Freshwater Gastropods of Equatorial Africa: Correlations Between Shell Isotope Ratios and Environment

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FRESHWATER GASTROPODS OF EQUATORIAL AFRICA: CORRELATIONS BETWEEN SHELL ISOTOPE RATIOS AND ENVIRONMENT

BY

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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1988
ABSTRACT

A stable oxygen isotopic study of modern African freshwater gastropod shells was carried out to ascertain the feasibility of the use of the stable oxygen isotope ratios of freshwater gastropods as paleoclimatic indicators.

In this study, the oxygen isotope ratios of the freshwater gastropod shell samples taken from the apertures of the individual shells collected at monthly intervals from one site were examined to ascertain their correlatability with weather, temperature, rainfall, water isotope ratios and other ambient conditions. The gastropod shell analysis was by the procedure of Abell (1985) and the water sample analysis by the method of Epstein and Mayeda (1953).

The monthly analyses of both water and gastropod shells from the tributary of the River Pra at Krobo, in the Western region of Ghana, approximately 700km from the Sahel, have shown amount effect, temperature effect and evaporative effect. Good parallelism between temperature plots and the $\delta^{18}O$ plots of the shells and the water was observed. The $\delta^{18}O$ values were also in agreement with vegetative cover map of Ghana and Africa in addition to their correspondence with seasonality information.

Application of these results to fossil gastropod shells, however, requires additional geological and geographical data.
ACKNOWLEDGEMENTS

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FRESHWATER GASTROPODS OF EQUATORIAL AFRICA : CORRELATIONS BETWEEN SHELL ISOTOPE RATIOS AND ENVIRONMENT.

INTRODUCTION

Stable oxygen isotope ratio information from modern African freshwater gastropods and water samples was examined to ascertain the reliability of such information as a proxy in the study of paleoclimates.

The geographical patterns of the stable oxygen isotope ratios obtained from whole shell analysis of individual African freshwater shells have already been established by Abell (1985). In this study reported here, the oxygen isotope ratios of freshwater gastropod shell samples, taken from the apertures of the individual shells collected at monthly intervals from one individual site were examined to ascertain their correlation with weather, temperature, rainfall, water isotope ratios and other ambient conditions. The gastropods and water samples studied were collected at monthly intervals from a tributary of the River Pra at Krobo in the Western region of Ghana, approximately 700km south of the Sahel in the tropical rainforest region of that country.

How this information on modern African freshwater gastropods can be applied to interpret the oxygen isotope ratios of some fossil shells is also examined. If clear correlations exist, then we may achieve our ultimate goal of interpreting paleoclimates from shell isotope data.
BACKGROUND

In pursuance of the study of paleoclimates many techniques and substrates have been examined for their utility and reliability, many of which have been reviewed by Schneider (1984). For example, among these tools are studies of the identification of pollen grains in sediments, with the attendant problems of differential production, distribution and preservation. A second example is the use in paleontology, of the assumption that modern species of animals inhabit environments similar to their ancestors. A third example is the distribution of Coleoptera beetles in sediments to give a rough indication of maximum winter temperatures. Also the deposition of layers of windblown, yellowish-brown dust called loess can serve as a paleoclimatic proxy, while the oceans with their accumulation of sand, mud, gravel, plant and animal fossils also provide geological paleoclimatic indicators (Schneider 1984). None of the aforementioned proxies focusses on short term climatic changes because of the inability of the substrates examined to provide clear evidence of short term climatic events. Other problems are the reworking of the proxy material within the sediments and lack of information on the longevity of the animal species. Thus, on the time scale of hundreds or thousands of years, many proxies can give us information about major climatic changes. However, such important activities as human habitability of an area depends as much or more on the annual range of temperatures and the length and severity of annual dry seasons as on average conditions. It is clear that seasonality will be recorded.
only in short term climatic conditions such as intra-annual rainfall and temperatures. Seasonal information will be useful in the establishment of seasonality in human activity. Since the proxies mentioned above do not have the capability of recording seasonality, alternatives need to be sought. One of the major tools that might be used to overcome this limitation could be the sequential measurements of the stable oxygen isotope ratios as preserved in the growth spirals of the shells of freshwater gastropods. Many freshwater gastropods have life spans of about a year, (Lévéque, 1968) and might be expected to preserve useful environmental records of that span of time. This technique involves the comparison of the relative amounts of the stable isotopes of oxygen using the two most common oxygen isotopes, with natural abundances of $^{16}O$, 99.76%; and $^{18}O$, 0.20%. Stable oxygen isotope measurements give the relative differences between the sample and the laboratory standard ratios of $^{18}O/^{16}O$ from the following formula:

$$
\delta^{18}O = \left\{ \frac{\left(\frac{^{18}O}{^{16}O}\right)_{\text{sample}} - 1}{\left(\frac{^{18}O}{^{16}O}\right)_{\text{standard}}} \right\} \times 1000 \%
$$

A negative $\delta^{18}O$ value means there is less $^{18}O$ in the sample than in the standard against which it is compared and the reverse if $\delta^{18}O$ is positive. It has also been found out that an increase in $\delta^{18}O$ of only 1 per mil in calcite shells corresponds to a change in water temperature of about $4.0^{\circ}C$ to $5.0^{\circ}C$ (Craig, 1953). The short life spans of most species of freshwater gastropods and their isotopic
ratio sensitivity to their environment makes them unique proxies to
the range of annual climatic conditions. This does not imply that
much is known about the life cycle or reproductive strategies of the
freshwater gastropods (Brown, 1980; Lèvêque, 1968; Brown, personal
communication, 1984). While the gastropods which we have examined
(mainly Melanoides tuberculata, Bellamya unicolor and Cleopatra
ferruginea) are believed to live for one to two years, these estimates
are based on aquarium-grown specimens, and need to be verified for
gastropods growing in natural habitats.

Since the application of stable isotope ratio measurements in
paleoclimatology, the volume of work done on freshwater mollusks with
this technique has not approached that done on marine mollusks
apparently due to complexity of data interpretation on freshwater
systems. Despite these complexities, we would like to see if it is
possible to apply this technique to the study of paleoclimates using
freshwater gastropods shells. We already know that some correlations
have been found to exist between isotopic ratios of modern shells and
the environment in which they grow (Abell, 1985).

Obviously, an understanding of how the oxygen isotope ratios of
freshwater gastropod shells vary with the environment in which they
grew could open wide the doors leading to the application of the
isotopic ratio measurements to continental paleoclimatology. This was
first suggested forty years ago when Harold Urey (1947) recognized
that naturally occurring carbonates might be employed in calculating
paleotemperatures, with subsequent verification by McCrea (1950).
Since then, various workers (Epstein et al., 1951, 1953; Mook, 1971,
1977; Burchardt, 1977; Keith et al., 1960, 1964, 1965) have used the technique with moderate success using mollusks as carbonate source material. A major drawback to this technique is that the use of mollusks in this way is not likely to provide the precise, quantitative information that is being furnished by foraminifera in the marine environment (Shackleton et al. 1984). This lack of complete success can be attributed to lack of background information on how environmental conditions translate into the oxygen isotope ratios of the mollusk shell. The fractionation of rainfall and post-precipitation evaporation combine to yield isotope ratios which are difficult to interpret quantitatively, although some qualitative interpretations are possible. This drawback, notwithstanding, some recent advances have been made in elucidating the potential of this technique. It might be noted here that despite quantitative assessment of ocean temperatures by stable oxygen isotope measurements in foraminifera, there is still controversy as to what portion of the oxygen isotope signal should be apportioned to temperature changes and what portion to ice volume changes. (Mix and Pisias, 1988)

The successes thus far have been in the marine environment. By carrying out oxygen isotope study on Pismo Clam (Tivela stultorem) off the coast of California, it has been demonstrated by Lee (1979) that seasonal temperatures are recorded in the growth bands of both modern and fossil clams. Micro-sampling technique along a section cut from the Pismo clam (Tivela stultorem) was effective in this study. Similarly, Jones et al. (1983) and Arthur et al. (1983) have employed the oxygen isotope technique in the study of Atlantic surf
clam (*Spisula solidissima*) and observed a record of environmental change in the shell growth increments. Similarly Schifano (1983) and Schifano and Censi (1983) have demonstrated that the growth habit of *Monodonta turbinata* along the west coast of Sicily correlated positively with sea water temperature. In yet another recent marine experiment, Grossman (1987) employed stable isotopes in modern benthic foraminifera to study the so called "vital effect" (different organisms taking up isotope ratios in differing proportions). In his work, the carbon and oxygen isotopic equilibrium in foraminiferal calcite and aragonite, the characteristics and causes of disequilibrium are examined.

Thus most of the stable isotope studies on mollusks as environmental indicators have employed marine species. This is because, apart from sporadic contributions from melting ice from the polar regions, the oxygen isotope ratio of the water in the ocean is almost constant (Mix and Pisias, 1988). Thus, analyses of the shells of marine mollusks may be expected to give information on marine temperatures with minimal effects from ice volume changes or evaporative alterations in the oxygen isotope ratios of the ocean. The latter effects can often be ignored in marine studies over short time spans when it is assumed that the ocean is a constant, unchanging reservoir of oxygen isotopes.

The disparity in the amount of work done on freshwater mollusks compared to that of marine mollusks since the work of Epstein et al. (1951) is attributable to the complexity of data interpretation on freshwater systems. The two major effects that hinder quantitative
interpretation of oxygen isotope ratios in freshwater mollusks are (1) 
variation in the $\delta^{18}O$ values of the rainfall, which supplies the 
water bodies in question, with time, topography, and latitude (Mook, 
1970) and (2) Alterations of the $\delta^{18}O$ values of the original 
precipitation with time because of evaporative losses, which may be 
associated with temperature, humidity and residence time (Craig, 
1961). Despite these complexities we believe it is possible to 
correlate oxygen isotope ratios of modern African freshwater 
gastropods with their environment at least semi-quantitatively and to 
use this information can be utilized in studying past African 
climates.

Why African climates? The geographical limitations of this study 
were dictated by both practical and theoretical reasons:

(1) The African continent provides a wide range of modern 
climates for comparisons with past climates.

(2) The latitudinal range of the continental land mass, from 
approximately 30°N to 30°S gives a useful range of climatic 
conditions, without encountering extremely low temperatures where 
molluscs may be dormant over large portions of the year.

(3) Initial surveys (Abell, 1985) were made possible by the 
availability of good museum collections of gastropod shells collected, 
at least in part, because of public health problems associated with 
freshwater gastropods.

(4) Finally, it was hoped that one consequence of this study 
would be application to paleoclimatic influences on the development of 
early man, whose original home was Africa.
Past African climates are of interest because we would like to know if the expansion of the Sahara desert in Africa is a cyclical process or not. Such knowledge would help in the formulation of land use policies on expectations of probable changes rather than merely hoping for the best.

Knowledge of ancient African climatic variations could provide some answers to some questions raised in the evolutionary process and in geology. The geographical conditions of past water basins could be deciphered, and the validity of the assumption linking environmental change to the process of evolutionary change could be confirmed. This assumption was engendered by the fact that the ancient environment had been profoundly different from that of the present at various times, not only in its physiography but also in its ephemeral aspects such as climate and vegetation, a view recognized by early natural scientists like Da Vinci, Lyell and Darwin. As an outgrowth of the recognition of the process of transformation from past to present environment, this assumption is held by many scientists in this field, e.g. Dobzhansky, (1962); Levins, (1953); Lewin, (1984); Matthew, (1915, 1939); Pearson, (1978); Simpson, (1953); and Vrba, (1980, 1984).

Of particular concern to anthropologists are the environmental changes that occurred in Africa during the latter half of the Cenozoic, and the role of this environmental change in the evolution of the higher primates including the hominids (Brain, 1981a, 1981b; Butzer, 1977, 1978; Livingston, 1971). Laporte and Zihlman (1983) observe that "...the environmental setting is a major driving force in hominoid evolution," and Brain (cited in Lewin (1984)) argues that
"... had it not been for temperature-based environmental changes in habitats of early hominids, we would still be secure in some hospitable forest, and would still be in the trees." However, while major trends in worldwide Cenozoic climate are well understood, details are scarce and the chronology, particularly in the first half of the Tertiary, is discontinuous, permitting anthropologists to invoke environmental change at nearly any juncture in a particular evolutionary scenario. As Butzer and Cooke, (1982) have observed, it would be useful to supplement essentially deductive approaches with "critical regional studies emphasizing empirical data that can be set into tightly controlled radiometric or stratigraphic frameworks."

To find an appropriate tool which can be used to decipher seasonality in past climates, that we have undertaken to examine the correlation of $\delta^{18}O$ of freshwater gastropod shells and the water in which they lived over a period of one year. Seasonality, which has been defined as marked cyclic annual alteration of temperature and rainfall, is presently being discussed for its role in the interplay between climate and the evolution of the hominoids, hominids and any organism. According to current climatic theory, global weather patterns exist because different parts of the globe receive and absorb varying amounts of solar insolation; upper air currents and ocean currents are mechanisms for restoring heat balance (Budyko, 1978; Barnett, 1978.) Inherent in the global weather patterns is seasonality. Knowledge regarding past seasonality on land has for the most part, been derived indirectly. None of the techniques can give climatic ranges (seasonality) within the year; all of the proxies
yield long term trends.

The influence of climatic factors and their interplay at one given time have greatly inhibited the use of oxygen isotope ratios in freshwater carbonates as continental climatic indicators. For example, in hot weather it is evident that the temperature effect (decreasing $\delta^{18}O$ as temperature rises) and evaporative effects (increasing $\delta^{18}O$ as evaporation increases) will tend to cancel each other. As it turns out, there is a good correlation between oxygen isotope ratios and general climatic conditions and some of the factors which influence the precipitation that eventually determines the immediate environment of the freshwater gastropods have been examined by Yurtsever (1975) and Dansgaard (1964).

**STABLE ISOTOPES IN PRECIPITATION AND CAUSES OF FRACTIONATION**

Dansgaard (1964) observed that the seasonal variations of $\delta^{18}O$ values in rain falling at low latitudes were due to what he called an "amount effect", while those at high latitudes are due to what he referred to as "temperature effect". It has also been observed that as condensation temperature increases, precipitation becomes more and more depleted in $\delta^{18}O$. This depletion of $\delta^{18}O$ has been observed (Dansgaard, 1954) to increase with high latitude and (Epstein, 1956) to increase with altitude, giving what Dansgaard refers to as "latitude effects" and "altitude effects". I will utilize these four named effects in the following discussion, although it is obvious that they are not truly independent effects.

Fractionation may occur in the evaporation of liquid precipitation
or in the condensation of water vapor. During any of these processes, it is the more volatile $H_2O^{16}$ which is readily exchanged as opposed to the heavy isotope counterpart. The fractionation of liquid precipitation in nature may be induced by biological processes or be engendered by mere exchange with other environmental materials. Irrespective of how the fractionation is brought about, it is ultimately dependent upon temperature and the rate of exchange.

In this work only simple equilibrium processes are considered. This is because the equilibrium and kinetic effects of the fractionation process of liquid precipitation are not fully understood yet. The environment in which this process occurs must be considered in any plausible explanation offered. Full consideration is therefore given to the environment in which there is an isotopic exchange between an evaporated water molecule and at the surrounding vapor. (Dansgaard, 1953; Friedman and Machta, 1962; Craig et al. 1963; Erickson, 1964). For example the $\delta^{18}O$ of liquid water in exchange with the atmosphere would be affected by a dry and cool environment differently than it would in a wet and humid environment.

The condensation process also plays an important role in the determination of the $\delta^{18}O$ of the liquid precipitate. This is demonstrated by water vapor in equilibrium with liquid water. The initial condensation of the initial vapor in equilibrium with the liquid water would have the same $\delta^{18}O$ as the original water by cancellation of the fractionation factors in going from liquid to vapor and then vapor to liquid. However, subsequent condensations deplete the heavy isotope of oxygen in the water leaving the
isotopically lighter H$_2$O in the vapor. The $s^{18}O$ of the condensation from the residual vapor then gives more negative values with greater rain-out producing increasingly isotopically lighter rain water. Condensation temperature cannot be determined generally from the amount of precipitation because the composition of any precipitation is a function of several parameters.

"Amount effect" correlation between monthly precipitation and $s^{18}O$ is demonstrated by low $s^{18}O$ values in rainy months and high $s^{18}O$ values in semi-arid months. This trend is observed in the summer months at mid-latitudes and all year round in the tropics. This pattern does not hold in the polar zones because the temperature effect is predominant. Thus, ascribing a rationale to this observed pattern has been complicated by the high isotopic turnover in the convective rain formation process. In this process, the vertically rising air could exchange with water droplets either in the clouds or just as the water droplets fall to the ground. In the tropics where high humidity exists, and the rainy seasons are long and heavy rains are recorded, low $s^{18}O$ values are attributed to deep cooling of the air followed by little enrichment by other processes. In areas with low humidity and light rains, the $s^{18}O$ is enriched by exchange and evaporation.

At higher latitudes where evaporation from falling raindrops is minimal, the amount effect becomes less pronounced. Direct evidence for the enrichment of falling drops through evaporation have been reported by Dansgaard (1953, 1961) and by Ehhalt et al. (1963).

The gross mean $s^{18}O$ over a year can be represented by a simple
mean over 12 months:

\[ s_m = \frac{1}{12} \sum_{i=1}^{12} s_i \]

or by a weighted mean value which is given by:

\[ s_m^w = \frac{1}{P} \sum_{i=1}^{12} (P_i \cdot s_i) \]

with \( P_i \) and \( P \) being monthly and annual amount of precipitation respectively as determined by prevailing conditions during the rainy season. The weighted mean can be utilized for comparative purposes if the climate of the pertinent site has a dry season. Weighted mean isotope ratio values provide information on major air mass movement while monthly isotope ratio values provide local isotope effect information. Since we are interested in local environmental information and record of seasonality in the isotope ratios of the shell and water, we would utilize the monthly \( s^{18}O \) values in our analysis.

By considering the monthly \( s^{18}O \) in the tropics, the amount effect can be observed to run antiphase to the monthly recorded amount of rain. The separation of amount effect from temperature effect in the tropics can be achieved by applying the seasonal variation of \( s^{18}O \) values. This is accomplished by taking the difference between \( s_s \), the unweighted mean \( s \) value for summer and \( s_w \), the unweighted mean \( s \) value
for winter. Summer in the Northern hemisphere is taken to be the period between May–October while November–April is taken as the winter and the vice versa in the Southern hemisphere. Less seasonal temperature variation, rainy summers and relatively dry winters have been observed to characterize the tropics. A negative $\delta_S - \delta_w$ therefore indicates the predominance of amount effect in the tropics. In mid-latitudes a positive oxygen isotope ratio value indicates the contribution of both temperature and amount effects. In high latitude samples where seasonal variation of temperature is very high, high $\delta_S - \delta_w$ are mainly influenced by temperature. If seasonal variation of $\delta^{18}O$ values is observed in Southern Ghana, then amount effect can be determined.

**EXPERIMENTAL**

Modern freshwater gastropods from a tributary of the River Pra (Figure 1) at Krobo, 5.2°N,1.6°W in the Western Region of Ghana in Africa, were collected at monthly intervals and analyzed together with water samples collected at the same time and location from the host body of water in which the gastropods lived. Various species of Melanoides, Cleopatra and Bellamya genera were collected from the tributary of River Pra, but for the purposes of uniformity and comparison in this work most of the analyses were done on Melanoides tuberculata. The ubiquity of *M. tuberculata* in Africa and the sturdy, robust character of the shells make it the ideal species for our study. When *M. tuberculata* shells were unavailable, *Bellamya unicolor* was our second choice, although identification at the species level was
FIGURE 1

RELIEF MAP OF GHANA

(ADAPTED FROM BOATENG, 1967)
sometimes more difficult. The third genus, Cleopatra, is widely distributed, usually as C. ferruginea, but is less common than the other two. See Brown, (1980) for distributions of these species throughout Africa.

The procedure involved collection on a monthly basis of water samples, freshwater gastropods and data on prevailing climatic conditions during the 12 month collection period from December 1985 to November 1986 (Table 1). The gastropods were collected at shallow (1 to 2 meters) depths, and were thus growing in water that was well-mixed, not deep or stagnant. Approximately 10 gastropods were collected at the bottom of the river (usually in a cluster), allowed to die and then dried before shipping to the laboratory. The water sample was collected in a 25ml septum capped vial, which was lowered down into the river at the proximity of the gastropods and then opened to fill up. It was recapped, labeled and kept sealed for analysis in the laboratory. Water temperatures were also measured monthly over the same period at the collection site.

The processing of the freshwater gastropod shells for the purpose of evolving their CO₂ content into ampoules for stable oxygen isotope ratio determination was by the procedure of Abell (1985). This involved longitudinal sectioning of a whole shell with a low speed diamond wafering saw in such a way that if a shell has 6 to 8 complete turns in the growth spiral, sampling from opposite edges of each turn (180°) in the sectioned shell would give 12 to 16 samples. Since adult Melanoides individuals generally have robust shells, long sequences of samples can be obtained along the growth spiral. The
TABLE 1

TEMPERATURES AND OTHER PREVAILING CONDITIONS DURING SAMPLING

SITE: The River Pra at Krobo, Western Region, Ghana.


<table>
<thead>
<tr>
<th>MONTH</th>
<th>WATER TEMP. °C</th>
<th>AIR TEMP. °C</th>
<th>REMARKS</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEC.</td>
<td>25.0</td>
<td>27.5</td>
<td>Cool, dry Harmattan</td>
</tr>
<tr>
<td>JAN.</td>
<td>24.8</td>
<td>27.0</td>
<td>Cool, dry, River drying up</td>
</tr>
<tr>
<td>FEB.</td>
<td>25.0</td>
<td>27.2</td>
<td>Extremely dry, Harmattan winds</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>River almost dried up.</td>
</tr>
<tr>
<td>MAR.</td>
<td>25.0</td>
<td>28.0</td>
<td>Light rainy season, River</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>level rising.</td>
</tr>
<tr>
<td>APR.</td>
<td>25.5</td>
<td>27.5</td>
<td>Light rains, River level</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>still rising.</td>
</tr>
<tr>
<td>MAY</td>
<td>25.0</td>
<td>31.0</td>
<td>River level normal but flowing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>faster due to heavy rains</td>
</tr>
<tr>
<td>JUN.</td>
<td>24.0</td>
<td>26.0</td>
<td>Heavy rains, River flooding.</td>
</tr>
<tr>
<td>JUL.</td>
<td>25.0</td>
<td>26.5</td>
<td>River completely flooded.</td>
</tr>
<tr>
<td>AUG.</td>
<td>23.5</td>
<td>27.5</td>
<td>Rainy season, River flooded.</td>
</tr>
<tr>
<td>SEP.</td>
<td>23.0</td>
<td>26.5</td>
<td>Major rainy season over,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Weather is cool.</td>
</tr>
<tr>
<td>OCT.</td>
<td>24.0</td>
<td>27.0</td>
<td>Started raining, River</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>flooding.</td>
</tr>
<tr>
<td>NOV.</td>
<td>24.0</td>
<td>28.0</td>
<td>Raining, River flooded.</td>
</tr>
</tbody>
</table>
samples of a fractional milligram size were baked under vacuum at 400°C for approximately 4hrs to destroy all organic matter. The carbon dioxide samples were prepared on a vacuum line by solution of shell fragments in 100% phosphoric acid at 55°C. The evolved CO₂ samples were sealed off in ampoules for isotopic ratio analysis on a V. G. Micromass 602-D mass spectrometer.

The results were corrected to 25°C, the temperature usually used for reporting isotope ratio results and recalculated to the PDB standard. Since all the samples analyzed were aragonitic, 0.6% was subtracted from the values to compensate for the difference between calcite and aragonite (Grossman, 1962).

Monthly water samples were analyzed for the oxygen isotope ratios according to the procedure of Epstein and Mayeda (1953). This involved the equilibration of approximately 24cc (STP) of carbon dioxide gas with 2.5g of water in a constant temperature bath maintained at 31°C for approximately 7 days and the analysis of approximately 3cc aliquot of the gas on a V. G. Micromass 602-D mass spectrometer. With the water samples having pH of 6 or lower, there was no need to adjust pH to facilitate rapid equilibration (Mills and Urey, 1940). The water sample was inserted into a 25cc round bottom flask provided with ground glass joints and a stopcock so as to be connectable to a vacuum manifold. The water was frozen in a liquid nitrogen-2-propanol slush bath and the air quickly pumped away. The ice was melted and warmed to room temperature to release gas which was trapped during the initial freezing. The water was then refrozen and pumped for a minute to remove the remaining non-condensible gases.
The ice was melted again and commercial cylinder carbon dioxide, 99.8% purity, was introduced into the flask to a pressure of about 73.5 cm Hg. After equilibration at 31°C for 7 days with frequent shaking, an approximately 3 cc aliquot of the carbon dioxide was withdrawn on a vacuum line by freezing into ampoules and analyzed on the V. G. Micromass 602-D mass spectrometer using the method described by McKinney et al (1950).

All mass spectrometric analyses are reported relative to the PDB carbon dioxide standard gas. The results were calculated from the formula:

\[ S^{18}O = \left[ \frac{R_x}{R_{std}} - 1 \right] 1000 \]

The probable error is ± 0.1%. Replicate samples measured on the same day are usually reproducible to ± 0.05%. Standards (usually NBS-20), were always run the same day as any unknowns were run.

Individual gastropods analyzed from a set collected at the same time at the Krobo tributary were accepted as representative by reference to experiments, conducted in this laboratory ( unpublished data ) by L. Buffington, which established that individual gastropods of all sizes of *M. tuberculata* from the same site record the same \( S^{18}O \) (Figure 2). A noticeable increase in the \( S^{18}O \) of all the shells as they grew reflects the known evaporative conditions at the Kawokudi stream. The drop in the \( S^{18}O \) values also reflect the temporary reprieve from the drying condition of the stream at the time of collection. Replicate samples measured were reproducible to ± 0.1%. Instrument reproducibility was ± 0.05%.
OXYGEN ISOTOPE RATIOS, COHORT OF SHELLS
(MELANOIDES TUBERCULATA) COLLECTED IN OCT.
1985 FROM KAWOKUDI STREAM IN ACCRA, GHANA.
Since the isotopic ratios in the shells are dependent on climatic and environmental conditions, a brief description of those conditions is necessary. Ghana lies between latitudes 4°45' N and 11°11' N, longitudes 3° W and 1°14' E and has two vegetational zones, the savannah grassland of the north and the rainforest of the south (Figure 3, Vegetation map of Ghana). The two vegetational zones experience significantly different climatic regimes. The northern savannah region has a single annual seasonal cycle consisting of a cool, rainy and windy period in August to October. For the rest of the year conditions are warm, dry and relatively calm. The climatic conditions prevailing in the southern forest zone consists of two rainy periods in March-July and September-October. The September-October rains in Ghana are followed by the north-east trade winds also called Harmattan winds, which are characterized by high daytime temperatures with low humidity, and dry cool nights. The Harmattan is intense during December and January and consists of dry winds from the Sahara desert, blowing toward the tropical rainforest across the savannah region (Beadle, 1974). Dry weather and clear skies during this period produce very elevated temperatures during the day, but with substantial radiational cooling at night. In the annual seasonal cycle of Ghana, the maximum temperature differential is experienced during the Harmattan because of the extreme daytime maximum and nighttime minimum temperatures (Boateng 1967).

The Harmattan certainly has a marked effect on the climate of the humid forest regions inland of the Guinea coast of West Africa due to
VEGETATION MAP OF GHANA

(ADAPTED FROM BOATENG, 1967)

FIGURE 3

22
its low humidity and effect on circulation of standing waters. The Harmattan winds are comparatively less powerful than the southeasterlies in August but they accelerate evaporation at the surface of standing waters and provide the necessary energy for stirring of lakes (Beadle, 1974). When the Harmattan winds are not blowing, the climate may alternate between hot and dry or rainy and humid. In general, climatic conditions in West Africa are determined by the effects of either the north-east winds or the south-west winds.

**FACTORS THAT INFLUENCE OXYGEN ISOTOPE RATIO IN PRECIPITATION AND IN SHELL INCORPORATION**

Correlation of oxygen isotope ratios with environmental information is complicated. Among the factors which influence shell isotope ratios are the temperature effect, evaporative effect, amount effect, latitudinal effect and altitudinal effect in precipitation as described by Dansgaard (1964) and Yurtsever (1975). In addition, evaporation and changes in temperature will influence the oxygen isotope ratios of gastropod shells as the gastropods grow in the bodies of water supplied by the precipitation. It would be impossible to interpret and utilize oxygen isotope ratios of freshwater samples if all of these factors were important and operational at a given site in a given period. We believe that this is not true and that the main determinant of the oxygen isotope ratio value of natural water is the fractionation from evaporation and condensation. Since this phase change is temperature dependent the influence of the other parameters are not as important as that of temperature.
Seasonal variations in oxygen isotope ratios are found to correlate well with monthly mean temperatures. By regression analyses, Yurtsever (1975) has shown that spatial variations observed in the mean oxygen isotopic composition of precipitation will be influenced mainly by temperature. This correlation is not considerably improved by the other parameters. Yurtsever (1975) performed a multiple linear regression analysis in an attempt to derive a relationship between the mean $s^{18}O$ of precipitation and basic geographical and climatological parameters. In the multiple linear regression analysis, the mean $s^{18}O$ values were taken as the dependent variable and were related to several selected independent variables with a linear equation of the following type:

$$( s^{18}O ) = a_0 + a_1 T + a_2 P + a_3 L + a_4 A$$

where

- $T$ = the average monthly temperature (°C)
- $P$ = the average monthly precipitation amount (mm)
- $L$ = Latitude (Degrees)
- $A$ = Altitude (meters)

and $a_0$, $a_1$, $a_2$, $a_3$, and $a_4$ are the regression coefficients.

By using data collected from the 91 network stations Yurtsever computed the regression equations by starting with the four independent variables, and then eliminating 3 of them progressively. The results of the multiple regression analyses derived from data collected from the 91 network stations have been adapted in Table 2 as follows:
<table>
<thead>
<tr>
<th>Dependent Variable</th>
<th>Independent Variables</th>
<th>Regression Equation</th>
<th>Multiple Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean ( s^{18}O )</td>
<td>( T, P, L, A )</td>
<td>( -18.723 + (0.597 \pm 0.088)T - (0.0035 \pm 0.0052)P + (0.106 \pm 0.048)L + (0.00102 \pm 0.0008)A )</td>
<td>0.833</td>
</tr>
<tr>
<td>( s^{18}O ) ( % )</td>
<td>( T, P, L )</td>
<td>( -16.279 + (0.545 \pm 0.082)T - (0.0067 \pm 0.0048)P + (0.074 \pm 0.044)L )</td>
<td>0.828</td>
</tr>
<tr>
<td>( s^{18}O )</td>
<td>( T, P )</td>
<td>( -11.781 + (0.418 \pm 0.033)T - (0.0084 \pm 0.0048)P )</td>
<td>0.821</td>
</tr>
<tr>
<td>( s^{18}O )</td>
<td>( T )</td>
<td>( -12.180 + (0.390 \pm 0.029)T )</td>
<td>0.815</td>
</tr>
</tbody>
</table>

where

\( T \) = average monthly temperature (°C)

\( P \) = average monthly precipitation (mm)

\( L \) = latitude (degrees)

\( A \) = altitude (meters)
That the spatial variations observed in the mean isotope composition of precipitation of the network stations are due essentially to temperature variations with somewhat reduced importance attached to latitude is evident from the values of multiple correlation coefficient. It may also be observed from the table that the improvement of the correlation is not significant with the other two parameters.

The partial correlation coefficient between the mean $^{18}O$ and the average monthly temperature is 0.815, whereas it is 0.303 for average monthly precipitation, -0.722 for latitude and 0.007 for the altitude. By virtue of being linearly correlated among themselves by a correlation coefficient of 0.938, the use of latitude as an additional parameter to temperature in the regression analyses does not improve the correlation. Also, the fact that the great majority of the network stations are located at low altitudes and consequently exhibit very small variations in altitude accounts for the poor correlation observed between $^{18}O$ and altitude. Yurtsever, therefore observed that the spatial variations in the mean isotope composition of precipitation in the network stations taken as a group are due mainly to the temperature effect. In Figures 4 and 5, adapted from Yurtsever (1975), the temperature effect is illustrated by plotting the mean $^{18}O$ against the mean temperature. Figure 4 illustrates data from continental stations while Figure 5 illustrates data from island and coastal stations.

This general conclusion is applicable on global scale using data from all network stations. However, other competitive parameters such
RELATION BETWEEN AVERAGE MONTHLY TEMPERATURE AND MEAN OXYGEN ISOTOPE RATIOS IN CONTINENTAL STATIONS
(ADAPTED FROM YURTSEVER 1975)

FIGURE 4
RELATION BETWEEN AVERAGE MONTHLY TEMPERATURE AND MEAN OXYGEN ISOTOPE RATIOS FOR ISLAND AND COASTAL STATIONS (ADAPTED FROM YURTSERVER, 1975)

FIGURE 5
as amount effect or evaporative effect may become important in
determining the spatial isotope variations when considering regional
data. For example, in Figure 5, the more negative mean $\delta^{18}O$ values in
one group of stations which is apparently due to the amount effect
deviate from the general $\delta^{18}O$-temperature relation, having signifi-
cantly higher mean precipitation values. Figure 6 clearly illustrates
the amount effect where the mean $\delta^{18}O$ values are plotted versus
average monthly precipitation for all equatorial island stations
having comparable average temperatures. The least square fit to the
data shown in Figure 6 is

$$(\delta^{18}O) = (-0.015 \pm 0.0024)P - (0.047 \pm 0.419)$$

With a correlation coefficient of $r = 0.874$ and standard error of
estimate of $\pm 0.783\%$. It is therefore, found that 76% ($r^2 = 0.76$) of
variations in mean $\delta^{18}O$ values in the island stations is due to amount
effect which results in an average depletion rate in $\delta^{18}O$ of -1.5% per
100mm of rainfall. Thus a high probability of improving the
parametric relations given in Table 2 exists if similar regression
analyses are performed on regional bases by employing some additional
climatological and geographical parameters. For example, altitude is
obviously not important as a variable when dealing with sea level
sites. In locations where altitude should be a factor, it should
still be influenced by temperature. This is because air temperatures
generally drop with increasing altitude and temperatures influence the
oxygen isotope ratios of precipitation as rain falls from the
\[(\Delta^{18}O) = -(0.015 \pm 0.001)Y - (0.470 \pm 0.419)\]

\[n=14\]
\[r=0.874\]
\[\sigma=0.783\%\]

Average Rate of Depletion:
-1.5±0.2 % per 100mm

(AVERAGE MONTHLY TEMP.
(°C) IS BY EACH POINT)

FIGURE 6

AMOUNT EFFECT IN ISLAND STATIONS. PLOT OF MEAN OXYGEN ISOTOPE RATIOS VERSUS AVERAGE MONTHLY RAINFALL. (ADAPTED FROM YURTSEVER, 1975)
atmosphere as well as when being incorporated into gastropod shells, altitudes should influence the $^{18}\text{O}$ of shells. Yurtsever (1975) has observed that precipitation at higher altitudes is more depleted in heavy isotopes than that at lower altitudes. In effect, it can be observed that the four major parameters considered by Yurtsever (1975) and Dansgaard (1964) may be important but are not truly independent as three of the parameters are to a large degree controlled by temperature. It is also known that the final composition of liquid precipitation on the ground would be different from the initial composition of a liquid precipitation in the clouds.

**FACTORS THAT INFLUENCE OXYGEN ISOTOPE RATIO IN SURFACE WATER**

Surface water is believed to be influenced by factors which are similar but are over and above those that influence precipitation in the cloud. Prominent among the factors that alter the oxygen isotope ratio in the post-precipitation phase are temperature and evaporation. The alteration of the oxygen isotope ratio may be caused by evaporation and exchange with environmental vapor. In dry air, relatively high evaporation causes the preferential escape of $\text{H}_2\text{O}^{16}$ (light water) creating a non-equilibrium conditions (Ephalt et al., 1963) resulting in heavy water being left behind. Dynamic equilibrium exchange between the precipitation and the environment which occurs in humid environment has been observed by Friedman and Machta (1962).

Should amount effect become important in the oxygen isotope ratios of a given precipitation, it would be expected that the environment
with a greater amount of precipitation in a given month, would be more depleted in oxygen-18 which would also be incorporated into the shell of gastropods that lived in that environment. Despite the different effects that can influence the oxygen isotope ratios in precipitation and in shell incorporation, it is still possible to correlate oxygen isotope ratios of a given body of water with the oxygen isotope ratios of the freshwater gastropods that inhabit it and even calculate the temperature at which the gastropod shells were formed (Epstein and Mayeda, 1953). The isotope temperature scale formulated for this calculation is:

\[ T = 16.5 - 4.3 (S - A) + 0.14 (S - A)^2 \]

where \( T \) is the temperature in °C, \( A \) is the \( S \) value for the \( H_2O \) in which the \( CaCO_3 \) was precipitated and \( S \) is the oxygen isotope ratio in the gastropod shell. Any considerable deviation from the above temperature formula would mean considerable fractionation or influence of the precipitation by other factors other than temperature.

The inability of freshwater gastropods shells to record the original \( S^{18}O \) of the rainfall as predicted by latitudinal influence, (as shown in Figure 7) is due to other effects over and above those discussed by Yurtsever (1975) and Dansgaard (1964) on post-precipitation isotope ratios. The main parameters that affect post-precipitation isotope ratio are amount, temperature and evaporation which Abell (1985) has rightly linked up with vegetation cover. As a
FIGURE 7

EXPECTED LATITUDINAL EFFECTS ON OXYGEN ISOTOPE RATIOS, IGNORING LAND MASS INFLUENCES

(ADAPTED FROM ABELL, 1985)
result of regional patterns in $s^{18}O$ of gastropods it is possible to sort out the major effects on post-precipitation isotope ratio. This is possible because some of the influential parameters on post-precipitation isotope ratio may be emphasized or discarded. This does not necessarily mean the same pattern of emphasis or discarding would apply for every site, but that some rules apparently apply.

Over much of Africa, the primary influence determining the isotope ratios in gastropod shells is the latitude. Rainfall is fractionated as air masses move and this is clearly manifested in the latitudinal effect on oxygen isotope ratios in precipitation as noted by Dansgaard (1964) and Yurtsever (1975). Gastropods, sampling the oxygen isotope ratios in that rainwater in their host body of water, will generally provide a faithful record of that isotope ratio, particularly if the gastropods lived in large deep bodies of water, resistant to evaporative changes or in areas where rainfall is persistent through much of the year and humidity is high enough to discourage evaporative fractionation. The deep lakes, Tanganyika and Malawi, are the obvious examples of these bodies of water large enough to resist evaporative change, while the rivers and lakes in the tropical forest of Central and West Africa are going to be characterized by low evaporation. On the other hand, there are a number of areas where control of $s^{18}O$ will be largely by evaporation. The shallower East Africa and Southern Saharan lakes will be maintained by seasonal rainfall in their source areas, but will be subject to continuous high evaporation rates. Lake Turkana, for example, fed largely (80%) by seasonal rainfall in the highlands of Ethiopia, has a climate of relatively unchanging
temperature, but the lake level, and the $^{18}O$ of the gastropod shells oscillates with this seasonal input. In all these arid locations, the average value of $^{18}O$ will be positive, reflecting the prevailing evaporative conditions.

Yet another scenario is to be found in the Transvaal region of South Africa and extreme southern Mozambique, where a cool and dry winter combine to produce major fluctuations in $^{18}O$. The combination of temperature and evaporation are enough to offset the latitudinal effects of several permil. These general climatic trends and their manifestation in the oxygen isotope ratios of gastropod shells are clearly visible in Figure 8 (Abell 1985). Thus latitudinal effects produce $^{18}O$ values near $-4$ to $-5\%$ at the equator, and extending to $-8$ to $-9\%$ at the northern and southern extremes of Africa. Evaporative situations in East Africa are clearly delineated with $^{18}O$ values near $+1$ to $+2\%$. The regional anomaly in the Transvaal area of South Africa is also obvious. This map supplies the norms for isotope ratios and climatic patterns of modern Africa, but it also supplies examples of regional effects which can be used for the interpretation of paleo-isotope ratios. Some general observations have emerged from the recent studies of $^{18}O$ values and their correlation with environmental conditions. One of such observations is that in cool, high and regular rainfall areas, where $^{18}O$ of shell is $-3$ to $-5\%$, in situ evaporation is probably much less important than temperature in controlling $^{18}O$. But where rainfall is light, and conditions are arid and hot, in most circumstances temperature variation is small, and the $^{18}O$ values are predominantly governed by evaporation. For
FIGURE 8

OBSERVED OXYGEN ISOTOPE RATIOS IN FRESHWATER GASTROPOD SHELLS
(ADAPTED FROM ABELL, 1985)
example, at both Lake Malawi and Lake Victoria (Winam Gulf) there is minimal temperature change with the seasons, but $\delta^{18}O$ of the shells varies considerably (Abell, unpublished data). There will be exceptions to these generalities, but they make a starting point.

In an attempt to apply these interpretations to paleoclimates we must not lose sight of the importance of the correlation between amount effect or rainfall and vegetation. The amount effect which according to Dansgaard (1964) is engendered by the deep cooling of air in heavy frequent rainfall, with minimum possible post-precipitation enrichments through evaporation, has been found to correlate well with vegetation cover (Tucker et al., 1985, Abell, 1985). With respect to the African climate, it has been found that areas with enough rainfall, and rainfall sufficiently well distributed throughout the year to ensure permanent vegetation cover (Figure 9), show $\delta^{18}O$ values ranging from $-3.5$ to $-0.9\%$, or lower. West African and Central African gastropods fall in this category of depleted $\delta^{18}O$, an indication of amount effect overwhelming latitudinal effect. Similar effect may be applicable in the coastal regions of East Africa, Malagasy and South Africa where latitudinal effect is masked by amount effect. By these observations, vegetational cover maps could be used to correlate $\delta^{18}O$ values of shells and environments because they integrate over time the effects of rainfall and provide topographically continuous information. In applying $\delta^{18}O$ values of gastropod shells to estimate paleoclimate, negative values of $\delta^{18}O$ will indicate environments of substantial rainfall while very positive $\delta^{18}O$ values will give an indication of areas of evaporative control of
Vegetation map of Africa redrawn from NASA imagery

FIGURE 9
the oxygen isotope ratios taking into consideration predicted latitudinal isotope ratio values.

RESULTS

Tables 3 and 4 summarize the oxygen isotope ratio information on the freshwater gastropod shells and the water samples respectively. In Table 1 the raw oxygen isotope ratio values were corrected to PDB by adding 0.84% to correct to the PDB standard from the Graduate School of Oceanography substandard and then subtracting 0.60% as an aragonitic correction factor. Since $\delta^{18}O$ values with reference to the PDB is reported at $25^\circ$C, the PDB values were corrected to $25^\circ$C by adding or subtracting $0.18\%$ for each $1^\circ$C of temperature change. The application of the $0.18\%$ to bring the shell and water samples to $25^\circ$C is to make the values comparable and also to correct for ambient temperature deviations in Ghana. The last column gives the $\delta^{18}O$ values after the PDB and temperature corrections which are plotted in Figure 10. In addition to the above corrections carried out on the raw $\delta^{18}O$ values for the water samples, the bath temperature which was equilibrated at $31^\circ$C was also corrected to $25^\circ$C to determine the final $\delta^{18}O$ values in the last column of Table 4 which is also plotted in Figure 10.

Plotted in Figure 10 are $\delta^{18}O$ values for both shells (aperture samples) and water corrected to PDB and temperature corrected. There is a good correlation between the $\delta^{18}O$ values of the gastropod shells and those of the water. It can be observed that the shell isotope ratios lag behind water isotope ratios by about 1 to 2 months.
Table 3

OXYGEN ISOTOPE RATIO VALUES OF FRESHWATER GASTROPOD SHELLS

SITE: The River Pra at Krobo, Western Region, Ghana.


SPECIES: Melanoides Tuberculata

<table>
<thead>
<tr>
<th>MONTH</th>
<th>$^{18}$O (raw)</th>
<th>$^{18}$O (PDB)</th>
<th>TEMP. CORRECTION</th>
<th>$^{18}$O (Aragonite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEC.</td>
<td>-3.49</td>
<td>-3.25</td>
<td>0.00</td>
<td>-3.25</td>
</tr>
<tr>
<td>JAN.</td>
<td>-3.87</td>
<td>-3.63</td>
<td>-0.04</td>
<td>-3.67</td>
</tr>
<tr>
<td>FEB.</td>
<td>-3.20</td>
<td>-2.96</td>
<td>0.00</td>
<td>-2.96</td>
</tr>
<tr>
<td>MAR.</td>
<td>-4.39</td>
<td>-4.15</td>
<td>0.00</td>
<td>-4.15</td>
</tr>
<tr>
<td>APR.</td>
<td>-4.06</td>
<td>-3.82</td>
<td>+0.09</td>
<td>-3.73</td>
</tr>
<tr>
<td>MAY</td>
<td>-2.44</td>
<td>-2.20</td>
<td>0.00</td>
<td>-2.20</td>
</tr>
<tr>
<td>JUN.</td>
<td>-3.36</td>
<td>-3.12</td>
<td>-0.18</td>
<td>-3.30</td>
</tr>
<tr>
<td>JUL.</td>
<td>-3.22</td>
<td>-2.98</td>
<td>0.00</td>
<td>-2.98</td>
</tr>
<tr>
<td>AUG.</td>
<td>-3.46</td>
<td>-3.22</td>
<td>-0.30</td>
<td>-3.52</td>
</tr>
<tr>
<td>SEP.</td>
<td>-4.61</td>
<td>-4.37</td>
<td>-0.36</td>
<td>-4.73</td>
</tr>
<tr>
<td>OCT.</td>
<td>-4.47</td>
<td>-4.23</td>
<td>-0.18</td>
<td>-4.41</td>
</tr>
<tr>
<td>NOV.</td>
<td>-4.39</td>
<td>-4.15</td>
<td>-0.18</td>
<td>-4.33</td>
</tr>
</tbody>
</table>
TABLE 4

OXYGEN ISOTOPE RATIO VALUES OF WATER SAMPLES

SITE: The River Pra at Krobo, Western Region, Ghana.


<table>
<thead>
<tr>
<th>MONTH</th>
<th>$^{18}O$(raw)</th>
<th>$^{18}O$(PDB)</th>
<th>BATH CORR.</th>
<th>TEMP. CORR.</th>
<th>$^{18}O$(final)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEC.</td>
<td>-5.82</td>
<td>-4.98</td>
<td>-3.98</td>
<td>0.00</td>
<td>-3.98</td>
</tr>
<tr>
<td>JAN.</td>
<td>-5.04</td>
<td>-4.20</td>
<td>-2.20</td>
<td>-0.04</td>
<td>-3.24</td>
</tr>
<tr>
<td>FEB.</td>
<td>-5.13</td>
<td>-4.29</td>
<td>-3.29</td>
<td>0.00</td>
<td>-3.29</td>
</tr>
<tr>
<td>MAR.</td>
<td>-4.20</td>
<td>-3.36</td>
<td>-2.36</td>
<td>0.00</td>
<td>-2.36</td>
</tr>
<tr>
<td>APR.</td>
<td>-5.30</td>
<td>-4.46</td>
<td>-3.46</td>
<td>+0.09</td>
<td>-3.35</td>
</tr>
<tr>
<td>MAY</td>
<td>-5.14</td>
<td>-4.30</td>
<td>-3.30</td>
<td>0.00</td>
<td>-3.30</td>
</tr>
<tr>
<td>JUN.</td>
<td>-5.09</td>
<td>-4.25</td>
<td>-3.25</td>
<td>-0.18</td>
<td>-3.43</td>
</tr>
<tr>
<td>JUL.</td>
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<td>-4.47</td>
<td>-3.47</td>
<td>0.00</td>
<td>-3.47</td>
</tr>
<tr>
<td>AUG.</td>
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<td>-5.25</td>
<td>-4.25</td>
<td>-0.30</td>
<td>-4.55</td>
</tr>
<tr>
<td>SEP.</td>
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<td>-4.49</td>
<td>-3.49</td>
<td>-0.36</td>
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</tr>
<tr>
<td>OCT.</td>
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<td>-3.65</td>
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<td>-3.83</td>
</tr>
<tr>
<td>NOV.</td>
<td>-5.14</td>
<td>-4.30</td>
<td>-3.30</td>
<td>-0.18</td>
<td>-3.48</td>
</tr>
</tbody>
</table>
Figure 10

OXYGEN-18 (PDB)

D-18 of water and shells vs month
Shifting the $^{18}O$ plot of the water by one month gives an almost complete correspondence of the $^{18}O$ plots of both water and shells as shown in Figure 11. Both water values and shell values give a fairly good picture of changing conditions, allowing for the lag. The $^{18}O$ values of the water samples are almost constant within $-3\%$ to $-4\%$ range throughout the period of collection except for March and August when $^{18}O$ values of $-2.36$ and $-4.55$ were recorded respectively. The high $^{18}O$ value recorded for March coincides with the period of maximum drought brought about by high temperatures and Harmattan winds from the Sahara. The low August $^{18}O$ value, on the contrary, corresponds well with the period of low temperature, highest rainfall and the flooding of the River Pra. Similar correspondence is observed for the shell $^{18}O$ values in Table 3 except for the 1 to 2 month’s slippage of the maximum $^{18}O$ from March to May and the minimum $^{18}O$ slipping from August to September. In general, the $^{18}O$ results are nearly constant except for a rise of $0.5\%$ in October for the shell and in December for the water samples. We attribute this general constancy to normal constancy of rainfall and temperature, and the one excursion as a consequence of the yearly arrival of the Harmattan.
0-18 of Water and Shells vs. Month.

---

**Diagram:**

- **Oxygen-18 (PDB):**
  - Shell 0-18
  - Water 0-18

- **Month:**
  - Dec.
  - Jan.
  - Feb.
  - Mar.
  - Apr.
  - May
  - Jun.
  - Jul.
  - Aug.
  - Sep.
  - Oct.
  - Nov.

**Figure 11**
Table 1 shows the temperature profile of the tributary of the River Pra at Krobo during the sampling period of December 9, 1985 to October 15, 1986. The water temperatures and the ambient temperatures tabulated in Table 1 are also shown on the bar graph plotted in Figure 12. The maximum, minimum, temperature range and average temperatures extracted from Table 1 are summarized in Table 5. The average temperature recorded in Table 5 was determined by the simple mean over 12 months period. Average summer and winter temperatures were obtained over 6 months period with summer in the Northern hemisphere defined by the months between May and October and winter months from November to April. Ambient temperature difference over the period of collection is twice that of the water temperature difference over the same period. The average summer temperature is lower than the average winter temperature.

By performing regression analysis on data collected from the tributary of the River Pra at Krobo, the regression equations were obtained with the correlation coefficients. Table 6 summarizes the correlation between water temperature, air temperature, precipitation and the oxygen isotope ratio values of both the water and the shell. The correlation factors for the water temperature values and the oxygen isotope ratios of the shell and water are 0.75 and 0.74 respectively. This correlation is further improved from 0.75 to 0.81 by shifting the oxygen isotope ratios of the shell one month to adjust for the lag in the $\delta^{18}O$ incorporation into the gastropods. The correlation plot for the water $\delta^{18}O$ and water temperature is shown in
MEAN MONTHLY TEMP.-RIVER PRA. KROBO

WATER TEMPERATURE  AMBIENT TEMP.

TEMPERATURE °C

23 23.5 24 24.5 25 25.5 26 26.5 27 27.5 28 28.5 29 29.5 30 30.5 31 31.5

DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV

MONTH (1985 - 1986)

FIGURE 12
### TABLE 5

**MAXIMA, MINIMA AND AVERAGE TEMPERATURES °C**

**SITE**: The River Pra at Krobo, Western Region, Ghana.


<table>
<thead>
<tr>
<th></th>
<th>WATER</th>
<th>AMBIENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Temperature</td>
<td>25.5</td>
<td>31.0</td>
</tr>
<tr>
<td>Minimum Temperature</td>
<td>23.0</td>
<td>26.0</td>
</tr>
<tr>
<td>Average Temperature</td>
<td>24.5</td>
<td>27.5</td>
</tr>
<tr>
<td>Average Summer Temperature</td>
<td>23.9</td>
<td>26.9</td>
</tr>
<tr>
<td>Average Winter Temperature</td>
<td>25.1</td>
<td>28.0</td>
</tr>
<tr>
<td>Temperature Fluctuation</td>
<td>2.5</td>
<td>5.0</td>
</tr>
</tbody>
</table>
**TABLE 6**

**SUMMARY OF CORRELATION VALUES**

<table>
<thead>
<tr>
<th></th>
<th>SHELL $\delta^{18}O$</th>
<th>WATER $\delta^{18}O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>* $R$</td>
<td><strong>$R^2$</strong></td>
<td>$R$</td>
</tr>
<tr>
<td>Water Temperature</td>
<td>0.74 (0.81)</td>
<td>0.55 (0.65)</td>
</tr>
<tr>
<td>Air Temperature</td>
<td>0.67 (0.33)</td>
<td>0.45 (0.11)</td>
</tr>
<tr>
<td>Precipitation</td>
<td>0.66 (0.62)</td>
<td>0.44 (0.39)</td>
</tr>
<tr>
<td>Shell $\delta^{18}O$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* $R$ = Coefficient of correlation  

** $R^2$ = Coefficient of determination  

Correlation coefficients of one month slippage are in brackets.
figure 13 while that of the shell $s^{18}O$ and water temperature with the one month slippage is shown in Figure 14.

The correlation of precipitation with shell oxygen isotope ratios, 0.66, and with water oxygen isotope ratios, 0.42, are good however the shell $s^{18}O$ values correlate better with precipitation than the water $s^{18}O$ values. Figure 15 shows the correlation plot of precipitation and water $s^{18}O$. Air temperature correlations with shell $s^{18}O$ and water $s^{18}O$ are as good as the precipitation correlation with shell $s^{18}O$ and water $s^{18}O$. The correlation plot of the air temperature and shell oxygen isotope ratios is shown in Figure 16. The correlation between the shell oxygen isotope ratio values and the water oxygen isotope ratios, 0.68, is also listed in Table 6.
WATER TEMPERATURE VS. WATER ISOTOPES

\[ y = 27.33 + 0.81x \quad R = 0.75 \]

FIGURE 13
SHELL ISOTOPE RATIOS VS. WATER TEMPERATURE

\[ y = 26.99 + 0.68x \quad R = 0.81 \]

SHELL ISOTOPE RATIO - SLIPPED ONE MONTH

FIGURE 14
RAINFALL VS. WATER ISOTOPES

\[ y = 196.75 + 27.98x \quad R = 0.42 \]

FIGURE 15
AIR TEMPERATURE VS. OXYGEN ISOTOPES

\[ y = 30.33 + 0.79x \quad R = 0.67 \]

FIGURE 16
DISCUSSION

A cursory look at the plot of the $^{18}$O values of the gastropod shells and that of the water in Figure 10 may not be enough to observe the convincing correlation between the shells and the water environment in which they lived. This is expected because the tributary of the River Pra at Krobo is not stagnant. The microenvironment of the gastropods is constantly changing due to mixing, water movement and the replenishing of the water in the immediate environment of the gastropods by precipitation from the northern tributaries which may have different oxygen isotope ratios and fresh local rains. Not only these but other factors such as the rate of incorporation of the $^{18}$O into the shells of the gastropods might be a factor as well as the chosen time interval of sampling. This parallelism between the $^{18}$O plots of the water and the shells, which is a good indicator as to the possibility of applying oxygen isotope ratios in paleoclimatology, is in accordance with an earlier observation by Epstein et al. (1953) that the oxygen isotope constant of calcite is dependent on both the $^{18}$O and temperature of ambient water.

The Collector's monthly remarks on water level of the River Pra which were requested as part of this research project, and the prevailing climatic conditions during the period of water and gastropod collection corresponds very well with the mean monthly rainfall values tabulated in Table 7 and also plotted in Figure 17 (Griffiths, 1972). The data given are from stations very close to Krobo (refer to Figure 18 which gives the annual mean rainfall adapted
FIGURE 17

(MEAN MONTHLY RAINFALL—NEAR R. PRA)

(ADAPTED FROM GRIFFITHS, 1972)
FIGURE 18

ANNUAL MEAN RAINFALL MAP OF GHANA

(ADAPTED FROM BOATENG, 1967)
from Boateng (1967)). In areas of Africa especially West and Central Africa where rainfall is high and well spread out over a period of one year, such that there is permanent vegetative cover, $\delta^{18}O$ values in gastropod shells have been observed to be between -3.5 to -0.9 per mil (Abell, 1985). Our values fall close to this range with the average monthly $\delta^{18}O$ for the one year period being -3.51 for the water samples and -3.60 for the gastropod shells, giving a 0.11 per mil average difference between the shells and the water samples. Without any land mass fractionation, the expected values of the $\delta^{18}O$ at this latitude should have been approximately -1.0 or -2.0 (Figure 7). The isotope ratio values in this region are more depleted in oxygen isotope ratios for this latitude. Even then, the $\delta^{18}O$ values of the shells are more depleted than that of the water samples. Here, this is attributable to amount effect, which is substantiated by the $S_s - S_w$ values of -0.52 from the water and -0.54 from the shell. This is in consonance with the observation of Tucker et al., (1985) and Abell (1985) where latitudinal effect is overwhelmed by amount effect which in turn correlates well with vegetation cover map of Ghana. (Figure 3)

The seasonality information summarized in Table 8 is to assist in the separation of amount effect from temperature effect in the tropics. By taking the difference between $S_s$, the unweighted mean $S$ value for summer and $S_w$, the unweighted mean $S$ value for winter. Summer in the Northern hemisphere is taken to be the period between May-October while November-April is taken as the winter and the vice versa in the Southern hemisphere. A negative $S_s - S_w$ indicates the predominance of amount effect in the tropics.
<table>
<thead>
<tr>
<th>MONTH</th>
<th>AXIM</th>
<th>TAKORADI</th>
<th>ACCRA</th>
</tr>
</thead>
<tbody>
<tr>
<td>JAN.</td>
<td>41</td>
<td>33</td>
<td>16</td>
</tr>
<tr>
<td>FEB.</td>
<td>54</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>MAR.</td>
<td>122</td>
<td>78</td>
<td>73</td>
</tr>
<tr>
<td>APR.</td>
<td>157</td>
<td>110</td>
<td>82</td>
</tr>
<tr>
<td>MAY</td>
<td>426</td>
<td>278</td>
<td>145</td>
</tr>
<tr>
<td>JUN.</td>
<td>613</td>
<td>249</td>
<td>193</td>
</tr>
<tr>
<td>JUL.</td>
<td>147</td>
<td>84</td>
<td>49</td>
</tr>
<tr>
<td>AUG.</td>
<td>56</td>
<td>41</td>
<td>16</td>
</tr>
<tr>
<td>SEP.</td>
<td>90</td>
<td>49</td>
<td>40</td>
</tr>
<tr>
<td>OCT.</td>
<td>205</td>
<td>127</td>
<td>80</td>
</tr>
<tr>
<td>NOV.</td>
<td>130</td>
<td>63</td>
<td>38</td>
</tr>
<tr>
<td>DEC.</td>
<td>74</td>
<td>45</td>
<td>18</td>
</tr>
<tr>
<td><strong>ANNUAL</strong></td>
<td><strong>2115</strong></td>
<td><strong>1182</strong></td>
<td><strong>787</strong></td>
</tr>
</tbody>
</table>
### TABLE 8

**SEASONALITY AND $^{18}$O VALUES**

**SITE:** The River Pra at Krobo, Western Region, Ghana.

**COLLECTION PERIOD:** December 1985 - November 1986

<table>
<thead>
<tr>
<th>$^{18}$O OF WATER</th>
<th>$^{18}$O OF SHELLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_w$</td>
<td>-3.25</td>
</tr>
<tr>
<td>$S_s$</td>
<td>-3.77</td>
</tr>
<tr>
<td>$S_s - S_w$</td>
<td>-0.52</td>
</tr>
</tbody>
</table>

$S_w$ = Winter oxygen isotope ratio  
$S_s$ = Summer oxygen isotope ratio  

Northern Hemisphere Summer Months: May - October.  
Northern Hemisphere Winter Months: November - April.
TABLE 9

METEOROLOGICAL DATA FROM THE AIRFORCE BASE AT TAKORADI


<table>
<thead>
<tr>
<th>MONTH</th>
<th>RAINFALL (mm)</th>
<th>NO. OF DAYS</th>
<th>MEAN TEMP. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCT.</td>
<td>64.8</td>
<td>3</td>
<td>29.7</td>
</tr>
<tr>
<td>NOV.</td>
<td>111.8</td>
<td>6</td>
<td>31.5</td>
</tr>
<tr>
<td>DEC.</td>
<td>0.0</td>
<td>-</td>
<td>31.3</td>
</tr>
<tr>
<td>JAN.</td>
<td>0.0</td>
<td>-</td>
<td>31.5</td>
</tr>
<tr>
<td>FEB.</td>
<td>62.3</td>
<td>7</td>
<td>31.6</td>
</tr>
<tr>
<td>MAR.</td>
<td>20.0</td>
<td>4</td>
<td>31.6</td>
</tr>
<tr>
<td>APR.</td>
<td>50.4</td>
<td>6</td>
<td>32.3</td>
</tr>
<tr>
<td>MAY.</td>
<td>99.4</td>
<td>16</td>
<td>31.6</td>
</tr>
<tr>
<td>JUN.</td>
<td>185.2</td>
<td>17</td>
<td>29.5</td>
</tr>
<tr>
<td>JUL.</td>
<td>163.6</td>
<td>12</td>
<td>28.2</td>
</tr>
<tr>
<td>AUG.</td>
<td>21.3</td>
<td>4</td>
<td>27.7</td>
</tr>
<tr>
<td>SEP.</td>
<td>18.5</td>
<td>8</td>
<td>28.3</td>
</tr>
<tr>
<td>OCT.</td>
<td>51.9</td>
<td>8</td>
<td>29.0</td>
</tr>
<tr>
<td>NOV.</td>
<td>61.4</td>
<td>6</td>
<td>28.2</td>
</tr>
</tbody>
</table>
The climatic conditions prevailing in the Southern rainforest region of Ghana consists of two rainy periods in March-July and September-October. The September-October rains in Ghana are followed by the Harmattan winds from the Sahara desert, which are characterized by high daytime temperatures with low humidity and dry cool nights. The Harmattan is usually intense during December and January (Beadle, 1974) however, during the sampling period, the intensity of the Harmattan winds was recorded in January and February. The Harmattan winds coupled with high daytime temperatures between December and May, as recorded by our collaborator shown under remarks in Table 1, brought about maximum evaporative effect which is recorded in both water and shell isotope ratios in March and April respectively. The highest $\delta^{18}O$ value of $-2.36$ for the water was recorded in March, the period of maximum drought, which was reflected in the shell value as $-2.20$ in May, a lag of approximately 2 months. The Harmattan winds are comparatively less powerful than the Southeasterlies in August but they accelerate evaporation at the surface of standing waters and provide the necessary energy for stirring. (Beadle, 1974) A lag of 1 month is observed between the $\delta^{18}O$ values of the shells and that of the water. A low $\delta^{18}O$ value of $-4.55$ is recorded in the $H_2O$ in August, while a low of $-4.55$ is recorded in the shell in September. The difference between the maximum and minimum $\delta^{18}O$ for the water is $-2.19$ per mil while that of the shell is $-2.53$ per mil. In general $\delta^{18}O$ results are nearly constant except for a rise of about 0.5% in
October for the shells and in December for the water samples. We attribute this general constancy to normal constancy of rainfall and temperature, and the one excursion as the consequence of the yearly arrival of the Harmattan.

The temperature effect is clearly demonstrated by the parallelism that exists between the $^{18}O$ plot of the water, the shell and the monthly temperature plot. The maximum ambient temperature, $31^\circ C$, and the maximum water temperature, $25.5^\circ C$, were both recorded in April while the minimum ambient temperature, $26.0^\circ C$, and the minimum water temperature, $23.0^\circ C$, were recorded for the month of August. Average monthly water temperature of $24.5^\circ C$ was calculated for the collection period. The maximum and minimum $^{18}O$ values recorded by both shell and water correspond very well with the months for which maximum and minimum temperatures were recorded. The average ambient temperature was $3.0^\circ C$ higher. The water temperature fluctuation was $2.5^\circ C$ while the air temperature fluctuated by $5.0^\circ C$ during the collection period. The average summer temperature is lower than the average winter temperature. A negative difference is obtained when the average winter temperature is subtracted from the average summer temperature. The conversion of this temperature difference to $^{18}O$ gives a negative $^{18}O$ value which substantiates the amount effect obtained by the difference between $S_s - S_w$.

Amount effect is further substantiated by the correlation between precipitation and $^{18}O$ of both the water (0.42) and the shells (0.66). By these correlation values it is observed that approximately 18% of the variations in the water $^{18}O$ values at the River Pra is due to
amount effect while approximately 44% of the variations in the shell $^{18}O$ values is attributable to amount effect (Table 6). Significant correlations exist between shell $^{18}O$ and water $^{18}O$ air temperature and precipitation, however, the correlation between shell $^{18}O$ and water temperature is even better (0.74). This is understandable because the microenvironment of the gastropod is greatly influenced by the water temperature. For all practical purposes, the correlation between water $^{18}O$, shell $^{18}O$ and water temperature are the same 0.75. Since it does not rain heavily all year round, the precipitation influences the $^{18}O$ variation by approximately 44% leaving the major influence, 55%, of the $^{18}O$ values to water temperature variation which improves considerably with the slippage (65%).

Application of these results to fossil samples must be carried out with caution as several other factors come into play and must be taken into consideration in the interpretation of $^{18}O$ ratios of fossil gastropod shells. Some of the factors that must be considered include altitude, latitude, reliability of dating, longevity of gastropods and knowledge of the hydrological regime from which the gastropod shell was collected. For example, the ancient site from where the shell is collected should be well documented and knowledge of the longevity of the individual species of gastropods must be known. It is essential to know the age of the shell in order to correlate it with other historical environmental information. Some fossil shells undergo diagenesis or recrystallization from aragonite to calcite, a process engendered by local weathering conditions. Whether a shell is aragonitic or calcitic can be detected by X-ray diffraction (XRD). In
order to extract seasonality information from a fossil shell, a sequential sampling along the growth spirals of the individual shells is necessary, while the average oxygen isotope ratios of whole shells will be useful in the characterization of major regional climatic trends.

Apart from gastropod shell information, some environmental information which can be acquired by other geological techniques has to be provided before applying oxygen isotope ratio values to the interpretation of paleoclimates. Among these are latitudinal, altitudinal, and hydrological information. For example, the $\delta^{18}O$ values of shells collected from a location where an ancient transient stream existed would be very difficult to interpret as compared with a location where a permanent body of water existed. Gastropods in areas with low rainfall and transient streams risk undergoing estivation which in turn will give only fragmentary seasonal information. Gastropod shells collected from areas where there was permanent vegetative cover, permanent lakes or tropical rainforest area with rainfall all year round will give interpretable results. Latitudinal and altitudinal information would also be useful in data interpretation. The geographical conditions of past water basins may be deciphered from remote sensing by the Shuttle Imaging Radar (SIR), Landsat images and Satellite navigation systems. For example, McCauley and his colleagues (1986) have applied SIR, Landsat images and Satellite navigation systems in their study of Miocene–Pliocene drainage system in Saharan Africa. Freshwater bivalves and gastropods were recovered at several points along the ancient waterways which
crossed the Sahara during the late Miocene and early Pliocene period, and could prove useful in characterizing that climatic episode.

In summary, the monthly analyses of both water and gastropod shells from a tributary of River Pra at Krobo, in the Western region of Ghana, approximately 700km from the Sahel, have shown amount effect, temperature effect and evaporative effect. Good parallelism between the $s^{18}O$ plots of the shells, water and temperature was observed. The $s^{18}O$ values were in agreement with vegetative cover maps of Ghana and Africa. Seasonality was also recorded by the shells of the gastropods. These results seem to pave the way for the application of $s^{18}O$ of shells in deciphering past climatic conditions, which is a boon to paleoclimatology. The application of this kind of study to samples collected from sites of different vegetation cover in the region would contribute to the data base upon which the application of $s^{18}O$ values in the study of past climate could be based.

**CONCLUSIONS**

Upon completion of this study, the following observation were made:

1. Freshwater gastropod shells are useful proxies of the prevailing climatic conditions during the life span of the gastropods.
2. Evaporative effect, temperature effect, and amount effect can be determined using the $s^{18}O$ of shells and water.
3. Time lag was observed between $s^{18}O$ of shell and the $s^{18}O$ of the
water.

4. $\delta^{18}O$ values of the shell and the water correlate well with vegetation cover maps of Ghana and Africa.

5. Seasonality was recorded in the $\delta^{18}O$ values of the shell and the water.

6. Information on the general character of the body of water is needed to apply shell oxygen isotope ratios as proxies in paleoclimatology.
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