

## EVALUATION OF TWO GENERA OF BENTHIC FORAMINIFERA FOR DOWN-CORE PALEOTEMPERATURE STUDIES IN THE WESTERN SOUTH ATLANTIC

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### ABSTRACT

In this study we have compared the oxygen isotopic composition of two genera of benthic foraminifera (*Uvigerina* and *Cibicidoides*) from core-top samples with modern oxygen isotopic composition of seawater ( $\delta^{18}\text{O}_w$ ). Based on a new relationship between  $\delta^{18}\text{O}_w$  and salinity for the mid-latitude western South Atlantic, we estimated the isotopic composition of equilibrium calcite ( $\delta^{18}\text{O}_{eq}$ ) using two different equations: (1) O'Neil *et al.* (1969), modified by McCorkle *et al.* (1997) and (2) Kim & O'Neil (1997). When using (1), the small difference between  $\delta^{18}\text{O}_{eq}$  and  $\delta^{18}\text{O}$  of *Uvigerina* suggests that this genus precipitates its shell close to equilibrium with ambient seawater. The  $\delta^{18}\text{O}$  *Cibicidoides* data are 0.82 ‰ lower than the predicted (equilibrium) oxygen isotopic composition. Conversely, using (2) the *Cibicidoides*  $\delta^{18}\text{O}$  data show excellent agreement with the oxygen isotopic composition predicted from  $\delta^{18}\text{O}$  and water temperature while *Uvigerina*  $\delta^{18}\text{O}$  data are 0.69 ‰ higher than predicted oxygen isotope equilibrium values. Based on the evidences presented here and on the results from previous studies we suggest using the genus *Cibicidoides* and applying Kim & O'Neil's (1997) equation for down-core paleotemperature investigations. In the absence of enough *Cibicidoides* specimens we suggest using *Uvigerina*  $\delta^{18}\text{O}$  data and applying a correction factor of -0.69 ‰.

### RESUMO

Neste estudo, compara-se a composição de isótopos de oxigênio de dois gêneros de foraminíferos bentônicos (*Uvigerina* e *Cibicidoides*) de amostras de topo de testemunho com a composição isotópica moderna da água do mar ( $\delta^{18}\text{O}_w$ ). Baseados em uma nova relação entre  $\delta^{18}\text{O}_w$  e salinidade para a latitude média do Atlântico Sul ocidental, estimou-se a composição isotópica da calcita em equilíbrio ( $\delta^{18}\text{O}_{eq}$ ) a partir de duas equações diferentes: (1) O'Neil *et al.* (1969), modificada por McCorkle *et al.* (1997) e (2) Kim & O'Neil (1997). Utilizando (1), a pequena diferença entre  $\delta^{18}\text{O}_{eq}$  e  $\delta^{18}\text{O}$  de *Uvigerina* sugere que este gênero precipita as suas testas próximo ao equilíbrio com a água. Já os dados de  $\delta^{18}\text{O}$  de *Cibicidoides* são 0,82 ‰ menores que a composição isotópica prevista. Ao contrário, utilizando (2) os dados de  $\delta^{18}\text{O}$  de *Cibicidoides* mostram uma concordância excelente com a composição isotópica esperada, enquanto que os dados de  $\delta^{18}\text{O}$  de *Uvigerina* são 0,69 ‰ maiores que os valores de equilíbrio previstos. A partir das evidências apresentadas neste trabalho e em estudos prévios sugerimos a utilização do gênero *Cibicidoides* e a aplicação da equação de Kim & O'Neil (1997) para pesquisas de paleotemperatura. Na ausência de suficientes espécimens de *Cibicidoides* sugerimos a utilização de  $\delta^{18}\text{O}$  de *Uvigerina* aplicando um fator de correção de -0,69 ‰.

*Descriptors:* Benthic foraminifera, Oxygen isotopes, Palaeoceanography, Paleothermometry.

*Descritores:* Foraminíferos bentônicos, Isótopos de oxigênio, Paleoceanografia, Paleotermometria.

## INTRODUCTION

The isotopic and elemental studies of benthic foraminifera species are fundamental to the knowledge of the circulation and chemistry of the oceans in the past, and are used to reconstruct variations in the models of intermediate and deep water circulation and their intensity in terms of glacial-interglacial oscillations. Glacial-interglacial fluctuations of foraminifera  $\delta^{18}\text{O}$  combine signs of changing temperature and changing  $\delta^{18}\text{O}$  of seawater ( $\delta^{18}\text{O}_w$ ) (Shackleton, 1967). The cyclical variations of benthic foraminifera  $\delta^{18}\text{O}$  values through time permit the determination of a stratigraphic time scale, from which it is possible to correlate different sediment cores. Because the  $\delta^{18}\text{O}$  of calcite ( $\delta^{18}\text{O}_c$ ) increases as calcification temperatures decrease, the  $\delta^{18}\text{O}$  in foraminifera can be used as a paleothermometer (Emiliani, 1955). Several paleotemperature equations have been proposed based on the oxygen isotopic composition of calcium carbonate. McCrea (1950) produced the first empirical relationship between temperature and  $\delta^{18}\text{O}$  for inorganically precipitated calcite. Epstein *et al.* (1953) calibrated the equation for mollusks precipitating their shells at known temperatures, showing the potential for paleothermometry of oxygen isotopes of biogenically precipitated calcite. Some improvements in the equation for mollusks were made by Craig & Gordon (1965) and in the equation based on calcite precipitated inorganically at temperatures of 0°-500°C by O'Neil *et al.* (1969). Based on the analysis of the oxygen isotopic composition of the benthic foraminifera *Uvigerina*, Shackleton (1974) suggested a linearization of the low temperature (<16.9°C) portion of the relationship originally proposed by O'Neil *et al.* (1969). The first paleotemperature equation developed for planktonic foraminifera was proposed by Erez & Luz (1983) based on laboratory culture experiments. Later, Kim & O'Neil (1997) re-examined the temperature- $\delta^{18}\text{O}$  relationship for inorganically precipitated calcite at low temperatures (10°-40°C) and proposed a new expression. Bemis *et al.* (1998) reassessed  $\delta^{18}\text{O}$  data for planktonic foraminifera and revised the available paleotemperature equations.

According to the equations proposed by O'Neil *et al.* (1969) and Kim & O'Neil (1997), for every 1°C decrease in temperature there is an increase in the fractionation of inorganically precipitated calcite and water of around 0.2 ‰. Although this relationship is generally observed in the isotopic composition of benthic foraminifera (Shackleton, 1974; Herguera, *et al.*, 1992), the absolute values of  $\delta^{18}\text{O}_c$  of some species may present a deviation from equilibrium (Lynch-Stieglitz, *et al.*, 1999). The exact  $\delta^{18}\text{O}$  value of

equilibrium calcite precipitation ( $\delta^{18}\text{O}_{eq}$ ) depends on the choice of the equilibrium equation.

An assumption implicit in all paleoceanographic studies is that the oxygen isotopic composition ( $\delta^{18}\text{O}$ ) of the foraminifera accurately reflects the temperature and oxygen isotopic composition of the seawater in which it grew. However, the isotopic record is not the same for every living organism because some of them (including some benthic foraminifera species) do not precipitate their shells in isotopic equilibrium with the surrounding seawater (Duplessy *et al.*, 1980). Some laboratory experiments using living foraminifera (Spero, 1992; Spero *et al.*, 1997) have demonstrated that the photosynthetic activity of algal symbionts and the carbonate ion concentration of water can affect the oxygen isotopic composition of the shells. Other experiments (Bijma *et al.*, 1999) suggest that pH is the controlling factor affecting the oxygen isotopic composition. The effect seems to be species dependent and, thus, the calibration of the response in Recent foraminifera is a necessary precondition for the quantitative interpretation of the down-core isotopic record.

The most straightforward approach to the evaluation of the paleoclimatic and paleoceanographic utility of isotopic measurements in benthic foraminifera is the analysis of core-top samples. Core-top calibration studies are based on comparisons of foraminiferal data and modern physical oceanographic parameters. This sort of study has made progress toward calibrating core-top benthic foraminifera isotopic measurements under modern oceanographic conditions in the Pacific (Keigwin, 1998), Indian (McCorkle *et al.*, 1998) and North Atlantic Oceans (Lynch-Stieglitz *et al.*, 1999). However, little attention has been paid to the western South Atlantic despite its fundamental role in global thermohaline deep water circulation as the pathway for the major deep water masses, the North Atlantic Deep Water (NADW), the Circumpolar Deep Water (CPDW), and the Antarctic Bottom Water (AABW) (Berger & Wefer, 1996).

In this study we focus on the calibration of two different oxygen isotopic equilibrium equations using western South Atlantic core-tops and water column data to determine oxygen isotope fractionation in the benthic foraminifera genera *Cibicides* and *Uvigerina* as a function of temperature. The relationship between isotopic variation in this data set and modern physical oceanographic parameters provides a realistic framework within which down-core isotopic records may be interpreted.

## METHODS

We compare the oxygen isotopic composition of two genera of benthic foraminifera

from core-top samples with modern oxygen isotopic composition of seawater from similar depths at neighboring Geochemical Ocean Sections Study (GEOSECS) stations (Bainbridge, 1981) (Fig. 1).

The oxygen isotope measurements were made on *Cibicidoides* and *Uvigerina* benthic foraminifera. The species generally used in paleoceanographic reconstruction is *Cibicidoides wuellerstorfi*. However, other species (e.g. *C. kullenbergi*) closely resemble *C. wuellerstorfi* for isotope analysis (McCorkle *et al.*, 1997). Whenever the abundance of *C. wuellerstorfi* was too low (less

than two individuals larger than 250  $\mu\text{m}$  per gram) we used *C. kullenbergi* for isotope analysis.

The foraminifera were picked from the top centimeters of six piston cores and four box-cores from intermediate depths (965-1995 m) on the Brazilian Continental Margin (Table 1, Fig. 1). Additional cores from the same depth range and deeper (Curry & Lohmann, 1982; Oppo & Horowitz, 2000) were included in our study in order to provide a more complete and confident dataset to be used in paleoceanographic reconstructions. The additional cores are close to the core-top locations of this study (Table 1, Fig. 1).

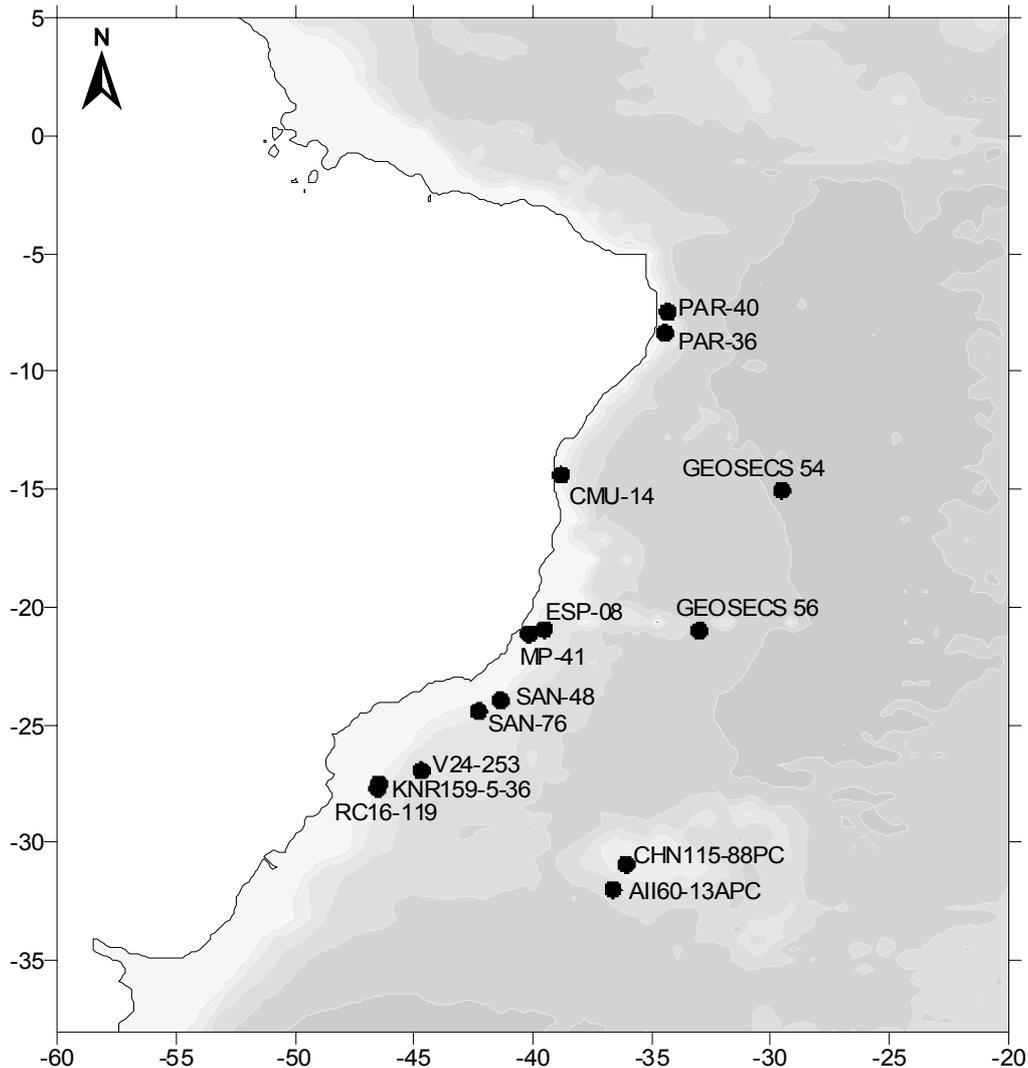


Fig. 1. Location of GEOSECS and core-top sampling stations. Box-cores MP-02, MP-14 and MP-33 are in the same area as box-core MP-41.

Table 1. Core locations and sample type (BC= box-core, PC= piston core).

Core	Latitude	Longitude	Depth	Type	Source
MP-02	21°08'19"S	40°10'15"W	903	BC	This study
MP-14	21°08'16" S	40°10'14"W	903	BC	This study
MP-33	21°08'25 "S	40°10'25"W	884	BC	This study
MP-41	21°08'29" S	40°10'01"W	928	BC	This study
CMU-14	14°24'00" S	38°49'12"W	965	PC	This study
PAR-40	7°28'48" S	34°19'48"W	1261	PC	This study
PAR-36	8°22'12" S	34°27'00"W	1315	PC	This study
SAN-48	23°58'12" S	41°21'00"W	1568	PC	This study
SAN-76	24°25'48" S	42°16'48"W	1682	PC	This study
ESP-08	20°57'00" S	39°31'48"W	1995	PC	This study
KNR159-5-36	27°30'36" S	46°28'12"W	1268	PC	Oppo & Horowitz (2000)
RC16-119	27°42'00" S	46°31'12"W	1567	PC	Oppo & Horowitz (2000)
V24-253	26°57'00" S	44°40'48"W	2069	PC	Oppo & Horowitz (2000)
All60-13APC	31°59'1" S	36°38'9"W	2739	PC	Curry & Lohmann (1982)
CHN115-88PC	30°55'0" S	36°04'8"W	2941	PC	Curry & Lohmann (1982)

The piston cores were sampled at intervals of 5 to 10 cm from 0 to 25 cm. Accelerator Mass Spectrometer (AMS) radiocarbon datings performed on three samples of planktonic foraminifera (Table 2) confirmed our Marine Isotopic Stage 1 age assignments. Although belonging to Marine Isotope Stage 1, these samples may not represent full interglacial Holocene conditions. In order to identify Holocene samples, the averages of the samples with the lowest  $\delta^{18}\text{O}$  values were used to estimate the isotopic composition of Holocene foraminifera. The piston cores oxygen isotope analyses were made on a Finnigan MAT 252 with an automated Kiel device at the Woods Hole Oceanographic Institution laboratory facilities. The standard deviation of the isotope values of the National Bureau of Standards (NBS) carbonate standard NBS-19 was  $\pm 0.08$  ‰. NBS-19 isotope values were used to calibrate for Pee Dee Belemnite ( $\delta^{18}\text{O} = -2.2$  Vienna Pee Dee Belemnite (VPDB)).

All the box cores sampled had clear overlying water and visual evidence of minimal sediment disturbance. We collected the top centimeter sediments. Core-top box core samples were

disaggregated in distilled water at room temperature, dry-sieved and for each sample 3 or 4 specimens were handpicked in the size fraction greater than the 250  $\mu\text{m}$  sieve to avoid ontogenetic artifacts. Oxygen isotope analyses of box corer samples were performed at the Pará-Iso Laboratory (CG-UFPA) using a Finnigan MAT 252 mass spectrometer.  $\text{CO}_2$  extraction of single foraminifera shells was done using an on-line KIEL-III system coupled to the instrument. Isotope ratios are reported relative to the Pee Dee Belemnite (PDB) standard, based on the analysis of NBS-19 carbonate standard, reacted with each set of samples. Results are reported in the standard  $\delta$  (‰) notation relative to the Chicago PDB standard. The precision of these foraminiferal isotopic analyses is better than 0.08 ‰, based on replicated analysis of the carbonate standard.

Prior to estimating the  $\delta^{18}\text{O}_{\text{eq}}$  for the South Atlantic, the regional  $\delta^{18}\text{O}_w$ -salinity relationship had to be established. The linear relationship between  $\delta^{18}\text{O}_w$  and salinity was estimated based on the GEOSECS data from station 56, considering the same depth range as that of the cores used in this study (884-2941 m).

Table 2. Accelerator Mass Spectrometer (AMS) Dates and Calendar Ages.

Cores	Sample depth (cm)	AMS Date (kyr)	Calendar Age (kyr)
SAN-76	13	3.010	2.756
ESP-08	07	3.370	3.219
CMU-14	12	4.010	3.987

## RESULTS

The  $\delta^{18}\text{O}$  of seawater primarily reflects patterns of evaporation and fresh water influx to the surface of the oceans. Because salinity also reflects these same processes, salinity and  $\delta^{18}\text{O}_w$  are often well correlated in the ocean (Craig & Gordon, 1965). Although the exact correlation varies in different areas of the ocean surface (Paul *et al.*, 1999), the vast majority of the surface and subsurface waters warmer than 5°C follow the surface water trend. The equation resulting from the linear regression of observed  $\delta^{18}\text{O}_w$  and observed salinity in the South Atlantic (Fig. 2) may be expressed relative to the Standard Mean Ocean Water (SMOW) as follows:

$$\delta^{18}\text{O}_w(\text{smow}) = (0.61 \times \text{salinity}) - 20.942 \quad (1)$$

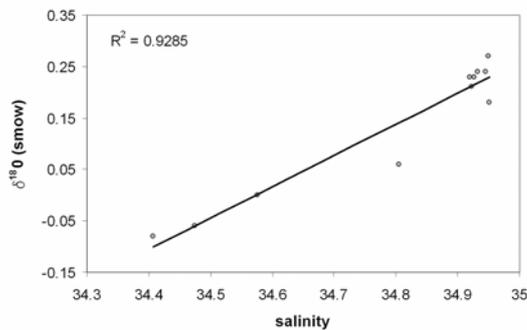


Fig. 2. Plot of  $\delta^{18}\text{O}_w$  (‰) versus salinity from GEOSECS station 56 for the depth range of the cores used in this study (884-2941m).

This equation agrees with that calculated by Paul *et al.* (1999) based on GEOSECS data for mid-latitudes. Applying the above relationship, the  $\delta^{18}\text{O}_w$  values for GEOSECS stations 54 were estimated.

Based on the  $\delta^{18}\text{O}_w$  values calculated from equation (1) and temperature data from the GEOSECS stations, the predicted isotopic values for calcite precipitated in equilibrium with modern bottom water chemistry were calculated using the equations of O'Neil *et al.* (1969) (eq. 2) and Kim & O'Neil (1997) (eq. 3) for the oxygen isotope fractionation as between calcite and water:

$$1000 \ln \alpha_{(\text{calcite-water})} = 2.78 (10^6 T^{-2}) - 3.39 \quad (2)$$

and

$$1000 \ln \alpha_{(\text{calcite-water})} = 18.03 (10^3 T^{-1}) - 32.42 \quad (3)$$

Both equations may be rearranged to give expressions for the calcite precipitated in equilibrium ( $\delta^{18}\text{O}_{\text{eq}}$ ) with local bottom water. McCorkle *et al.* (1997) rearranged the original equation of O'Neil *et al.* (1969) incorporating a revised estimate of the calcite-water fractionation factor (Friedman & O'Neil, 1977) as follows:

$$\delta^{18}\text{O}_{\text{eq}(\text{smow})} = \{e^{[(2.78 \times 1000/T^2) - (2.89/1000)]} \times (\delta^{18}\text{O}_w + 1000)\} - 1000 \quad (4)$$

The equation derived from (3) to yield the calcite precipitated in equilibrium ( $\delta^{18}\text{O}_{\text{eq}}$ ) may be written as:

$$\delta^{18}\text{O}_{\text{eq}(\text{smow})} = \{e^{[(18.03/T) - (32.42/1000)]} \times (\delta^{18}\text{O}_w + 1000)\} - 1000 \quad (5)$$

In equations (4) and (5) temperature values are in degrees Kelvin (°K) [ $T(^{\circ}\text{K}) = 273.15 + T(^{\circ}\text{C})$ ] and  $\delta^{18}\text{O}_{\text{eq}}$  is relative to the SMOW standard. Values of  $\delta^{18}\text{O}_{\text{eq}(\text{smow})}$  were converted to the PDB scale using Friedman & O'Neil's (1977) equation:

$$\delta^{18}\text{O}_{\text{eq}(\text{PDB})} = (0.97006 \times \delta^{18}\text{O}_{\text{eq}(\text{smow})}) - 29.94 \quad (6)$$

Table 3 reports the foraminifera oxygen isotopic composition ( $\delta^{18}\text{O}_{\text{foram}}$ ), the corresponding predicted isotopic values for calcite precipitated in equilibrium with ambient conditions ( $\delta^{18}\text{O}_{\text{eq}}$ ) using, respectively, the O'Neil *et al.*'s (1969) equation, modified by those of McCorkle *et al.* (1997) and Kim & O'Neil (1997) equations and the offset values. Benthic foraminiferal  $\delta^{18}\text{O}$  values increase regularly with increasing water depth (mirroring the decrease in water temperature). A different behavior is observed as between the *Cibicides* and *Uvigerina* isotopic record (Fig. 3).

Table 3. Measured  $\delta^{18}\text{O}_{\text{foram}}$ , predicted oxygen isotope values for foraminifera shells if precipitated in isotopic equilibrium with seawater ( $\delta^{18}\text{O}_{\text{eq}}$ ), and offset from equilibrium values for all samples and for both equations tested. The table also includes the temperature and salinity values for each sample and the corresponding calculated  $\delta^{18}\text{O}_w$ . Except for  $\delta^{18}\text{O}_w$  which is relative to the SMOW standard, all values are relative to the PDB standard.

Core	Genus	Temp (K)	Salinity	$\delta^{18}\text{O}_w$ (SMOW) (‰)	$\delta^{18}\text{O}_{\text{foram}}$ (PDB) (‰)	O'Neil <i>et al.</i> (1969)		Kim & O'Neil (1997)	
						$\delta^{18}\text{O}_{\text{eq}}$ (PDB) (‰)	$\delta^{18}\text{O}$ offset	$\delta^{18}\text{O}_{\text{eq}}$ (PDB) (‰)	$\delta^{18}\text{O}$ offset
MP-02	<i>Uvigerina</i>	276.83	34.41	-0.10	2.90	2.99	0.09	2.21	-0.69
MP-14	<i>Uvigerina</i>	276.83	34.41	-0.10	2.94	2.99	0.05	2.21	-0.73
MP-33	<i>Uvigerina</i>	276.83	34.41	-0.10	2.88	2.99	0.11	2.21	-0.67
MP-02	<i>Cibicoides</i>	276.83	34.41	-0.10	2.30	2.99	0.69	2.21	-0.09
MP-14	<i>Cibicoides</i>	276.83	34.41	-0.10	2.21	2.99	0.78	2.21	0.00
MP-33	<i>Cibicoides</i>	276.83	34.41	-0.10	2.19	2.99	0.80	2.21	0.02
MP-41	<i>Cibicoides</i>	276.83	34.41	-0.10	2.48	2.99	0.51	2.21	-0.27
CMU-14	<i>Cibicoides</i>	276.83	34.53	-0.03	2.36	3.07	0.71	2.29	-0.07
PAR-40	<i>Cibicoides</i>	277.28	34.74	0.10	2.35	3.07	0.72	2.31	-0.04
PAR-36	<i>Cibicoides</i>	277.45	34.79	0.13	2.26	3.06	0.80	2.30	0.04
SAN-48	<i>Cibicoides</i>	276.61	34.89	0.19	2.55	3.34	0.79	2.56	0.01
SAN-76	<i>Cibicoides</i>	276.61	34.89	0.19	2.54	3.34	0.80	2.56	0.02
ESP-08	<i>Cibicoides</i>	276.58	34.95	0.23	2.56	3.39	0.83	2.60	0.04
KNR159-5-36	<i>Cibicoides</i>	276.30	34.50	-0.05	2.40	3.19	0.79	2.40	0.00
RC16-119	<i>Cibicoides</i>	276.26	34.71	0.08	2.29	3.33	1.04	2.54	0.25
V24-253	<i>Cibicoides</i>	276.39	34.93	0.21	2.39	3.42	1.03	2.63	0.24
RC16-84	<i>Cibicoides</i>	276.25	34.94	0.22	2.50	3.47	0.97	2.67	0.17
All60-13APC	<i>Cibicoides</i>	276.00	34.91	0.21	2.63	3.52	0.89	2.72	0.09
CHN115-88PC	<i>Cibicoides</i>	275.84	34.91	0.20	2.62	3.56	0.94	2.75	0.13

Equation Derived from O'Neil *et al.* (1969)  
(McCorkle *et al.*, 1997)

The *Cibicoides*  $\delta^{18}\text{O}$  values increase, from minimal values (2.19 ‰) to maximal values (2.63 ‰), while the  $\delta^{18}\text{O}$  predicted for calcite precipitated in equilibrium with ambient water values increases from 2.99 ‰ to 3.56 ‰. In this way, the *Cibicoides*  $\delta^{18}\text{O}$  data do not agree well with the  $\delta^{18}\text{O}$  profile calculated from equations (4) and (6). The average offset value is 0.82 ‰. In other words, the  $\delta^{18}\text{O}$  *Cibicoides* data are 0.82 ‰ lower than the  $\delta^{18}\text{O}_{\text{eq}}$  data. A similar pattern of large shifts between  $\delta^{18}\text{O}$  predicted for calcite precipitated in equilibrium with ambient water and  $\delta^{18}\text{O}$  *Cibicoides* using equations like O'Neil *et al.*'s (1969) were recorded by Shackleton & Opdyke (1973) (0.64 ‰), Shackleton (1974) (0.82 ‰), Erez & Luz

(1983) (0.48 ‰) and Herguera *et al.* (1992) (0.84 ‰). These studies noted that *Cibicoides* do not precipitate their shells in isotopic equilibrium with ambient water and suggested a correction factor for  $\delta^{18}\text{O}$  *Cibicoides*.

In contrast to the  $\delta^{18}\text{O}$  *Cibicoides* data, the  $\delta^{18}\text{O}$  *Uvigerina* shows a better agreement with the  $\delta^{18}\text{O}$  predicted from the GEOSECS data profile (Fig. 3, Table 3).  $\delta^{18}\text{O}$  *Uvigerina* values range from 2.88 ‰ to 2.94 ‰ and  $\delta^{18}\text{O}$  predicted for calcite precipitated in equilibrium with ambient water using equations (4) and (6) is 2.99 ‰. The average offset value based on the *Uvigerina* dataset is 0.08 ‰. In other words,  $\delta^{18}\text{O}$  *Uvigerina* data are 0.08 ‰ lower than the  $\delta^{18}\text{O}$  predicted for the GEOSECS data stations 54 and 56. Assuming that the equation applied is correct, the small difference between  $\delta^{18}\text{O}_{\text{eq}}$  and  $\delta^{18}\text{O}$  *Uvigerina*

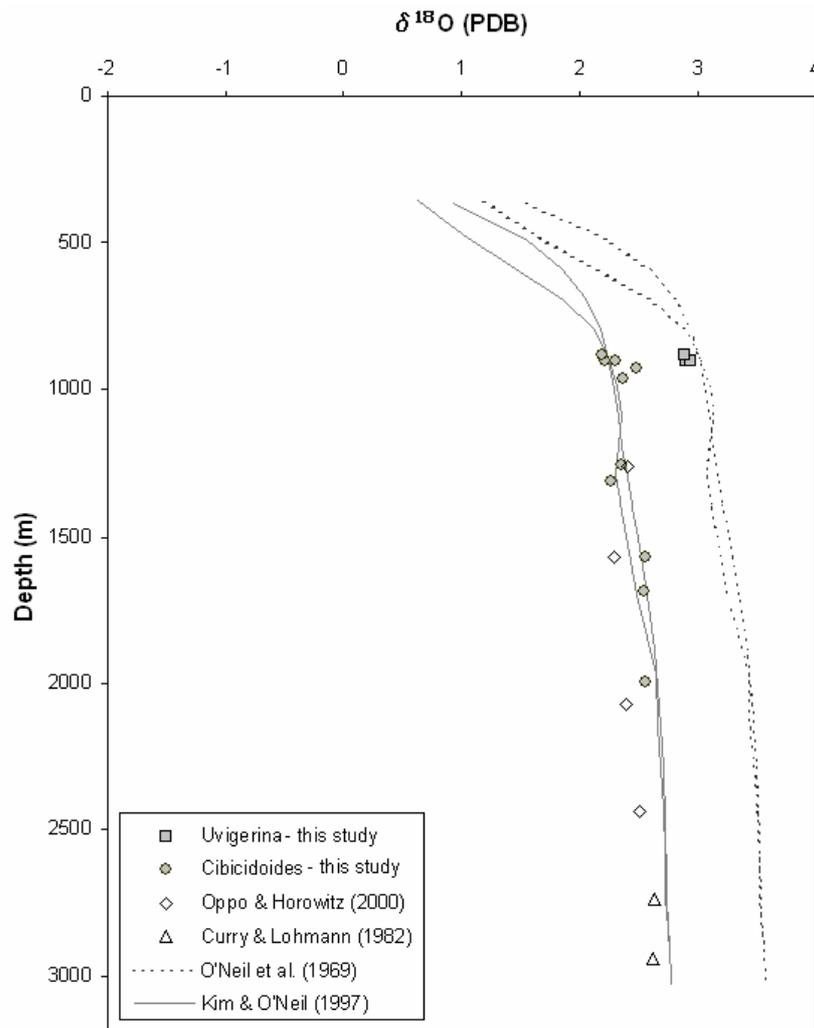


Fig. 3. Comparison of  $\delta^{18}\text{O}$ (‰) values from core-top benthic foraminifera *Cibicidoides* and *Uvigerina* with  $\delta^{18}\text{O}_{\text{eq}}$  values calculated using the equation of O'Neil *et al.* (1969) modified by McCorkle *et al.* (1997) and Kim & O'Neil (1997). Data from Curry and Lohmann (1982) and from Oppo and Horowitz (2000) are of *Cibicidoides*.

suggests that this latter genus precipitates its shells close to equilibrium with ambient seawater. Several authors (Shackleton & Opdyke, 1973; Duplessy *et al.*, 1984; Zahn & Mix, 1991; Herguera *et al.*, 1992; McCorkle *et al.*, 1997) observed a similar response for this genus.

Equation Derived from Kim & O'Neil (1997)

The *Cibicidoides*  $\delta^{18}\text{O}$  data are in good agreement with the predicted profile calculated from equations (5) and (6). Values range from 2.19 ‰ to 2.63 ‰, while the  $\delta^{18}\text{O}$  predicted for calcite

precipitated in equilibrium with ambient water values range from 2.21 ‰ to 2.75 ‰ (Fig. 3). The offset calculated for the *Cibicidoides* dataset has an average value of 0.03 ‰. In other words, the  $\delta^{18}\text{O}$  *Cibicidoides* data are 0.03 ‰ lower than the  $\delta^{18}\text{O}$  predicted for GEOSECS data stations 54 and 56.

Conversely, the  $\delta^{18}\text{O}$  *Uvigerina* do not show an agreement with the  $\delta^{18}\text{O}$  values predicted for the GEOSECS data profile (Fig. 3, Table 3). The  $\delta^{18}\text{O}$  *Uvigerina* values range from 2.88 ‰ to 2.94 ‰ and the  $\delta^{18}\text{O}$  predicted for calcite precipitated in equilibrium with ambient water using equations (5) and (6) is 2.21 ‰. The offset between the predicted

and observed  $\delta^{18}\text{O}$  values for the *Uvigerina* dataset has an average value of  $-0.69\text{‰}$ . In other words,  $\delta^{18}\text{O}$  *Uvigerina* data are  $0.69\text{‰}$  higher than the  $\delta^{18}\text{O}$  predicted for GEOSECS data stations 54 and 56.

## DISCUSSION

The  $\delta^{18}\text{O}$  data set as a whole is internally consistent. The small scattering within data is probably easily accounted for by foraminiferal calcification, imperfection of our  $\delta^{18}\text{O}_w$ -salinity relationship, post-depositional physical or chemical alterations, and the fact that although the piston core samples were chosen to represent full interglacial conditions they may not be synchronous. Some authors (e.g. Dunbar & Wefer, 1984; Schmiedl *et al.*, 2004) observed ontogenetic influences on the stable isotopic composition of deep-sea benthic foraminifera. However, it seems unlikely that these influences should have had any effect on our study because exclusively adult specimens were picked for analyses. The enrichment of *Uvigerina* shells relative to *Cibicides* would be consistent with the habitat differences of the genus. *Uvigerina* is infaunal and experiences lower pH and decreased  $\text{CO}_2^{-3}$  concentration in pore waters, whereas *Cibicides* inhabits the sediment surface where bottom water pH and  $\text{CO}_2^{-3}$  concentration are higher (McCorkle *et al.*, 1990). In such a scenario the isotopic offset between the foraminifera genus should partially reflect the  $\text{CO}_2^{-3}$  concentration gradient in the sediments. On the other hand, Mulitza *et al.* (2003) suggest that the pH in the vicinity of the shell might be important for the recorded  $\delta^{18}\text{O}_{\text{foram}}$  and not the overall pH gradient in the porewater that determines the difference between the species. This is because local pH gradients in the upper centimeters of the sediment seem to be too low in most places to explain the differences observed.

It was not previously believed that benthic foraminiferal genus *Cibicides* precipitated its shell in equilibrium with  $\delta^{18}\text{O}_w$ . The  $\delta^{18}\text{O}$  of *Cibicides* appeared to have a consistent "vital effect" offset of  $0.64\text{‰}$  (Shackleton & Opdyke, 1973) or  $0.83\text{‰}$  (Shackleton, 1974; Herguera *et al.*, 1992) from the calculated  $\delta^{18}\text{O}_{\text{eq}}$  using equations such as O'Neil *et al.*'s (1969). Similarly, for many years the benthic foraminifera genus *Uvigerina* was widely believed to precipitate its shell in oxygen isotopic equilibrium with ambient seawater (Shackleton, 1974). However, core-top *Uvigerina* from the NW-Pacific are more depleted in  $^{18}\text{O}$  than may be predicted from Shackleton's equation, and recent evaluation of the problem indicates that *Uvigerina* is not in equilibrium (Keigwin, 1998).

Bemis *et al.* (1998) reevaluated  $\delta^{18}\text{O}$  data for planktonic foraminifera from core tops in the North

Atlantic, Pacific and Indian Oceans and in the Arabian Sea and Gulf of Mexico and revised the available paleotemperature equations. The authors proposed a more accurate paleotemperature equation and showed that the *Cibicides* data are in excellent agreement with it and with the equation of Kim & O'Neil (1997). This agreement suggests that *Cibicides* precipitates its shell near  $\delta^{18}\text{O}$  equilibrium with ambient seawater. Conversely, the *Uvigerina* are relatively rich in  $^{18}\text{O}$  and fall primarily into or between the equations of Shackleton (1974) and Erez & Luz (1983).

Although the two equations tested here yield conflicting results, we believe that as long as we are interested in evaluating relative temperature changes, both equations are useful. However, in order to calculate absolute calcification temperatures it is necessary to know which is the most accurate paleotemperature equation and which genus (if any) precipitates in equilibrium or precipitates with a predictable offset from equilibrium. Among the available equations, that of Kim & O'Neil (1997) seems to be the most reliable mainly because of the large number of experiments performed with it, the large temperature range and the consistency of the data. According to this equation, *Cibicides* precipitates its shell in oxygen isotopic equilibrium with ambient seawater.

Considering that the oxygen and carbon isotopic analyses are performed on the same foraminifera shells, it is necessary to take into account whether the analyzed benthic foraminifera also precipitates its shell in carbon isotopic equilibrium. It is generally accepted that *Cibicides* is the best recorder of bottom water dissolved inorganic carbon (Belanger *et al.*, 1981; Graham *et al.*, 1981; Duplessy *et al.*, 1984), allowing for reconstructions of past deep-ocean circulation changes, biological production and nutrient cycling (Broecker & Peng, 1982; Curry *et al.*, 1988; Oppo *et al.*, 1990). Being epibenthic, *Cibicides* is not affected by pore-water chemistry. Therefore, in paleoceanographic studies the use of *Cibicides* is preferable to the use of *Uvigerina*.

## CONCLUSIONS

The new relationship between  $\delta^{18}\text{O}_w$  and salinity developed in this study is particularly important for the estimation of  $\delta^{18}\text{O}_w$  based on salinity data in the mid-latitude western South Atlantic. Using the  $\delta^{18}\text{O}_w$  values calculated from the new equation and temperature data from GEOSECS stations, predicted isotopic values for calcite precipitated in equilibrium with modern bottom water chemistry were calculated applying the equations of O'Neil *et al.* (1969) as modified by McCorkle *et al.* (1997) and Kim & O'Neil (1997).

For down-core paleotemperature investigations we suggest applying the latter equation and using the benthic foraminifera *Cibicidoides*. Our conclusion is supported by several evidences. First of all, Kim & O'Neil's (1997) equation is considered to be more accurate. According to this equation, *Cibicidoides* precipitates its shell closer to predicted oxygen isotope equilibrium values (no vital effect). In addition, being epibenthic, *Cibicidoides* is free from the influence of pore water chemistry. This genus is also considered to precipitate in carbon isotopic equilibrium with ambient seawater. In the absence of sufficient *Cibicidoides* specimens for oxygen isotopic analyses, <sup>18</sup>O *Uvigerina* may be used data after applying a correction factor of -0.69 ‰ to account for vital effects.

The results presented here are substantially in agreement with those of other studies of oxygen isotopic variations of benthic foraminifera for the various oceans (McCorkle *et al.*, 1990; Keigwin, 1998; Lynch-Stieglitz *et al.*, 1999) and may potentially improve paleoceanographic interpretations from foraminiferal δ<sup>18</sup>O values in the western South Atlantic.

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