , where *T* is in Kelvin. This relationship gives similar temperature dependence to the earlier relationship of Emrich *et al.* (1970), but the predicted values are systematically about 1.5 ‰ less enriched than those predicted with the Emrich *et al.* (1970) relationship (which has an intercept at 12.02 rather than 10.51) (see also **Figure 5**). Grossman (1984b) ascribes this to the fact that the Emrich *et al.* (1970) equation was based on a mixture of aragonite and calcite, while his equation is based purely on calcite. Romanek *et al.* (1992) observed a straightforward relationship between the  $\delta^{13}\text{C}$  of equilibrium carbonate and  $\delta^{13}\text{C}$  of bicarbonate where, within errors of  $\pm 0.2 \text{ ‰}$ ,  $\delta^{13}\text{C}_{\text{eqcarb}} = \delta^{13}\text{CHCO}_3^- + 1.0$ . In their analyses of aragonitic species, Grossman (1984b) and Grossman and Ku (1986) found a weak inverse temperature relationship (see also Wefer and Berger, 1991).

Many studies report carbonate  $\delta^{13}\text{C}$  equilibrium relative to the  $\delta^{13}\text{C}$  of total dissolved inorganic carbon (i.e., the  $\delta^{13}\text{C}$  of  $\Sigma\text{CO}_2 = \delta^{13}\text{C}_{\text{DIC}}$ ) rather than relative to the  $\delta^{13}\text{C}$  of bicarbonate. This is because the value for  $\delta^{13}\text{C}_{\text{DIC}}$  can be either analytically determined (Kroopnick, 1974), or estimated from apparent oxygen utilisation rates ( $\text{AOU} = \text{O}_2^{\text{saturation}} - \text{O}_2^{\text{measured}}$ ) as  $\delta^{13}\text{C}_{\text{DIC}} = 1.5 - 0.0075 \text{ AOI}$  (Kroopnick, 1985), whereas the  $\delta^{13}\text{C}$  of bicarbonate is obtained through calculations from  $\delta^{13}\text{C}_{\text{DIC}}$  rather than direct measurement, using  $\delta^{13}\text{C}_{\text{DIC}} = (f \delta^{13}\text{C})\text{HCO}_3^- + (f \delta^{13}\text{C})\text{CO}_3^{2-} + (f \delta^{13}\text{C})\text{CO}_2^{\text{aq}}$ , where *f* indicates the mole fraction per dissolved inorganic species. The mole fraction for  $\text{CO}_2^{\text{aq}}$  is very small at normal sea water pH of 7.8–8.3, so that  $\delta^{13}\text{C}_{\text{DIC}}$  is only slightly (0.2 to 0.4 ‰) lower than  $\delta^{13}\text{CHCO}_3^-$  because of the abundance dominance of  $\text{HCO}_3^-$  over  $\text{CO}_3^{2-}$ . The high degree of uncertainty concerning the isotopic depletion of  $\text{CO}_3^{2-}$  relative to  $\text{HCO}_3^-$  (**Figure 5**) becomes particularly troublesome for the deconvolution of  $\delta^{13}\text{C}_{\text{DIC}}$  at pH >9.0, where  $\text{CO}_3^{2-}$  becomes the dominant species. Below pH 7.5 the proportion of  $\text{CO}_2^{\text{aq}}$  increases drastically, which causes a strong increase in the offset between  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{13}\text{CHCO}_3^-$  (Romanek *et al.*, 1992). Therefore,  $\delta^{13}\text{C}_{\text{DIC}}$ , a discrete quantifiable parameter, is more useful than  $\delta^{13}\text{CHCO}_3^-$ . However, information on the concentrations of the various inorganic carbon species and pH still remains desirable to assess equilibrium/disequilibrium carbonate precipitation (see following sections). In the oceans, the very high or low pH ranges mentioned above are not normally reached.

### 3.3.1.2. Apparent disequilibria: differential depth habitats/microhabitat effect

In planktonic Foraminifera, changes in depth of calcification during growth and differences between preferred depths of different species may cause apparent  $\delta^{13}\text{C}$  deviations from surface water equilibrium, because the gradient in  $\delta^{13}\text{C}_{\text{DIC}}$  is steep between the very surface and the thermocline (where the majority of organic matter is remineralised) (Kroopnick *et al.*, 1972; Garlick, 1974; Kroopnick 1985; Tan, 1989). Hence, growth/size related intra-specific variations, and inter-species differences, in preferred depth of calcification must be taken into account before decisions are made on the degree of disequilibrium and its potential causes (among many others Bouvier-Soumagnac and Duplessy, 1985; Wefer and Berger, 1991; Ravelo and Fairbanks, 1995; Ortiz *et al.*, 1996). Since temperature drops in the oceans with increasing depth, there is also a strong  $\delta^{18}\text{O}$  relationship with calcification depth (see *section 2.2.1*). Bouvier-Soumagnac and Duplessy (1985) argue that enriched  $\delta^{18}\text{O}$  and depleted  $\delta^{13}\text{C}$  values in several planktonic Foraminifera indicates that calcification at later growth stages occurs well below the mixed layer. Ravelo and Fairbanks (1995) employed the covariation to assess the potential of using  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  pairs from fossil Foraminifera to reconstruct past surface water hydrography, concluding that non-spinose species offer the greatest potential because they are less affected by biological effects on isotope fractionation.



Concerning benthic Foraminifera, it has been argued that the question of equilibrium should be viewed within the context of ambient pore water  $\delta^{13}\text{C}$  at the species' preferred living depth/microhabitat, rather than those of bottom waters, in which case the disequilibria are less pronounced (Woodruff *et al.*, 1980; Belanger *et al.*, 1981; Grossman, 1984a, b; 1987; McCorkle *et al.*, 1985; 1990; Zahn *et al.*, 1986; Wefer and Berger, 1991; Loubere *et al.*, 1995). McCorkle *et al.* (1990) consistently found more  $\delta^{13}\text{C}$  depleted values in deep dwelling taxa than in shallow dwelling taxa. Gradients of  $\delta^{13}\text{C}$  within sediments (pore waters) may be of order 1 ‰ depletion per cm depth within sediment (Grossman, 1984a, b; McCorkle *et al.*, 1985; Grossman, 1987) and are caused by the decomposition of sedimentary organic matter with a  $\delta^{13}\text{C}$  around  $-22$  ‰. There may be additional intra-specific control on the magnitude and variability of depletions in some species by the amount (Zahn *et al.*, 1986; Loubere, 1987) and mechanisms (Loubere, 1987) of food supply within the sediment. It has become widely accepted that the epiphytic species *C. wuellerstorfi* (in the literature described under genus-names *Cibicides*, *Cibicidoides*, *Planulina*, and *Fontbotia*) forms its test nearest to equilibrium with dissolved carbon in bottom waters and so is the best measure for bottom water  $\delta^{13}\text{C}_{\text{DIC}}$  variations through time (among others Woodruff *et al.*, 1980; Graham *et al.*, 1981; Zahn *et al.*, 1986; Grossman, 1987; Wefer and Berger, 1991; Mackensen *et al.*, 1993).

### 3.3.2. Deviations from equilibrium $\delta^{13}\text{C}$ in foraminiferal carbonate

Disequilibrium in foraminiferal  $\delta^{13}\text{C}$  values relative to dissolved carbon in ambient sea water may be caused by: (1) utilisation of metabolic  $\text{CO}_2$  during shell formation; (2) photosynthetic activity of symbionts; (3) growth rate; and (4) variation in carbonate ion concentrations in ambient waters. The various effects are not strictly separate, and there may be strong overlaps between their regulating processes. Structured overviews and an attempt to model the combined influences of each effect - except (4) which had not yet been discovered - were presented by Grossman (1987), Ravelo and Fairbanks (1995), and Spero *et al.* (1991; 1997).

#### 3.3.2.1. Respiratory $\text{CO}_2$

Grossman (1987) summarised that carbon isotope ratios in almost all biogenic carbonates are to some extent influenced by vital effects, which almost invariably cause depletion relative to equilibrium. The vital effects are thought to be caused by incorporation of isotopically light metabolic  $\text{CO}_2$  into the carbonate skeleton (among others Keith and Weber, 1965; Weber and Woodhead, 1970; Vinot-Bertouille and Duplessy, 1973). The magnitude of the vital effect seems to be proportional to the amount of metabolic  $\text{CO}_2$  within the organisms internal  $\text{CO}_2$  pool (Erez, 1978), which, in turn, should be a function of the organisms ability for gas-exchange with ambient water. Grossman (1984a; 1987) relates this reasoning to his assessment that organisms from oxygen minimum zones around the world show the least influence of vital effects, suggesting that these organisms are specially adapted for efficient gas-exchange, which would appear to be corroborated by the observations of Leutenegger and Hansen (1979).

Grossman (1987) attempted to quantify the amount of metabolic  $\text{CO}_2$  used in calcification by assessing the degree of  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  covariation in various benthic foraminiferal species, since there is a  $\delta^{18}\text{O}$  depletion in the oxygen used in respiration relative to unused oxygen while the  $\delta^{13}\text{C}$  of metabolic  $\text{CO}_2$  likely reflects the very low  $\delta^{13}\text{C}$  values of the food source, i.e. sedimentary organic matter (cf. Lane and Doyle, 1956; Degens *et al.*, 1968; Kroopnick, 1975; De Niro and Epstein, 1978). On the basis of these arguments, the incorporation of metabolic carbon-oxygen compounds should result in depletions of both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in the test. Grossman (1987) found that the expected relationship holds only to a limited extent.

Clearly, there still are too many unknowns to finally quantify the vital effect. Note, however, that it has recently been found from laboratory cultures that even large variations in  $\delta^{13}\text{C}$  of food to the planktonic species *Orbulina universa* and *Globigerina bulloides* cause only negligible shifts in shell  $\delta^{13}\text{C}$ , amounting from 0 to 0.08 ‰ per 1 ‰ change in dietary  $\delta^{13}\text{C}$  (Spero and Lea, 1993; 1996; see also Ortiz *et al.*, 1996). Ortiz *et al.* (1996) re-evaluated carbon isotope disequilibria and concluded that temperature, instead of food  $\delta^{13}\text{C}$ , plays the major role in the observed  $\delta^{13}\text{C}$  disequilibria, through its control on metabolic rates. Wefer and Berger (1991) discussed strong early summer  $\delta^{13}\text{C}$  depletions in shells of gastropods of reproductive age, reflecting greater metabolic activity associated with spawning events. Similar depletions associated with spawning events have been reported from corals (Gagan *et al.*, 1994). Larger photosynthetic symbiont-bearing Foraminifera also show a shift to very low  $\delta^{13}\text{C}$  values in the reproductive period (Wefer and Berger, 1991). These observations corroborate the contention of Ortiz *et al.* (1996) that fluctuations in metabolic rates are a prime determinant for the magnitude of carbon isotope disequilibria caused by vital effects.

#### 3.3.2.2. Symbiont photosynthesis

There is much evidence for a relationship between decreasing skeletal  $\delta^{13}\text{C}$  enrichment with decreasing light intensity from a wide range of photosynthetic (symbiont bearing) organisms that precipitate calcium carbonate (McConnaughey, 1989a). In laboratory cultures, Spero and Lea (1993) noted a distinct average chamber  $\delta^{13}\text{C}$  increase with increasing irradiance levels in the planktonic species *Globigerinoides sacculifer*, which they ascribe to elevated utilization of  $^{12}\text{CO}_2$  by photosynthetic symbiont. This increases the calcifying microenvironment in  $\text{H}^{13}\text{CO}_3^{2-}$  and so produces  $\delta^{13}\text{C}$  enriched chambers. A similarly strong relationship had been previously observed for the planktonic species *Orbulina universa*, while the relationship disappeared when photosynthetic activity was prevented, i.e. the photosynthetic symbionts were removed, or specimens containing symbionts were kept in the dark (Spero and Williams, 1988).

It is interesting to note that the  $\delta^{13}\text{C}$  values of *G. sacculifer* at very low light levels shift slightly below equilibrium, suggesting that photosynthetic effects are suppressed and that some respired  $\text{CO}_2$  becomes incorporated in the shell, but only to a proportion of 0-3% of the shell carbon (Spero and Lea, 1993). Similar values have been observed for *O. universa* (Spero, 1992). Light intensity/photosynthetic activity influences cannot be too easily accounted for in data from Foraminifera that have grown in natural dark-light alternations, unless the proportions are known of the shell fractions deposited during the dark and the light periods. For *Orbulina universa*, these proportions are 40 and 60%, respectively (Spero *et al.*, 1991).

#### 3.3.2.3. Changes with growth

Romanek *et al.* (1992) presented new experiments and re-interpreted the results of Turner (1982), concluding that both indicate that - over two orders of magnitude of change in precipitation rate - no significant  $\delta^{13}\text{C}$  fractionations need to be taken into account due to differences in calcification rates alone. However, most Foraminifera experience major physiological changes during growth. In symbiont-bearing species *Globigerinella aequilateralis* and *Orbulina universa*, symbiont density has been observed to increase with test size (Faber *et al.*, 1988; Spero and Parker, 1985), which in turn increases total gross photosynthesis so that each new chamber is calcified under a different physiological regime, with progressive increase of the photosynthetically induced shell  $\delta^{13}\text{C}$  enrichment. An analysis of whole-shell  $\delta^{13}\text{C}$ , therefore, gives an integrated value of the masses and different  $\delta^{13}\text{C}$  compositions of all individual chambers (Spero *et al.*, 1991), and will be different for the same species in different size-classes. Ravelo and Fairbanks (1995), however, argued that progressive increases in  $\delta^{18}\text{O}$  in *Orbulina*

*universa* in the natural environment suggest migration to progressively deeper habitats with lower light intensity during growth, the influence of which may partially offset that of the increase in symbiont density. The end-result would be weakening of the size-related photosynthetic effects to shell  $\delta^{13}\text{C}$  due to a shift from high light-low symbiont density conditions to low light-high symbiont density conditions.

In non-symbiont-bearing species, a change with size would be expected in the depletion caused by contamination of shell  $\delta^{13}\text{C}$  with metabolic/respiratory  $\text{CO}_2$ . Such depletions should be strongest in small specimens from early life stages with high metabolic rates, decreasing in later growth stages which would tend towards equilibrium (cf. Berger *et al.*, 1978; Wefer and Berger, 1991). Bouvier-Soumagnac and Duplessy (1985) reported such trends for the species *Globorotalia menardii* and *Neogloboquadrina dutertrei*, which do not contain symbionts. Ravelo and Fairbanks (1995) also found such a trend in *N. dutertrei*, but observed little to no size-dependent fractionation in *G. menardii*, *Globorotalia tumida*, *Globorotalia inflata*, *Globorotalia crassaformis*, *Globorotalia truncatulinoides*, or *Pulleniatina obliquiloculata*.

There appears to be no significant change in the skeletal  $\delta^{13}\text{C}$  with size in deep dwelling benthic Foraminifera (Vincent *et al.*, 1981; Dunbar and Wefer, 1984; Grossman, 1984a; 1987; Wefer and Berger, 1991).

#### 3.3.2.4. Carbonate ion concentration

In their laboratory experiments (see section 2.2.2.4.), Spero *et al.* (1997) observed a constant  $\delta^{13}\text{C}$  offset between high and low irradiance experiments, while the ratio of change in shell  $\delta^{13}\text{C}$  with change in  $[\text{CO}_3^{2-}]$  remained similar for both groups. These results were obtained from three different experiments, and Spero *et al.* (1997) concluded that, similar to  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$  in foraminiferal carbonate decreases with increasing  $[\text{CO}_3^{2-}]$ , that the magnitude of this response is strongly species-specific, that the process is not related to symbiont photosynthesis, and that their data combined with those for abiogenic carbonates (McCrea, 1950) point at a common, a-biological, kinetic fractionation effect. The effect was considered to be related to calcification rates and the pH dependent balance between  $\text{CO}_2$  hydration and hydroxylation reactions (for detailed discussions, see McCrea, 1950; McConnaughey, 1989b; Usdowski and Hoefs, 1993; Spero *et al.*, 1997; and references therein).

#### 3.4. Aragonite versus Calcite

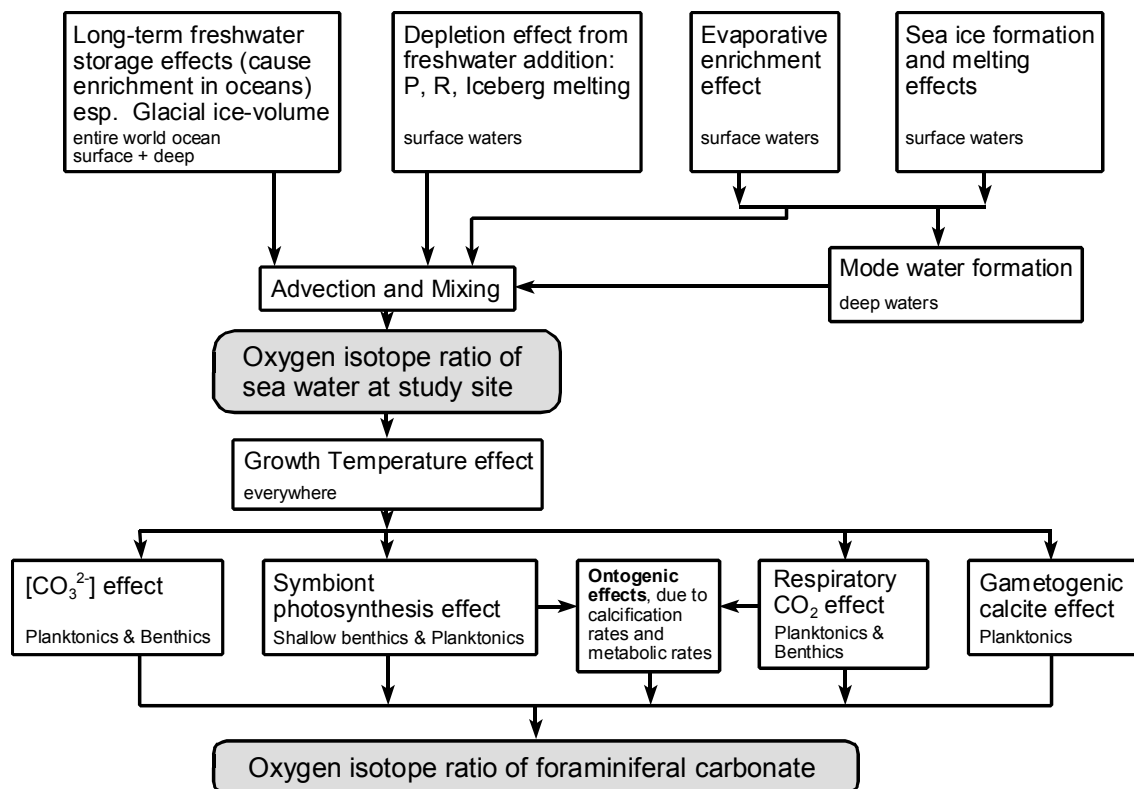
The aragonitic benthic foraminifer *Hoeglundina elegans* constructs its test with a  $\delta^{13}\text{C}$  enrichment that is constant with depth in the California borderland study area, whereas  $\delta^{13}\text{C}_{\text{DIC}}$  increases with depth (Grossman, 1984a). This may suggest a negative temperature dependence of the bicarbonate-aragonite fractionation (with temperature decrease offsetting the  $\delta^{13}\text{C}_{\text{DIC}}$  increase) (see also Grossman, 1984b; Grossman and Ku, 1986). To date, there is only very limited knowledge of the differences between fractionation associated with aragonite formation and those with calcite formation.

#### 4. Summary

**Figure 7** and **Table 2** illustrate and summarise the main processes determining sea water  $\delta^{18}\text{O}$  at any study site and those determining the fractionation between  $\delta^{18}\text{O}$  of foraminiferal carbonate and  $\delta^{18}\text{O}$  of that sea water, including typical magnitudes of the isotopic changes due to each effect. It is indicated which processes dominantly influence surface and/or deep waters, and planktonic and/or benthic foraminifera. **Figure 8** and **Table 3** are similar, for  $\delta^{13}\text{C}$ .

To investigate the main controlling processes and eliminate the noise introduced by minor ones, specific analytical strategies have been adopted in palaeoceanographic research. The vital effect is commonly considered to be species-specific, and avoided by study of monospecific records. The effects of symbiont density, gametogenic calcite formation, and changes in calcification depth during growth are avoided by analysing either thin-walled, or thick-walled, specimens of the selected species from similar ontogenic stages, using narrowly constrained size-fractions. No studies have yet established in sufficient detail the temporal changes in oceanic  $[\text{CO}_3^{2-}]$  to allow assessment of its impact on foraminiferal isotope records.

**Figure 7.** Schematic overview of the various effects involved in the determination of oxygen isotope ratios in Foraminiferal carbonate.



The ice volume effect exerts by the most important control on  $\delta^{18}\text{O}$  records, allowing both global correlations and absolute dating (Figure 1). Also very important is the influence of ambient temperature during calcification. In a 'glacial world', this influence is less relevant for deep-sea benthics, since oceanic deep-sea temperature fluctuations are unlikely to exceed 1 to 2°C. However, larger deep-sea temperature fluctuations may have prevailed in previous geological periods when the deep-sea was filled with so-called warm saline deep water, such as found today in isolated basins like the Red Sea and Mediterranean. For planktonic foraminiferal  $\delta^{18}\text{O}$  records, temperature influences are always very important. Temperature effects may be constrained

through the use of other palaeotemperature indicators, such as transfer functions or geochemical proxies (*e.g.* alkenone records).

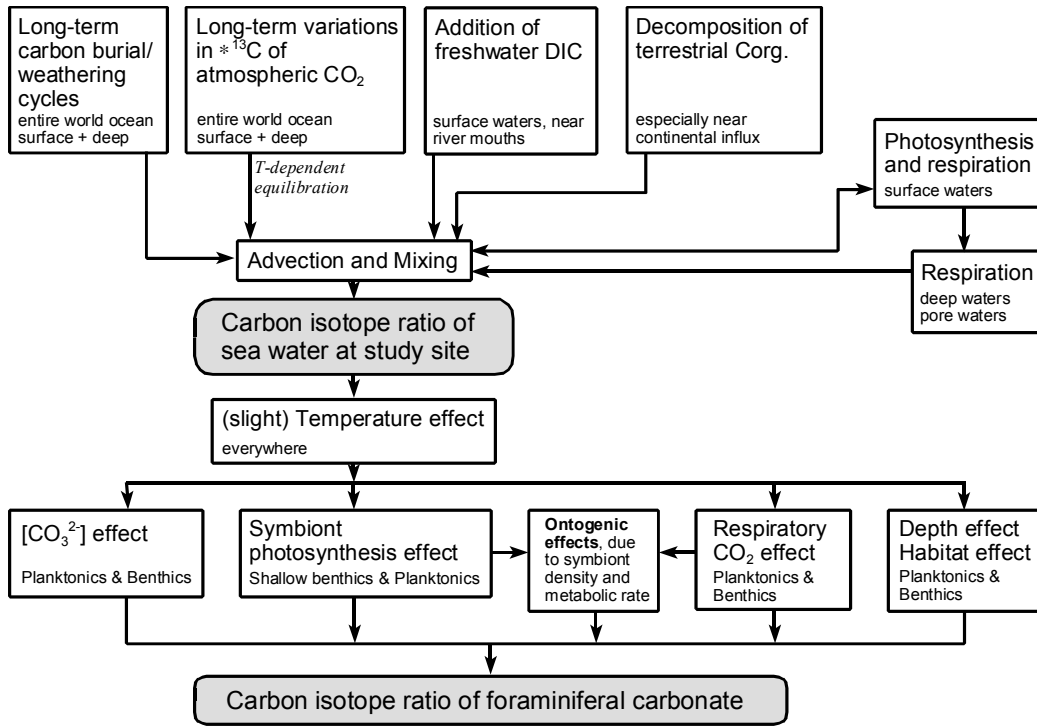
**Table 2.** Processes influencing  $\delta^{18}\text{O}$  in seawater (white) and carbonate  $\delta^{18}\text{O}$  (shaded)

<b>Oxygen isotopes</b>			
<b>Process</b>	<b>Deep/ Benthic</b>	<b>Surface/ Planktonic</b>	<b>Impact and typical magnitude</b>
evaporation; ice-volume effect	✓	✓	global; up to 2 ‰ (0.012 ‰ m <sup>-1</sup> sea level change)
evaporation; 'normal' effect	✓ <sup>(1)</sup>	✓	local; surface 1 ‰, <sup>(1)</sup> may affect deeper waters through mode water formation
precipitation	✓		local; 1 ‰
runoff		✓	local; >1 ‰ near river mouth or melting ice
sea ice freezing	✓ <sup>(1)</sup>	✓	local; surface 1 ‰, <sup>(1)</sup> may affect deeper waters through mode water formation
sea ice melting		✓	local; 1 ‰
watermass transport and mixing	✓	✓	everywhere; magnitudes under investigation
equilibrium fractionation	✓	✓	everywhere, temperature dependent; 0.2 ‰ °C <sup>-1</sup>
depth habitat / vertical migrations		✓	1 ‰ depending on local temperature gradient
microhabitat effect	✓		1 ‰ depending on local gradient in pore-water
ontogenic effects		✓	species specific < 1 ‰
photosynthetic symbiont effect		✓	species (or specimen?) specific < 1 ‰
vital effect	✓	✓	(?) < 1 ‰, not well known for Foraminifera
gametogenic calcite		✓	species (?) specific (?) < 1 ‰
changing carbonate ion concentration	✓	✓	< 1 ‰, poorly known for natural conditions

Secondary influences on benthic foraminiferal  $\delta^{18}\text{O}$  records originate from the microhabitat and  $[\text{CO}_3^{2-}]$  effects, which likely are related, but still are not fully understood/quantified. Away from sea-ice margins, secondary controls on planktonic  $\delta^{18}\text{O}$  records are exerted by local freshwater cycle effects and  $[\text{CO}_3^{2-}]$  variations. Temporal variations due to the  $[\text{CO}_3^{2-}]$  effect are not yet sufficiently known. The assumption that - through time - a systematic relationship should exist between salinity and  $\delta^{18}\text{O}$  due to action of the freshwater cycle has given rise to the term 'salinity effect'. Recent work is casting doubt on this assumption, and so on the potential to use oxygen isotopes for determination of palaeosalinity. Temporal changes in subsurface water sources, advective pathways, and mixing of watermasses appear to complicate interpretation of  $\delta^{18}\text{O}$  records, especially for planktonics.

For  $\delta^{13}\text{C}$ , the major controls are: global shifts related to changes in terrestrial vegetation and/or large-scale burial/oxidation of sedimentary organic matter; and the interrelated influences of export production, respiration at depth, and age of deep water. The global effects are established by inter-comparison of a large number of records from various locations worldwide. The export production, etc. effect may be estimated from comparison of planktonic records with benthic records for epiphytic species known to calcify near equilibrium. This approach is most successful when paired with analyses of other nutrient-proxies, such as Cd/Ca ratios. The age of deep water is assessed similarly, but in a wider geographical context.

**Figure 8.** Schematic overview of the various effects determining the carbon isotope ratios in Foraminiferal carbonate.



**Table 3.** Processes influencing  $\delta^{13}\text{C}$  in seawater (white) and carbonate  $\delta^{13}\text{C}$  (shaded)

<b>Carbon isotopes</b>			
<b>Process</b>	<b>Deep/ Benthic</b>	<b>Surface/ Planktonic</b>	<b>Impact and typical magnitude</b>
photosynthesis		✓	global, but locally variable; <1 ‰
respiration	✓	✓	local; <1 ‰
export production	--- causes	gradients ---	function of photosynthesis, respiration, ‘age’ of deep water
‘age’ of deep water	✓		along deep water path; up to >1 ‰
shifts in terrestrial vegetation	✓	✓	global; >1 ‰
burial / oxidation sedimentary organic matter	✓	✓	global; >1 ‰
equilibrium fractionation	✓	✓	everywhere; <1 ‰ to negligible (uncertain!)
depth habitat / vertical migrations		✓	up to 1 ‰ depending on local temperature gradient
microhabitat effect		✓	1 ‰ or more depending on local gradient in pore-water (very strong near gas-hydrate seepage)
growth-related effects		✓ (some)	species (or specimen ?) specific < 1 ‰
photosynthetic symbiont effect		✓	specimen specific < 1 ‰
vital effect	✓	✓	species specific < 1 ‰, not well known for Foraminifera
changing carbonate ion concentration	✓	✓	< 1 ‰, poorly known for natural conditions

Other influences on benthic foraminiferal  $\delta^{13}\text{C}$  are due to the microhabitat effect, and the  $[\text{CO}_3^{2-}]$  effect, which likely are related to one another. Seepage of clathrates may cause very strong anomalies in the  $\delta^{13}\text{C}$  values of infaunal benthic species. Additional control on planktonic foraminiferal  $\delta^{13}\text{C}$  records is exerted by  $[\text{CO}_3^{2-}]$  fluctuations through time. This effect may be important, but is not yet well quantified.

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