Problems and prospects of stable isotope applications to marine microfossils for palaeoceanography and palaeoclimate reconstruction

MANISH TIWARI AND RENGASWAMY RAMESH

Physical Research Laboratory, Ahmedabad, 380 009, India.
Email: rramesh@prl.res.in

ABSTRACT

Tiwari M & Ramesh R 2008. Problems and prospects of stable isotope applications to marine microfossils for palaeoceanography and palaeoclimate reconstruction. The Palaeobotanist 57(1-2) : 303-309.

Stable isotopes of oxygen and carbon in marine microfossils (such as Foraminifera) have been extensively applied to reconstruct past oceanographic and climatologic conditions. But great care needs to be taken while interpreting the data, as there are many factors governing the isotopic composition of the shells of microfossils. This paper is an attempt to outline and elucidate these factors with special reference to the most widely used microfossil, viz. Foraminifera.

Key-words—Foraminifera, Stable isotopes, Palaeoclimate, Arabian Sea.

पुरासमुद्रविज्ञान एवं पुराजलवायु पुनर्संरचना हेतु समुद्री सूक्ष्मजीवाश्मों के स्थायी समस्थानिक अनुप्रयोगों की समस्याएं एवं संभावनाएं

मनीष तिवारी एवं रंगास्वामी रमेश

सारांश

विगत समुद्रविज्ञान एवं जलवायु स्थितियों की पुनर्संरचनाओं में समुद्री सूक्ष्मजीवाश्मों (जैसे फोरैमिनीफेरा) में ऑक्सीजन एवं कार्बन के स्थायी समस्थानिक व्यापक रूप से अनुप्रयुक्त किए गए हैं। चूँकि सूक्ष्मजीवाश्मों की कोशिकाओं के समस्थानिक के संघटन को नियंत्रित करने वाले कई घटक हैं अतः आँकड़ों की व्याख्या करते समय ज्यादा ध्यान देने की जरुरत है। यह शोध-पत्र इन घटकों की रुपरेखा एवं अत्यंत बृहत् रुप से प्रयुक्त सूक्ष्मजीवाश्म अर्थात फोरैमिनीफेरा के विशेष संदर्भ सहित समझाने का प्रयास है।

संकेत-शब्द—फोरैमिनीफेरा, स्थायी समस्थानिक, पुराजलवायु, अरब सागर।

INTRODUCTION

TO understand the anthropogenic effect on climate, it is very necessary to understand and delineate the natural variability exhibited by climatic systems. Recorded meteorological data spans at best the past ~150 years. To retrieve the full variability we need climatic records spanning thousands of years. One of the best places to get such records is the marine sediments, which preserve various signals continuously and spanning geological time periods. At this stage, marine microfossils that get preserved in sediments enter the picture as their shells store in them the isotopic signatures of the ambient seawater with the help of which we can deduce past climatic conditions. One of such groups of microfossils is foraminifera, which has been comprehensively used for palaeoclimatic reconstruction.

FORAMINIFERA

Foraminifera are eukaryotic (possessing a distinct nucleus), unicellular (single celled, characterized by the absence of tissue or organs) organisms belonging to the Phylum Protozoa. They secrete calcium carbonate shells of incredible beauty and structural complexity, which get preserved in sea sediments as fossils. Their size ranges from 0.01 mm (10 μm) to 10 mm but the average representative size range is 0.1 mm (100 μm) to 1.0 mm. The living organism consists of protoplasm encapsulated in the shell, which is further divided into different chambers. The typical life spans of Foraminifera are 2-4 months. They are both planktonic and benthic. **Benthics** are the bottom dwelling form and have existed since the Cambrian time (~570 Ma). They may be sessile, i.e. constantly attached to the bottom or vagile, i.e. free bottom-dwelling organisms. They inhabit all depths ranging from continental shelf to abyssal plain. **Planktonic** Foraminifera float in the water column. They are more recent in origin than benthics and have existed since Jurassic (~200 Ma). Most of the planktonic species inhabit the top 150 m of the water column but their habitat can be upto 1000 m. On the basis of depth habitats, planktonic foraminifers can be grouped into three categories, viz. "Shallow-water", "Intermediate-water" and "Deep-water" dwelling species. "Shallow-water" species live predominantly in the upper 50 m of the water column, e.g. all the species of genus *Globigerinoides* and some species of *Globigerina*. "Intermediate-water" species include those that inhabit the upper 100 m but predominantly dwell in the 50-100 m of the water column. "Deep-water" group consist of those species, which live in the euphotic zone as the juveniles, and predominantly below 100 m as adults, e.g. all the species of genus *Globorotalia* (Bé, 1977).

ISOTOPIC PROXIES STUDIED IN MICROFOSSILS

The variations in the physical and chemical properties due to the presence of different isotopes (the so called "isotope effect") arise due to very small, albeit finite mass differences among them. These differences are most significant for lighter elements such as hydrogen, carbon, nitrogen, oxygen, etc. Urey (1947) was the first to explain the variations in physico-chemical properties in isotopic systems on the basis of thermodynamic considerations and proposed that a palaeotemperature scale can be constructed based on the fractionation of oxygen isotopes in the calcites. The absolute abundances of minor isotopes as well as absolute values of isotope ratios cannot be determined precisely enough for geochemical purposes. Moreover to aid the measurements in mass spectrometers, the isotope abundances are reported in "δ" values, which are relative differences of isotopic ratios from an international standard expressed in per mil (‰) units:

$$\delta_A = [\,(R_A/R_{st}) - 1\,] \times 10^3 \text{‰}$$

Where,

R_A is the ratio of the abundances of the less abundant (heavier, e.g. ^{18}O) to more abundant (lighter, e.g. ^{16}O) isotope of the element in the sample, and

R_{st} is the ratio of the abundances of less abundant (heavier) to more abundant (lighter) isotope of the element in the standard (e.g. $^{18}O/^{16}O$ in the standard)

For oxygen isotopic studies of foraminifera PDB is used as the international standard. It is a carbonate obtained from fossilized rostrum (cigar shaped internal shell) of *Belemnitella americana*, a belemnite (an extinct cephalopod) from the Peedee Formation of Cretaceous Period in South Carolina, USA.

OXYGEN ISOTOPES

Oxygen has three stable isotopes, viz. ^{16}O, ^{17}O and ^{18}O with 99.763%, 0.0375% and 0.1995% abundances respectively. The fractionation (defined as the relative partitioning of the heavier and lighter isotopes between two co-existing phases) of these isotopes in nature is caused by an equilibrium or kinetic process. **Kinetic fractionation** is associated with incomplete and unidirectional processes such as evaporation, diffusion, biologically mediated reactions, etc. No isotopic equilibrium is attained in this case. **Equilibrium fractionation** is a special case of chemical equilibrium reaction in which there is no net reaction but an exchange of isotopes takes place. In this case isotopes can move to and fro and equilibrium is attained when there is no more change in the isotopic ratios with time. The fractionation is temperature dependent in such a way that calcites precipitated from water of constant isotopic composition but at different temperatures will possess different $^{18}O/^{16}O$ ratios. This is the basis for the palaeotemperature scale, by which various empirical palaeotemperature equations are deduced. The overall effect is that approximately 0.25‰ depletion in carbonate $\delta^{18}O$ occurs for every 1°C temperature increase (Erez & Luz, 1983). The palaeotemperature equation is given below:

$$T\,(^\circ C) = 17.0 - 4.52\,(\delta^{18}O_c - \delta^{18}O_w) + 0.03\,(\delta^{18}O_c - \delta^{18}O_w)^2$$

T, $\delta^{18}O_c$, $\delta^{18}O_w$, are the estimated temperature (°C), the isotopic composition of the shell carbonate and the seawater respectively.

To apply this equation we must know the $\delta^{18}O$ value of the seawater with which a given specimen of $CaCO_3$ has equilibrated. This is not easy to establish with certainty because the isotopic composition of seawater as a whole depends on the amount of ice stored on the continents, which gives rise to the so called "ice-volume effect". When water evaporates from the ocean surface, the water vapour gets enriched in the lighter isotopes, as vapour pressure of $H_2^{16}O$

^{13}C	^{18}O	^{13}C	^{18}O	^{13}C	^{18}O	^{13}C	^{18}O
1.98	-2.26	2.05	-2.07	1.94	-2.12	1.99	-2.11
2.04	-2.21	2.06	-2.03	1.92	-2.30	1.98	-2.14
1.99	-2.35	2.05	-2.02	2.10	-1.78	1.96	-2.17
1.90	-2.45	2.01	-2.21	1.98	-1.89	1.87	-2.17
1.92	-2.63	1.93	-2.44	1.97	-2.03	1.87	-2.25
1.84	-2.32	2.01	-2.14	2.02	-2.08	2.09	-1.79
1.95	-2.35	2.04	-2.00	1.96	-2.05	1.90	-2.15
1.96	-2.47	1.92	-2.32	1.96	-2.06	1.92	-1.87
1.92	-2.49	1.97	-2.29	2.03	-1.92	1.97	-2.25
1.99	-2.36	2.08	-1.98	2.22	-2.17	2.03	-1.97
1.92	-2.30	2.03	-1.96	2.18	-2.07	1.92	-2.16
2.03	-2.08	1.90	-2.24	2.25	-1.96	1.94	-2.11
2.10	-1.77	1.81	-2.51	2.07	-2.13	1.97	-2.00
2.03	-2.12	1.89	-2.26	1.94	-2.09	1.85	-2.19
2.06	-1.89	1.89	-2.32	2.04	-2.22	1.95	-2.17
1.99	-2.00	1.82	-2.34	1.99	-2.31	2.02	-2.00
2.11	-1.85	1.98	-2.22	2.12	-2.14	1.88	-2.22
1.98	-2.12	2.09	-1.73	2.06	-2.35	1.94	-2.09
1.99	-2.09	2.04	-1.90	2.02	-2.43		
1.99	-1.93	2.04	-2.11	2.02	-2.21		
2.00	-1.86	2.00	-2.03	2.00	-2.25		
2.05	-2.05	1.81	-1.94	2.08	-1.96		
2.08	-1.92	2.06	-1.89	2.03	-2.08		
1.90	-2.32	2.03	-2.01	1.98	-2.15		
1.90	-2.35	2.02	-1.95	1.84	-2.36		
2.07	-1.76	1.99	-2.06	1.98	-2.12		
2.08	-1.95	1.96	-2.08	2.02	-2.22		
2.10	-1.82	2.03	-2.00	1.95	-2.24		
2.10	-1.88	2.00	-1.97	1.97	-2.19		
2.06	-2.09	2.09	-1.94	1.95	-2.31		
2.06	-1.88	1.93	-2.13	2.04	-1.87		
2.03	-1.94	1.99	-1.91	2.03	-2.01		
2.10	-1.70	2.01	-1.91	2.17	-1.96		
2.07	-1.86	2.01	-2.03	1.98	-2.12		
2.06	-1.81	1.99	-2.20	1.97	-2.15		
2.06	-1.75	2.06	-1.90	2.08	-1.76		
2.07	-1.87	2.00	-1.88	1.92	-2.08		
2.06	-1.82	1.93	-2.25	1.98	-1.94		
2.07	-1.83	1.79	-1.89	1.89	-2.28		

Mean ^{13}C = 2.00 ± **0.08**; Mean ^{18}O = -2.09 ± **0.19**, total no. of measurements=135
(numbers in bold denote single standard deviation, 1•)

Fig. 1—Z-Carrara (internal laboratory standard) d^{13}C and d^{18}O values with respect to PDB in per mil, measured from 19.7.2003 to 4.4.2004.

is more than H$_2$$^{18}O$. Kinetic effects also take place that further depletes the vapour phase in the heavier isotope. As more and more evaporation takes place and as this isotopically lighter water gets locked in the form of continental ice sheets, the remaining ocean water gets more and more enriched in the heavier isotope. It is believed that during the LGM (Last Glacial Maximum; ~21,000 calendar years BP) the average seawater $\delta^{18}O$ was 1.2 ‰ heavier than present (Fairbanks, 1989).

The depletion of heavier isotope in freshwater gives rise to the correlation of salinity with $\delta^{18}O$. As evaporation takes place, the salinity as well as $\delta^{18}O$ of the seawater increases. In the Arabian Sea it has been found that 1‰ increase in salinity causes a 0.33 ‰ increase in $\delta^{18}O$ of water (Duplessy et al., 1981, Sarkar et al., 2000). Separately analyzing planktonic and benthic foraminifera from the same site can help to resolve the

ice volume effect. The $\delta^{18}O$ values of the planktonics reflect the changes in both the temperature as well as $\delta^{18}O$ of water whereas the bottom water is mostly believed to be unaffected by the temperature changes, hence the benthics could record only the change in the isotopic composition of seawater.

There are several effects associated with the biology of foraminifera that cause deviation from the equilibrium. Isotopic disequilibrium effects can be classified as either metabolic or kinetic (McConnaughey, 1989 a, b). Metabolic effects result from the incorporation of dissolved carbon and oxygen produced due to respiration or photosynthesis into the shell material. Kinetic effects are due to the preferential uptake of lighter isotopes during the hydration and hydroxylation of CO$_2$ and are generally associated with rapid calcification. These effects, collectively called "vital effects", include effects due

to respiration, ontogeny, secretion of gametogenic calcite, etc. The respiration products are depleted in the heavier isotopes (Lane & Doyle, 1956) and their utilization for shell secretion results in depleted $\delta^{18}O$ values. Progressive $\delta^{18}O$ enrichment from juvenile to mature chambers has been observed and is assigned to the incorporation of the respired CO_2 during early calcification. The higher metabolic rates in the juvenile specimen would cause the strongest depletions, which then decreases in the adult specimen that has reduced metabolism (Berger *et al.*, 1978; Wefer & Berger, 1991). Furthermore, planktonic foraminifera inhabit different depths at various stages of their ontogeny. In the later part of their lifecycles they tend to secrete shells at deeper and cooler waters resulting in enhanced $\delta^{18}O$ values (Bouvier-Soumagnac & Duplessy, 1985; Emiliani, 1971). Towards the end of their life cycle foraminifera secrete gametogenic calcite. Before gamete release, foraminifera move to deeper, cooler waters and secrete a layer of calcite that is enriched in $\delta^{18}O$ over its shell. This calcite layer can comprise 18 to 28% of the shell mass of foraminifera (Bé, 1980; Duplessy *et al.*, 1981). Furthermore $\delta^{18}O$ has been found to vary with varying light intensities (photosynthetic activities in the symbiont carrying foraminifera) and carbonate ion concentrations. The $\delta^{18}O$ was found to decrease with increasing irradiance that caused enhanced photosynthesis. Enhanced rate of skeletogenesis ensues increased photosynthesis that favours stronger kinetic fractionation resulting in depleted $\delta^{18}O$ (Spero & Lea, 1993; Wefer & Berger, 1991). $\delta^{18}O$ in foraminiferal carbonate decreases with increasing carbonate ion concentration that was ascribed to a-biological, kinetic fractionation effect (Spero *et al.*, 1997) as it was also observed in rapidly precipitating inorganic $CaCO_3$ (McCrea, 1950). The disequilibria due to vital effects can be avoided by choosing the particular species, which are known to precipitate their shells in equilibrium with seawater and by picking mature shells from a particular size range. Also diagenetic alteration after the death of the organism can modify its isotopic composition significantly. The $\delta^{18}O$ values of planktonic foraminifera from warm subtropical seas are particularly sensitive to alteration as the secondary calcite precipitates in equilibrium with the cold pore fluids at the sediment-water interface (Schrag, 1999). Also shells may get recrystallized at the micron scale (preserving the shell features and ornamentation) unlike the previous case in which euhedral calcite crystals precipitate on the outer and inner surfaces of the shell (Pearson *et al.*, 2001). This obstacle can be overcome by selecting pristine shells, which appear glassy under the microscope and are without any overgrowths.

CARBON ISOTOPES IN FORAMINIFERA

Carbon has two stable isotopes, viz. ^{12}C and ^{13}C with an abundance of 98.89% and 1.11% respectively. Kinetic isotope effects during photosynthesis cause preferential uptake of ^{12}C in the organic matter. Phytoplanktons prefer lighter isotope (^{12}C) during photosynthesis enriching the ambient surface seawater in the heavier isotope (^{13}C). The organisms secreting calcareous shells (such as foraminifera) in equilibrium with the ambient water will record these isotopic signatures. Thus the higher $\delta^{13}C$ value of the $CaCO_3$ of the organism's shell could correspond to an enhanced rate of photosynthesis in the euphotic layer that may indicate an increase in productivity.

As $\delta^{13}C$ has a steep gradient in the water column so the species secreting their shells at different depths in equilibrium with the ambient water during their ontogeny will exhibit deviation from the surface seawater equilibrium values (Kroopnick *et al.*, 1972). Disequilibria in the $\delta^{13}C$ values are caused by vital effect as discussed in the case of oxygen isotopes (see Sec. 2.4.1). Respiration products are depleted in heavier isotopes, the incorporation of which causes depletion relative to equilibrium (Weber & Woodhead, 1970; Vinot-Bertouille & Duplessy, 1973; Grossman, 1987). Higher metabolic rates have been found to cause increased depletion in $\delta^{13}C$ values (Wefer & Berger, 1991; Oritz *et al.*, 1996). Symbionts present in the foraminifera carry out photosynthesis in which they preferentially utilize the lighter isotope. With increased irradiance photosynthesis also increases resulting in enhanced $H^{13}CO_3^-$ in the ambient microenvironment, resulting in chambers enriched in $\delta^{13}C$ (Spero & Lea, 1993). $\delta^{13}C$ in foraminiferal carbonate decreases with increasing carbonate ion concentration similar to the effect experienced by $\delta^{18}O$ that was ascribed to be a-biological, kinetic fractionation effect (Spero *et al.*, 1997). Diagenetic alteration at the sediment-water interface or beneath the sediments will shift $\delta^{13}C$ values toward the lighter side as degradation of organic matter produces ^{12}C depleted CO_2 making the ambient water depleted in the heavier isotope.

To avoid the above-mentioned problems as far as possible, pristine foraminifera from a certain size range should be chosen. For further information, please look at the excellent review article by Rohling and Cooke (1999).

PRECISION OF MEASUREMENTS: $\delta^{13}C$ AND $\delta^{18}O$ OF FORAMINIFERA

Precision deals with estimating that how well the same value is reproduced in repeated measurements (i.e. what is the deviation from the mean) and is estimated by calculating the standard deviation. In isotopic measurements involving mass spectrometers, it is mainly of two types, viz. "internal" and "external". Internal precision provides an estimate of the reproducibility by the mass spectrometer itself without involving the sample (i.e. CO_2 gas) preparation procedure. The gas once injected into the mass spectrometer is measured repeatedly. The typical value of internal precision for $\delta^{13}C$ and $\delta^{18}O$ comes out to be ±0.01‰. For this purpose "Check Standard", which is CO_2 gas with values already determined by repeated measurements (e.g. the check standard used by us has $\delta^{13}C$ and $\delta^{18}O$ values of 0.33‰ and 2.33‰ with respect

S. No.	Sample Name Core name (Depth, in cm)	Globigerinoides ruber (in ‰)		Globigerinoides sacculifer (in ‰)		Globorotalia menardii (in ‰)	
		$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
1.	SK 145-9 (0-2)	1.37	-3.38			1.09	-1.69
		1.83	-3.38			1.64	-1.21
		1.17	-3.04				
2.	SK 145-9 (2-3)	0.82	-3.41	1.76	-2.71		
		0.93	-3.53	1.68	-2.65		
3.	SK 145-9 (9-10)					1.26	-1.94
						1.11	-1.84
4.	SK 145-9 (18-19)			1.92	-2.67		
				1.93	-2.76		
5.	SK 145-9 (25-26)					1.26	-1.12
						1.47	-1.20
6.	SK 145-9 (39-40)			2.46	-1.89		
				2.16	-1.91		
7.	SS 3827 (1-2)			1.84	-2.35		
				1.73	-2.73		
8.	SS 3827 (4-5)	2.13	-4.70				
		1.32	-4.61				
9.	SS 3827 (6-7)	1.53	-2.57				
		1.87	-2.03				
10.	SS 3827 (7-8)			1.78	-2.63		
				1.86	-2.67		
				2.06	-2.70		
11.	SS 3827 (25-26)	1.25	-2.47	1.67	-2.07	1.18	-0.32
		1.07	-2.56	1.92	-2.11	1.13	-0.80
12.	SS 3827 (37-38)			1.88	-0.93		
				1.69	-0.67		
13.	SS 3827 (50-51)	1.19	-1.89				
		1.12	-1.02				
14.	SS 3827 (59-60)	1.30	-1.03				
		1.37	-0.84				
15.	SS 3827 (60-61)	1.16	-0.87				
		1.18	-0.82				
16.	SS 3827 (74-75)	1.32	-1.83	2.04	-1.18		
		1.34	-1.98	1.94	-1.42		
17.	SS 3827 (77-78)	1.21	-2.10	1.96	-2.02		
		1.29	-2.09	1.64	-1.59		
18.	SS 3827 (90-91)	1.48	-1.01	1.91	-0.91	1.47	-0.19
		1.39	-1.36	1.89	-0.93	1.53	0.38
19.	SS 4018 (2-4)			1.31	-4.44		
				1.20	-4.95		
20.	SS 4018 (10-12)	1.07	-1.93				
		1.30	-1.97				
21.	SS 4018 (36-38)			1.93	-1.44		
				1.82	-1.48		
22.	SS 4018 (38-40)	1.05	-1.95	1.70	-1.60		
		1.21	-1.98	1.57	-1.53		
		1.16	-1.72	1.61	-1.13		
23.	SS 4018 (52-54)	1.31	-1.66				
		0.84	-1.53				

Fig. 2— $\delta^{13}C$ and $\delta^{18}O$ values of three different species of foraminifera with respect to PDB in per mil, measured from July, 2003 to August, 2004.

to PDB), is used. Thus it also helps in determining the stability of the mass spectrometer, i.e. whether the machine is yielding correct numbers or not. External precision, on the other hand, estimates the deviation from the mean value after taking into account the sample preparation procedure, i.e. evolution of CO_2 from calcitic sample. It is determined by three measurements of a laboratory standard (Z-Carrara, a marble powder, $\delta^{18}O$ and $\delta^{13}C$ values of which have been determined by repeated measurements to be -2.11‰ and 2.11‰ respectively) daily. The typical value of external precision for $\delta^{18}O$ for daily measurements is ±0.1‰ and for the year-long

measurements, it is ±0.2‰ whereas for $\delta^{13}C$, it is ±0.05‰ (daily measurements) and ±0.1‰ (year-long measurements) (Fig. 1).

To obtain a good precision, following precautions should be taken:

(i) CO_2 is extracted from the purified carbonate by the acid decomposition of the carbonate with 100% phosphoric acid as shown:

$$3CaCO_3 + 2H_3PO_4 \rightarrow 3CO_2 + 3H_2O + Ca_3(PO_4)_2$$

This reaction shows that only two-thirds of the carbonate oxygen is liberated in the product CO_2. Many precautions have to be taken to follow the acid decomposition technique
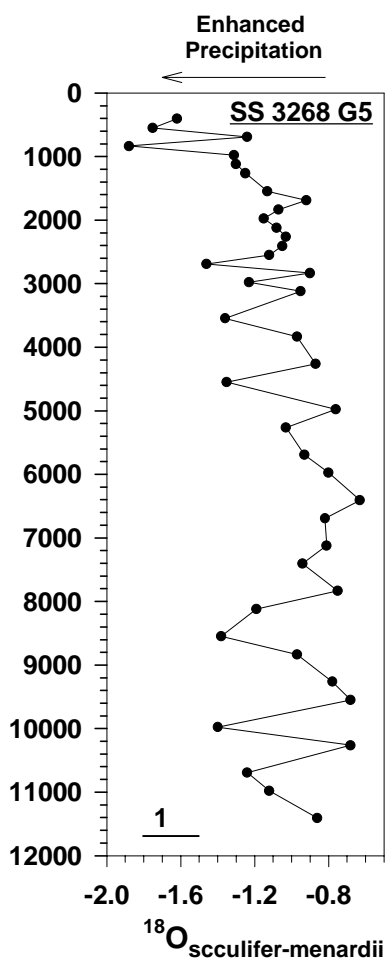
Fig. 3—Differences in the $\delta^{18}O$ value of the two species, viz. *Gs. sacculifer* and *Gr. menardii* in the core SS 3268 G5. The bar at the lower left hand corner represents the error, i.e. ±0.3‰ (1σ).

during acid decomposition at 25°C is 1.01025 (Rosenbaum & Sheppard, 1986).

(iii) Reaction time, i.e. the time allowed for acid decomposition to take place should be kept uniform. Even if there is any contamination due to microscopic leak, etc. it will be equal for all the samples and standard and can be corrected later.

(iv) Sample preparation system and mass spectrometer should be clean, i.e. no impurity should be present that can exchange isotopes with the sample gas. Further care should be taken that the needle in the acid dropping system, which sucks in the sample gas, should not get obstructed (special attention is required when treating powdered samples from corals, etc.).

(v) Lastly, there should be no moisture (H_2O) adsorbed inside the tubes of mass spectrometer or else isotopic exchange with it will widely fluctuate the $\delta^{18}O$ values.

Beyond the quoted external precision, there may be significant variability in the mean $\delta^{18}O$ and $\delta^{13}C$ values measured on a set of 30 foraminifera of the same species from the same depth interval in a sediment core. This has been determined by repeated measurements. The results are shown in Fig. 2.

As evident from the Fig. 2, in most of the cases the overall precision for a full year is ±0.2‰ for $\delta^{18}O$ and $\delta^{13}C$ with respect to PDB. However in some cases it reaches upto ±0.3‰ because foraminifera might have grown at different depths or during different seasons.

NEW WAYS OF INTERPRETING OXYGEN AND CARBON ISOTOPIC DATA

It is sometimes more useful to look at the differences in $\delta^{18}O$ or $\delta^{13}C$ values of foraminifera living at different water depths (i.e. $\Delta^{18}O$ or $\Delta^{13}C$) rather than the absolute values. For example, the foraminiferal species such as *Globigerinoides ruber*, *Globigerinoides sacculifer* and *Globorotalia menardii* dwell at different water depths. *Gs. ruber* and *Gs. sacculifer* are surface dwelling species predominantly inhabiting top 25 m and 50 m respectively whereas *Gr. menardii* is a deeper dwelling species predominantly inhabiting 100-150 m [Bé, 1977; Fairbanks *et al.*, 1982].

The $\Delta^{13}C$ value between the surface and deeper water dwelling species ($\Delta^{13}C_{sur-dep}$, i.e. differences in $\delta^{13}C$ values of *Gs. ruber* or *Gs. sacculifer* and *Gr. menardii*) can illuminate the water column stratification. As discussed earlier $\delta^{13}C$ value is an indicator of productivity (higher $\delta^{13}C$ values depict enhanced productivity). The sea surface is depleted in nutrients due to consumption by microorganisms whereas the deeper layers (~150-200 m) have abundant nutrients due to the oxidation of the organic matter. These nutrients are injected into the photic zone *via* upwelling or wind induced mixing of the water column. When the water column is well mixed, it is

to obtain good reproducibility (precision). The salt produced ($Ca_3(PO_4)_2$) should be soluble in the solution produced by the interaction of the acid with the carbonate, or else a protective covering will form on the latter that will inhibit further reaction. Also, the acid should not produce radicals in the mass range 44-46 (the dominant mass range of CO_2 species), which excludes nitric acid (HNO_3) that decomposes to form nitrous oxide (NO_2). Most importantly, isotopic exchange between water and CO_2 is known to take place that necessitates an acid that has no free water. For these reasons, orthophosphoric acid is chosen as it has an extremely low vapour pressure and also the concentration of water is very low in comparison to other acids. The acid is prepared following Coplen *et al.* (1983). We used the mass spectrometer "Europa–Scientific GEO 20–20 stable isotope ratio mass spectrometer" with an attached Carbonate Preparation System (CAPS).

(ii) The temperature of the reaction should be kept constant as the fractionation factor varies with temperature. The oxygen isotopic fractionation factor for CO_2-calcite system

isotopically homogenized and $\Delta^{13}C_{sur-dep}$ will be less. On the other hand, when water column is stratified due to reduced upwelling or wind strength, the nutrient supply to the surface layers will be hindered; but nutrients can be supplied *via* surface run-off, which will enhance the productivity and hence $\Delta^{13}C$ of the surface dwelling foraminifera will be higher than that of the deeper dwelling one. In such a case $\Delta^{13}C_{sur-dep}$ will be more and will depict episodes of water column stratification.

Similarly $\Delta^{18}O_{sur-dep}$ can also help in demarcating various properties of seawater column. For example, eastern Arabian Sea receives large amount of fresh water as surface run off from Western Ghats during Southwest Monsoon (SWM), which reduces the sea surface salinity (SSS) and is depleted in heavier isotope of oxygen (in the way that for every per mil decline in SST, the $\delta^{18}O$ value reduces by 0.33‰, Sarkar *et al.*, 2000). This isotopically lighter water will have more effect on the surface dwelling foraminiferal species (*Gs. ruber* or *Gs. sacculifer*) as compared to the deeper dwelling species (*Gr. menardii*). During periods of intense SWM, the difference in $\delta^{18}O$ values between the surface and deeper dwelling species will be more, i.e. $\Delta^{18}O_{sur-dep}$ will be more than the arid episodes. For example, Sarkar *et al.* (2000) analyzed a core (SS 3268 G5) from the eastern Arabian Sea, off the Mangalore Coast (600 m water depth) and reported the $\delta^{18}O$ values for surface dwelling *Gs. sacculifer* and deeper dwelling *Gr. menardii*. We have calculated the difference between the $\delta^{18}O$ values of the two species as shown in the Fig. 3.

As evident from the Fig. 3, there are various peaks on multi-centennial time scales, but they fall within the error range. But it is also clear that in the Late Holocene, the precipitation enhanced as evident from the increasing trend observed in $\Delta^{18}O_{sacculifer-menardii}$.

REFERENCES

Bé AWH 1977. An Ecological, Zoogeographic and Taxonomic Review of Recent Planktonic Foraminifera. *In*: Ramsey ATS (Editor)—Oceanic Micropaleontology, Academic Press, London: 1-100.

Bé AWH 1980. Gametogenic calcification in a spinose planktonic foraminifer, *Globigerinoides sacculifer* (Brady). Marine Micropaleontology 5: 283-310.

Berger WH, Killingley JS & Vincent E 1978. Stable isotopes in deep carbonates: box core ERDC-92, West equatorial Pacific. Oceanologica Acta: 203-216.

Bouvier-Soumagnac Y & Duplessy JC 1985. Carbon and isotopic composition of planktonic foraminifera from the laboratory culture, plankton tows and recent sediment: implications for the reconstruction of paleoclimatic conditions and of the global carbon cycle. Journal of Foraminiferal Research 15: 302-320.

Coplen TB, Kendall C & Hopple J 1983. Comparison of stable isotope reference samples. Nature 302: 236-238.

Duplessy JC, Bé AWH & Blanc PL 1981. Oxygen and carbon isotopic composition of planktonic foraminifera in the Indian Ocean. Palaeogeography Palaeoclimatology Palaeoecology, 33: 9-46.

Emiliani C 1971. Depth habitats of the growth stages of pelagic foraminifera. Science 173: 1122-1124.

Erez J & Luz B 1983. Experimental palaeotemperature equation for planktonic foraminifera. Geochimica et Cosmochimica Acta 47: 1025-1031.

Fairbanks RG, Sverdlove M, Free R, Wiebe PH & Bé AWH 1982. Vertical distribution and isotopic fractionation of living planktonic foraminifera from the Panama Basin. Nature 298: 841-844.

Fairbanks RG 1989. A 17,000-year glacio-eustatic sea level record: influence of glacial melting rates on the Younger Dryas event and deep ocean circulation. Nature 342: 637-642.

Grossman EL 1987. Stable isotopes in modern benthic foraminifera: a study of vital effects. Journal of Foraminiferal Research 17: 48-61.

Kroopnick P, Weiss RF & Craig H 1972. Total CO_2, ^{13}C, dissolved oxygen – ^{18}O at GEOSECS II in the north Atlantic. Earth and Planetary Science Letters 16: 103-110.

Lane GA & Doyle M 1956. Fractionation of oxygen isotopes during respiration. Science 123: 574-576.

McConnaughey T 1989a. ^{13}C and ^{18}O disequilibrium in biological carbonates.1. Patterns. Geochimica et Cosmochimica Acta 53: 151-162.

McConnaughey T 1989b. ^{13}C and ^{18}O disequilibrium in biological carbonates. 2. In vitro simulation of kinetic isotope effects. Geochimica et Cosmochimica Acta 53: 163-171.

McCrea JM 1950. The isotopic chemistry of carbonates and a paleotemperature scale. Journal of Chemical Physics 18: 849-857.

Oritz JD, Mix AC, Rugh W, Watkins JM & Collier RW 1996. Deep dwelling planktonic foraminifera of the northeastern Pacific Ocean reveal environmental control of oxygen and carbon disequilibria. Geochimica et Cosmochimica Acta 60: 4509-4523.

Pearson PN, Ditchfield PW, Singano J, Harcourt-Brown KG, Nicholas JC, Olsson RK, Shackleton NJ & Hall MA 2001. Warm tropical sea surface temperatures in the Late Cretaceous and Eocene epochs. Nature 413: 481-487.

Rohling EJ & Cooke S 1999. Stable oxygen and carbon isotopes in foraminiferal carbonate shells. *In*: Sengupta BK (Editor)—Modern Foraminifera, Kluwer Academic Publications: 239-258.

Rosenbaum J & Sheppard SMF 1986. An isotopic study of siderites, dolomites and ankerites at high temperature. Geochimica et Cosmochimica Acta 50: 1147-1150.

Sarkar A, Ramesh R, Somayajulu BLK, Agnihotri R, Jull AJT & Burr GS 2000. High resolution Holocene monsoon record from the eastern Arabian Sea. Earth and Planetary Science Letters 177: 209-218.

Schrag DP 1999. Effects of digenesis on the isotopic record of late paleogene tropical sea surface temperatures. Chemical Geology 161: 215-224.

Spero HJ & Lea DW 1993. Intraspecific stable isotope variability in the planktic foraminifera *Globigerinoides sacculifer*: results from laboratory experiments. Marine Micropaleontology 22: 221-234.

Spero HJ, Bijma J, Lea DW & Bemis BE 1997. Effect of seawater carbonate concentration on foraminiferal carbon and oxygen isotopes. Nature 390: 497-500.

Urey HC 1947. The thermodynamic properties of isotopic substances. Journal of Chemical Society, 1947: 562-581.

Vinot-Bertouille AC & Duplessy JC 1973. Individual isotopic fractionation of carbon and oxygen in benthic foraminifera. Earth and Planetary Science Letters 18: 247-252.

Weber JN & Woodhead PJJ 1970. Carbon and oxygen isotope fractionation in the reef building corals. Chemical Geology 6: 93-117.

Wefer G & Berger WH 1991. Isotope paleontology: growth and composition of extant calcareous species. Marine Geology 100: 207-248.