ATTAINMENT OF ISOTOPIC EQUILIBRIUM BETWEEN OCEAN WATER AND THE BENTHONIC FORAMINIFERA GENUS *UVIGERINA* : ISOTOPIC CHANGES IN THE OCEAN DURING THE LAST GLACIAL

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ABSTRACT

It is shown that even when the oxygen isotopic composition of foraminiferal tests is examined using non-standard analytical methods, the measurements may be expressed in terms of the PDB standard. In order to investigate departure from isotopic equilibrium, comparison must be made not with an empirical relationship determined for molluscs in a limited temperature range, but with a relationship based on inorganic calcite precipitation in the temperature range of interest. By such a comparison it is found that *Uvigerina* deposits its test at or near isotopic equilibrium in the temperature range 0.8 ºC to 7 ºC. Values for the isotopic composition of tests of this genus which lived during the last glacial can only be explained in terms of a change in the mean oxygen isotopic composition of the oceans which probably exceeded 1 ‰ for about 20 000 years, and exceeded 0.5‰ for about 70 000 years.

RÉSUMÉ

On montre que, même lorsque l'on étudie la composition isotopique de l'oxygène des tests de foraminifères en utilisant des méthodes analytiques non standard, les mesures peuvent être exprimées par rapport au standard PDB. Pour étudier les écarts à l'équilibre isotopique il ne faut pas faire une comparaison avec une relation empirique obtenue à partir des mollusques dans une gamme de température limitée, mais avec une relation obtenue à partir de précipitation inorganique de calcite dans la gamme de température que l'on étudie. En utilisant cette comparaison, on trouve que *Uvigerina* forme son test à l'équilibre ou très près de l'équilibre dans la gamme de température de 0,8 à 7 °C. Les valeurs pour la composition isotopique des tests de ce genre qui a vécu pendant la dernière période glaciaire ne peuvent être expliquées qu'en terme de changement de la composition isotopique moyenne des océans qui a été probablement supérieure à 1 ‰ pendant environ 20 000 ans et supérieure à 0,5 ‰ pendant environ 70 000 ans.

The oxygen isotope method of determining palaeotemperatures [1] is widely regarded as a tool of unique potential in the investigation of past changes in the temperature of the earth's surface. As regard the Pleistocene, oxygen isotope studies have a second interest, as a method of estimating changes in the isotopic composition of the oceans and hence the extent of Northern Hemisphere glaciation [2].

The potential of Urey's idea was realised by Epstein et al. [3], [4]. To this day, the majority of investigators use an analytical system and interpretation based almost entirely on their work. It is the purpose of this paper to describe some significant changes in both technique and interpretation which have become necessary to the application of oxygen isotope analysis by the writer.

The procedure for performing the oxygen isotope analysis of carbonate may be considered in three stages. First, the carbonate to be analysed is cleaned so as to ensure that a pure carbon dioxide sample can be obtained. Many workers have followed Epstein et al. [4] and heated the powdered sample

in a stream of helium at 475 °C for 30 minutes. Others [5], [6] (and the writer) have heated the crushed sample in vacuo rather than in helium. A third method [7] involves using a chlorate solution (Chlorox) to digest organic contaminants.

The second stage in analysis is the extraction of carbon dioxide for mass spectrometric analysis. McCrea [8] tried several different methods before concluding that reaction with 100 % orthophosphoric acid in vacuo at 25 °C yielded the most reproducible results. The reaction is performed in an enclosed and evacuated vessel and must be allowed some time if a high yield is to be obtained; Oba [9] leaves the sample to react overnight in a thermostat. Water is evolved in the reaction, so that when the carbon dioxide is extracted from the vessel it must be passed through a trap cooled with dry ice before being transferred to the mass spectrometer.

The third stage in the analysis involves comparing the isotopic composition of the gas with that of a laboratory standard in a mass spectrometer. When Urey proposed this method of estimating palaeotemperatures in 1947 this posed a major challenge, solved by McKinney et al. [10]. Today there are mass spectrometers available commercially which are capable of a precision considerably better than is essential for the work.

Most workers achieve a standard deviation among replicate analyses of aliquots of the same sample of about 0.1 ‰ or better, and this is generally taken to be a valid indication of the precision of analyses made for geological purposes. This value corresponds to 95 % confidence limits of a little under ± 1 deg. C. However, a few years ago it was rumoured that results varied systematically according as to whether or not the sample was ground to a powder before carbon dioxide extraction. Emiliani [6] discussed this problem, stating that grinding his laboratory standard of the time, 'Marble V', changed its oxygen isotopic composition by 0.2 ‰. He also stated that this effect was not detected if the grinding was performed under chloroform. It appeared from this work that grinding actually induced some change, perhaps by encouraging isotopic exchange with atmospheric oxygen or water vapour.

A more detailed analysis of the problem was undertaken by Fritz and Fontes [11], who analysed a limestone in grain-sizes ranging from 250-315 μ down to less than 40 μ. Over this range they determined a variation in the isotopic composition of the evolved carbon dioxide of over 0.6 ‰. They were forced to conclude that it is impossible to make palaeotemperature determinations with a useful precision unless all samples are analysed in the same grain-size; failure to observe this precaution could lead to errors of up to 3 deg. C or even more in palaeotemperature estimation.

Although the advice offered can easily be followed by workers analysing macro-fossils such as belemnites, it would be out of the question in our work, involving as it does the analysis of foraminifera in minute quantities. On the one hand it is not practicable to reduce a single specimen of *Globigerinoides sacculifer* to grains of a uniform size, while on the other hand the effective grain size of a small species is determined by its wall thickness.

In view of the seriousness of this problem, we embarked on a series of experiments designed to reinvestigate the nature of the effect of grain-size on the rate of reaction with the phospheric acid and on the isotopic composition of the evolved carbon dioxide. Fritz and Fontes interpreted the variation they detected as a kinetic effect, and we had in mind the possibility of correcting measured isotopic compositions on the basis of the observed rate of reaction.

Whereas Fritz and Fontes [11] used McCrea's system [8] for extracting carbon dioxide, our system in significantly different, having been modified during our attemps to reduce the amount of sample used. A description of an early version of the system is available [12] but as the mode of operation has been changed in the past years we will describe the essential features of the procedure here.

EXPERIMENTAL PROCEDURE

First, the sample is heated in vacuo at 450 °C for 30 minutes to remove impurities. The sample is at this stage contained in a small quartz thimble; when cool, it is transferred in this thimble to the reaction vessel. The reaction vessel, with 100 % orthophosphoric acid in the side arm, is pumped for an hour or more while kept at 50 °C in an oven, after which the reaction is performed at this temperature. The reaction is very rapid, and three minutes is ample for complete dissolution. As the gas is evolved, it is frozen down in a thimble cooled with liquid nitrogen, passing through a trap cooled with dry ice slush. This ensures that the reaction takes place at low pressure, and that carbon dioxide and water are not in contact with each other or with

the walls of the vessel after evolution. After briefly opening the valve to the pumping line to remove any non-condensible gases (which should be negligible), the sample is transferred to the mass spectrometer inlet bulb, using melting acetone to retain any remaining water. The mass spectrometric analysis is substantially as described in Ref. 13, although several minor modifications have been made since that time. Recently we have coupled a similar system to another mass spectrometer (VG Micromass 602 C), with equal success.

INVESTIGATION OF THE VALIDITY OF THIS METHOD : GRAIN-SIZE.

A few grams of white crystalline marble were crushed in a pestle and mortar, and seived to a series of size-fractions between 180μ and less than 40μ. Samples from each size-fraction were processed and the isotopic composition of the carbon dioxide evolved compared with that of a bulb of laboratory standard gas. Results, displayed in Figure 1,
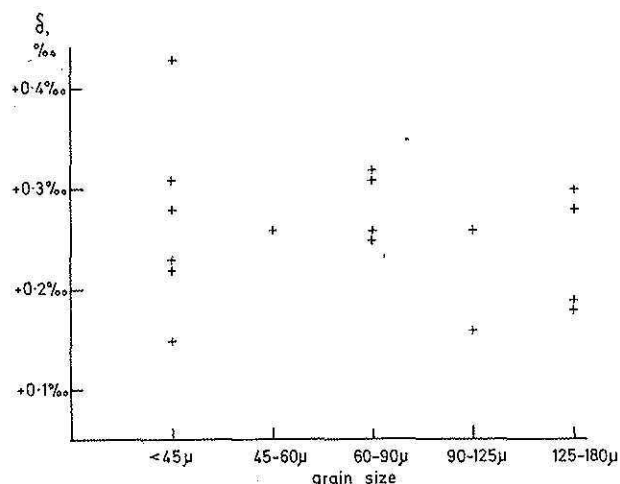

Fig. 1. — Oxygen isotopic composition of carbon dioxide released from Marble in various grain-size fractions. Expressed as a deviation in parts per thousand (‰) from a laboratory standard gas.

are expressed as δ-values in parts per thousand, with respect to this arbitrary gas. The standard deviation among the sixteen analyses of standard-sized samples (about 0.3 mgm) was 0.07 ‰, the best figure ever obtained with the present mass spectrometer in oxygen isotope analyses. There is no evidence of any systematic variation with grain

size. Fritz and Fontes [11] found a large variation, equivalent to about 0.5 ‰ over the range of our determinations. Whether all users of the McCrea method would detect the same variations as did Fritz and Fontes, or whether the geometry of the glassware, the relationship between sample size and vessel volume, or other factors affect the result, should be investigated by users of the McCrea system.

EFFECT OF ACID STRENGTH, SAMPLE QUANTITY, AND OF SAMPLE ROASTING.

Some samples were also analysed after roasting in vacuo for 30 minutes at 450 °C; after roasting immediately following wet-sieving; using low strength (88 %) acid; in very small quantity (0.04 mgm). It is intended that the effects of these variations in procedure should be re-investigated using a higher-precision mass spectrometer : we can conclude from the present series of measurements that an analytical precision of ± 0.1 ‰ [1-σ] can be achieved using the experimental system described for extracting carbon dioxide, even if no precaution is taken to standardise acid strength, roasting procedure or sample weight. Our routine acid is prepared from 85 % AnalR orthophosphoric acid by heating in vacuo for several hours using a magnetic stirrer.

IMPLICATIONS FOR STANDARDISATION.

The relationship used to derive palaeotemperatures from oxygen isotope determinations [4], [14] was set up using as a reference standard a belemnite from the Cretaceous Pee Dee formation of South Carolina. This isotope standard is known as PDB, and its isotopic composition corresponds to a temperature of 16.9 °C for an organism living in water whose isotopic composition is + 0.2 ‰ on the SMOW (Standard Mean Ocean Water) scale [14].

By some workers, PDB appears to have been regarded as a carbonate standard, in the sense that palaeotemperatures were derived by comparing the isotopic composition of the sample with the isotopic composition of the PDB standard. However, others have regarded PDB as a carbon dioxide standard extracted from the standard carbonate under McCrea conditions. There are good reasons for this view. As Craig [14] pointed out, the determination of palaeotemperatures is only rigorously possible through

the measurement of the fractionation between water and carbonate, and when this is done then the result is not dependent on any laboratory standard. He derives the relation :

$$t = 16.9 - 4.2\ (\delta_c - \delta_w) + 0.13\ (\delta_c - \delta_w)^2 \quad A$$

where $(\delta_c - \delta_w)$ is the corrected isotopic difference between carbon dioxide extracted from the carbonate and carbon dioxide equilibrated with the water, both under specified conditions.

In geological circumstances one cannot of course analyse δ_w, but the importance of the relationship is that it permits the use of a gas equilibrated with standard water as a comparison, instead of gas extracted from standard carbonate. This has two advantages. Firstly, many laboratories find that water equilibration is more reproducible than carbonate decomposition, so that a more stable standard ensues. Secondly, PDB itself is used up, whereas SMOW is widely available.

The implication of Fritz and Fontes work is that equation A) is only valid for carbonates having the same grain-size distribution as did those analysed in [4]. However, we are of the opinion that since our method appears to enable us to compare the isotopic composition of two carbonates regardless of their grain-size, we should be able to use the equation, providing that we have a carbonate comparison standard which is tied in to the equation in the sense that it has been calibrated as representing a particular temperature if referred to SMOW. As we have seen, PDB itself should fulfill that role, but it does not exist.

In principal another carbonate standard such as NBS20 [15] ought to be as good, but here we run into a second problem. Although NBS20 has been calibrated agaihst PDB, it was calibrated in McCrea conditions : we cannot now be certain that it was compared in the same grain-size, so that the calibration may not be exactly valid. In any case only three analyses were made without best reproducibility [16].

We are at present calibrating to PDB through two other belemnite standards : LJ1 (ex H. Craig, La Jolla, $\delta = + 0.41\ \%_0$) and B1 (ex C. Emiliani, Miami, calibrated by I. Friedman, U.S.G.S. Denver, $\delta = + 0.29\ \%_0$). Being belemnites and hence perhaps similar to PDB, and being calibrated by careful workers whose experience extends back into the period when PDB was still available, these calibrations are likely to be reliable.

PURIFICATION PRETREATMENT.

Emiliani [6] reported that the method of sample pretreatment (helium roasting, chlorox treatment, no cleaning, vacuum roasting) affected oxygen isotope analyses of foraminifera and other materials. He reported that the analyses performed in Chicago (while PDB standard was still in use) were systematically 0.55 $\%_0$ isotopically light due to having been roased in helium. We believe that this is not the case, and that in fact the discrepancy noticed by Emiliani was caused by the unsatisfactory 'Marble V' standard which he was using at that time, and which proved to be highly variable and/or unstable (Emiliani, personal communication). We have re-analysed samples from core Al79-4 [17] using vacuum roasting, and obtained essentially identical values to those obtained by Emiliani in Chicago. Van Donk [18] obtained values for another Caribbean core (V12-122) which are rather closer to those obtained by Emiliani in Chicago [17] than to those he reported later from Miami [6], although he (van Donk) did not roast the samples at all. We conclude that the procedure that we here describe, by means of which foraminifera and well-calibrated belemnite carbonate standards are analysed under identical conditions, does in fact enable us to express the oxygen isotopic composition of the carbonate of these foraminifera in terms of the carbonate represented by the (non-existent) PDB standard.

CALIBRATION OF THE PALAEOTEMPERATURE SCALE.

Equation A represents an empirical best fit to analyses of mollusc carbonate deposited between 7° and 29 °C. More recently, O'Neil et al. [19] have shown that in the temperature range 0 to 500 °C, the calcite water fractionation factor α can be well represented by :

$$1000\ \ln\alpha = 2.78\ (10^6\ T^{-2}) - 3.39 \quad B$$

and that the mollusc data [4] fit this relation as well as they do equation A. B may be expanded about 16.9 °C to yield a relationship in the same form as A :

$$T = 16.9 - 4.38\ (\delta_c - \delta_w) + 0.10\ (\delta_c - \delta_w)^2 \quad C$$

Equations C and A are similar in the temperature range 15° to 25°, and diverge significantly only at low temperatures (at high temperatures, outside the oceanic range, neither relation is useful). O'Neil et al. show that in fact experimental points fall a little

above this line at 0°C, and also show that theory predicts such a deviation. Thus although C is almost certainly a better representation of isotopic equilibrium in the temperature range 0 to 30 °C than A, it may not be exact. Consideration of the actual low temperature data [19], [20] suggests that perhaps a line :

$$T = 16.9 - 4.0 \; (\delta_c - \delta_w) \qquad\qquad D$$

might approximate the data below 16.9 °C.

LOW-TEMPERATURE CALIBRATION WITH BENTHONIC FORAMINIFERA.

We have investigated the approach to isotopic equilibrium in the benthonic foraminifera *Uvigerina* in the recent sections of three cores covering a temperature range of nearly seven degrees; relevant data are given in Tables 1 and 2. Mean values are plotted in Figure 2. It appears that the values are close to the line representing Equation D which, as we have said, probably represents a good approximation to isotopic equilibrium. We therefore conclude that *Uvigerina* does in fact deposit its test in isotopic equilibrium with sea water.

In collaboration with the CLIMAP project, we analysed core V28-238, from the Western Equatorial Pacific Ocean [21]. The top $2\frac{1}{2}$ metres were sampled at 5 cm intervals, and at each level three independent analyses of *Globigerinoides sacculifera*, each sample of eight individuals, were made. Where sufficient were present, we analysed *Uvigerina* spp., *Pyrgo murrhina*, and *Planulina wuellestorfi*. *Pyrgo murrhina* appears to give similar values to *Uvigerina* spp.; on the other hand, *P. wuellestorfi* appears to deviate from what we now show to be the isotopic equilibrium oxygen isotopic composition by 0.64

per mil. This deviation is somewhat smaller than the published deviation for this species [22]; it may prove to be a temperature dependent effect. In order to obtain the best estimate of the isotopic composition of equilibrium carbonate through the time of deposition of the sediment, we have taken the mean
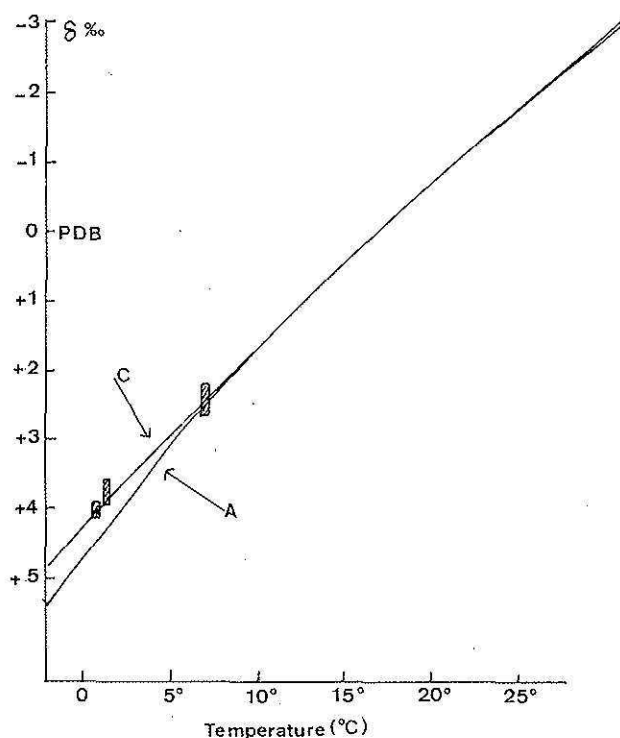

FIG. 2. — Analyses of *Uvigerina* sp from recent section of three cores (Tables 1 and 2) plotted against temperature, and compared with two alternative expressions of isotopic equilibrium.

$$A \quad T = 16.9 - 4.2 \; (\delta_c - \delta_w) + 0.13 \; (\delta_c - \delta_w)^2$$
$$C \quad T = 16.9 - 4.38 \; (\delta_c - \delta_w) + 0.10 \; (\delta_c - \delta_w)^2$$

TABLE I

Data on cores used for *Uvigerina* calibration

Core	Latitude	Longitude	Depth	Temperature	σ_w
V21-30	01°13'S	89°40'W	617 m	7°C	− 0.3 °/oo
RC11−120	43°31'S	79°52'E	3193 m	0.8°C	− 0.4 °/oo
Box Core 2	47°01'N	129°34'W	2650 m	1.3°C	− 0.4 °/oo

Cores V21-30 and RC11-120 from Lamont-Doherty Geological Observatory, studied in collaboration with CLIMAP. Box Core 2 from University of Washington, studied in collaboration with A.W. Fairhall and A.W. Young. Bottom temperature estimates from (23), δ_w estimates based on data in (24), referred to the PDB standard.

TABLE 2

Analyse of *Uvigerina* samples from cores in Table 1

V21-30 :	10 cm, + 2.26 : 20 cm, + 1.81, + 1,93, + 2.20 ; 40 cm, + 2.34.	
RC11-120 :	5 cm, + 3.52 ; 15 cm, + 3.70, + 3,50 ; 25 cm, + 3,58 ; 30 cm, + 3.62 ; 35 cm, + 3.66	
Box Core 2 :	2C02, +·3.50, + 3.11, + 3.49 ; 2C03, + 3.05, + 3.22, + 3,35, + 3.31	
	2C04, + 3.59, + 3,27, + 3.58	

All analyses referred to PDB standard, deviations per mil. Each sample analysed comprised five or more individuals.

of all analyses after adding 0.64 per mil to the *P. wuellestorfi* values.

Analyses in V28-238 were originally published with reference to the Emiliani B1 standard; we now show that the analyses may be corrected to PDB. Subject to the limitations imposed by sediment mixing by benthonic organisms, we believe that departures of these analyses from the line representing isotopic equilibrium between carbonate and present-day Pacific bottom water at 1.2 °C, can only be interpreted in terms of glacio-isotopic changes in bulk oceanic isotopic composition.

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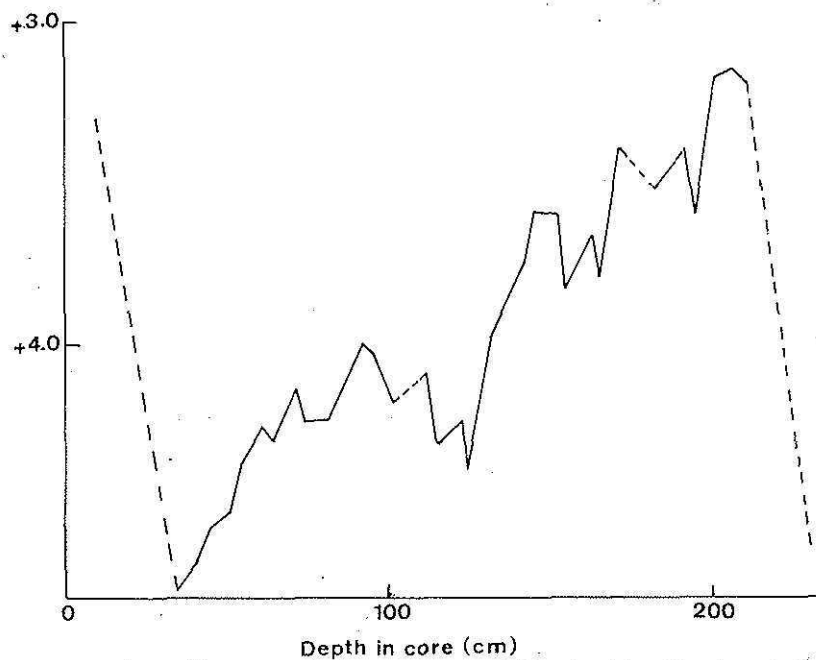
FIG. 3. — Oxygen isotopic composition of benthonic foraminifera in core V28-238, covering the past 130 000 years, expressed as deviation per thousand (‰) from PDB. Core V28-238 [21] is from 01 °01′N, 160 °29′E, depth 3 120 m.

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DISCUSSION

S.M. SAVIN : The peaks and valleys of the planktonic and benthonic foraminifera records of your Pacific core do not exactly coincide. Is it a real effect ? Have you or others observed this in other cores. If it is real it implies important climatic or oceanographic information.

N.J. SHACKLETON : In core V28-238 sharp changes in the ratio of benthonic to planktonic foraminifera mean that sediment mixing can give rise to small ofsets; that is to say, the effects you noticed are probably real but of no climatic significance. However, in cores with a higher sedimentation rate it will be interesting to see if we can detect effects due to the delay in ocean mixing. To do this one would need sedimentation rates of 10 cm or more per 1000 years.

(La discussion générale sur l'utilisation des isotopes est reportée après la communication de J. C. DUPLESSY).