Isotopic Equilibrium between Shells and Their Environment

Abstract. *The carbon-isotopic composition of shell carbonate is shown to be in isotopic equilibrium with bicarbonate dissolved in the water. By measurement of both ^{13}C and ^{18}O in a series of brackish-water shells a mean growth temperature can be deduced.*

One problem in work on isotope paleotemperatures is the question of whether the carbonate sample to be analyzed for ^{18}O is of purely marine origin or not. There is always the possibility that freshwater contamination of the seawater in which the shell grew caused more or less severe changes in the ^{18}O content. Because freshwater is mostly depleted in ^{18}O relative to ocean water, admixture causes the temperature derived from the shell carbonate to be too high. We attempted to find a criterion for the determination of whether conditions were truly oceanic or not.

Shells of the species *Mytilus edulis, Cardium edule, Mya arenaria,* and *Macoma balthica* were collected alive from two estuaries in which the ratio of freshwater to seawater slowly varies. One estuary, the Westerschelde, Netherlands, has a rather uniform chlorinity gradient of 0 to 18 ppt (parts per thousand), over a distance of about 90 km, caused by mixing of freshwater from the River Schelde with water of the North Sea; the other is the former Zuiderzee, a shallow, brackish, inland sea that received its water largely from the river Ijssel, an arm of the Rhine.

An average portion of each shell was analyzed after removal of organic material. Analysis of the relative abundances of ^{18}O and ^{13}C in the shell carbonates showed a linear relation between the two (Fig. 1). Also there appeared to be correlation between the isotopic contents and the freshwater: saltwater mixing ratio, the suggestion being that not only the ^{18}O (*1*), but also the ^{13}C, is determined by the chemical environment in which the mollusks live.

For investigation of this point, samples of water were collected along the estuaries and analyzed for ^{18}O of the water and ^{13}C of the dissolved bicarbonate. The $\delta^{13}C$ of bicarbonate was deduced from the measured $\delta^{13}C$ values of the total dissolved carbon by use of the known isotope-fractionation factor between CO_2 and HCO_3^- (*2*).

Besides the normal linear relation between ^{18}O and chlorinity (*3*), ^{13}C and chlorinity also proved to be linearly dependent (*4*), so that plotting of $\delta^{13}C$ of the bicarbonate against the $\delta^{18}O$ of water [values relative to SMOW (*5*)] from the Westerschelde yields a straight line (Fig. 1).

Figure 1 shows also a mean value for samples collected in the English Channel where little contamination by freshwater can be expected; this point fits the same straight line. One must conclude that both the $\delta^{18}O$ (water) and the $\delta^{13}C$ (bicarbonate) of such an estuary are defined solely by the mixing ratio and the values of the end points of the curves, which in this case are: $\delta^{13}C$ (freshwater bicarbonate), -12 ppt; $\delta^{13}C$ (seawater bicarbonate), $+0.9$ ppt; $\delta^{18}O$ (river water, Schelde), -6.5 ppt; $\delta^{18}O$ (North Sea), $+0.2$ ppt.

These remarks are true only when the duration of contact between water and atmosphere is relatively short (some days). When the contact is prolonged, the possibility of carbon-isotopic exchange between dissolved bicarbonate and atmospheric carbon dioxide is much greater; such exchange leaves the $\delta^{18}O$ undisturbed, but tends to shift the $\delta^{13}C$ to higher values (less negative), until eventually equilibrium is reached—as in the ocean. Such a situation apparently occurred in the Zuiderzee. One cannot compare shells with water from the former Zuiderzee, which is now a freshwater lake; samples from different points in the lake, in which the water now has a residence time of several months, clearly indicate a gradual increase in the ^{13}C. This increase must be ascribed to isotopic exchange with the atmosphere. Although the mean residence time of water in the Zuiderzee was much shorter (some weeks), isotopic exchange is presumably the reason for the gradient of the curve for the Zuiderzee shells being smaller than would result from mere mixture of seawater and freshwater of the Ijssel having $\delta^{18}O = -8.5$ ppt; $\delta^{13}C = -12$ ppt.

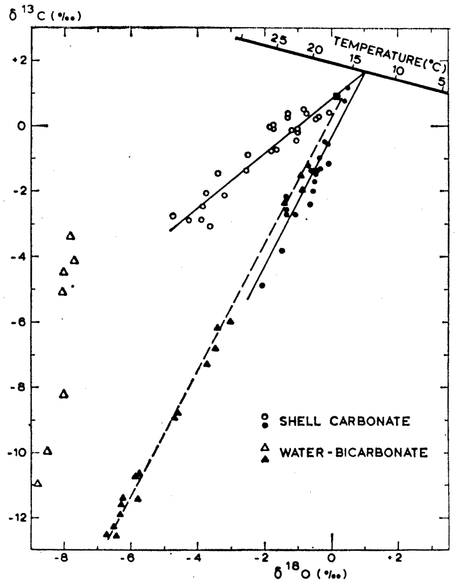

Fig. 1. Relative abundance of ^{13}C versus relative abundance of ^{18}O. $\delta^{13}C$ and $\delta^{18}O$ represent per mille deviations from the PDB standard (*8*); $\delta^{18}O$ of the water samples is relative to the SMOW standard (*5, 6*). The measurements are accurate within 0.1 ppt. Solid circles (solid line), shell carbonate; solid triangles (dashed line), dissolved bicarbonate and water of the Westerschelde; open circles, shell carbonate of the former Zuiderzee; open triangles, bicarbonate and water of the present Zuiderzee. The lines are least-squares fits to the points. The heavy line indicates the temperature-dependence of the isotopic composition of carbonate under true marine conditions; it is deduced from samples of water from the open sea (solid square). Results from both Westerschelde and Zuiderzee shell carbonates extrapolate to an average temperature of 13.5°C.

The bicarbonate curve for water from the Westerschelde clearly parallels that for the shells. The distance between the two lines should be defined by two fractionation factors: one for the oxygen isotopes in the carbonate-water equilibrium, the other for carbon in the carbonate-bicarbonate system. The fractionation depends on temperature only, so that at any given temperature the two lines should be parallel.

When known fractionation factors are applied to the isotopic composition of bicarbonate and water from the North Sea, the isotopic composition of a shell from the open sea can be deduced. At a temperature of 16.9°C the oxygen-isotope fractionation is such that $\delta^{18}O$ of the water on the SMOW scale equals the carbonate $\delta^{18}O$ on the PDB scale, while the temperature-dependency is so derived (*6*):

$$t = 16.9 - 4.2\,(\delta^{18}O_{PDB} - \delta^{18}O_{SMOW}) + 0.13\,(\delta^{18}O_{PDB} - \delta^{18}O_{SMOW})^2$$

The carbon-isotope fractionation factor is not yet accurately known. Our measurements give (*2*):

$$\alpha^{13} = \frac{(^{13}C/^{12}C)_{CaCO_3}}{(^{13}C/^{12}C)_{HCO_3^-}} = 1.0015 \text{ ppt at } 25.0\,^{\circ}C$$

and

$$(d\alpha/dt) = +\,0.07 \text{ ppt}/{}^{\circ}C$$

On the basis of these figures and the measured isotopic composition of North Sea water, the heavy line in Fig. 1 is obtained; each point on it represents the carbon and oxygen isotopic composition of a true North Sea shell at a specific temperature.

It is interesting to note that the intersection of the carbonate lines of the two estuaries falls on the equilibrium line for true marine conditions. The point of intersection corresponds to an average temperature of about 13.5°C, which is a reasonable average for the main growth period of mollusks (April to June) in this region (*7*); thus it seems evident that isotopic equilibrium exists between the shell carbonate and the surrounding water.

If one assumes equilibrium for ^{18}O and a temperature of 13.5°C ($\alpha^{18} = 1.00083$), a fractionation factor for the $CaCO_3-HCO_3^-$ equilibrium can be derived from the samples from the Westerschelde; the value $\alpha^{13} = 1.00096$ yielded is in good agreement with results from laboratory experiments: α^{13}, 1.00075 (13.5°C). The fact that mean deviation of an individual sample (± 0.36 ppt) is surprisingly small means that, for the shells we used, equilibrium is very likely not only for oxygen but also for carbon isotopes. For different regions, different δ^{18}O and (possibly) δ^{13}C values of the freshwater contaminant are to be expected, so that a straight carbonate line can only be expected in a restricted area.

Besides the mentioned effect of atmospheric exchange, quite large deviations from our figures on shell isotopic compositions can presumably result from local conditions. Local production of metabolic CO_2 or high photosynthetic activity by water flora could easily lower or increase the ^{13}C content, respectively, while the ^{18}O content can be changed, for instance, by local freshwater contamination or by evaporation in more or less closed basins. In a region of flowing water and under mild climatic conditions, such as we have considered, the correlation seems to hold remarkably well.

Thus one may draw the following conclusions:

1) In an estuary of fast-running brackish water there is a similar linear relation between the ^{13}C of the dissolved bicarbonate (ranging from −12 to +1 ppt) and chlorinity as there is known to be for the δ^{18}O of the water.

2) At least for the shells we investigated, there is a state of isotopic equilibrium between carbonate and solution, not only for the oxygen but also for the carbon isotopes.

3) An average growth temperature can be deduced for shells from an estuary by extrapolation of the $\delta^{13}C/\delta^{18}O$ plot to oceanic conditions.

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References and Notes

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Palinspastic Restoration Suggesting Late Paleozoic North Atlantic Rifting

Abstract. *Palinspastic restoration of sinistral wrench faults in Britain and of dextral wrenches in Canada, starting with the palinspastic pre-continental-drift map, implies the possibility of as much as 424 kilometers of rifting between Newfoundland and Ireland. The wrench-faulting and postulated resultant rifting are of Devonian and Carboniferous age.*

The development of a rift between Newfoundland and Ireland during the Late Paleozoic is postulated on the basis of the occurrence of both sinistral and dextral slips in the once continuous Great Glen–Cabot Fault system; it may be termed the Labrador-Biscay Rift.

Recent recognition of continuing spreading of the ocean floor in the North Atlantic (*1*) is a compelling argument in favor of the continental-drift theory. Assuming continental drift, Wilson (*2*) has called attention to the striking predrift continuity of the Great Glen Fault (or fault system) and of what he terms the Cabot Fault—in fact a system of faults extending southwestward across Newfoundland, the Maritime Provinces, the Bay of Fundy, the Gulf of Maine, and southeastern New England; he suggested a history of Devonian-to-Early Carboniferous sinistral slip for the entire Great Glen–Cabot system. Two facts argue against the sinistral-slip history as proposed:

1) A probable age distinction exists between the British wrenches and the wrenches of the northern Appalachians. The former are Devonian where dated, as in the case of the Great Glen Fault (*3*), the Fintona Fault (*4*), and the Highland Boundary Fault (if a wrench, *5*, *6*); more loosely dated otherwise on the Leannan (*7*) and the Minch (*8*) faults. By contrast, the Canadian wrenches cut Lower to Upper Carboniferous, where dated (*9*, *10*); while the ages may overlap in part, as some of the British faults have had post-Devonian history (*11*) and the Canadian faults may have had pre-Carboniferous movements, the major displacements apparently were not synchronous.

2) Probably of greater significance is the apparent discrepancy in slip directions. Sinistral slip dominates the major faults trending from northeast to southwest in the British Isles (*3–5*, *7*, *8*), although the Highland Boundary Fault may be an exception (*6*). Late Carboniferous sinistral slip did occur along the Cabot Trend on one fault—the Harvey-Hopewell of eastern New Brunswick (*9*)—but otherwise the dominant sense of displacement is dextral on most of the Cabot Fault system (*9*, *10*, *12*, *13*), possibly including an earlier phase on the Harvey-Hopewell Fault itself. Thus, aside from the question of age, the opposition of slip directions precludes a single shear history of the Great Glen–Cabot Fault system. However, palinspastic analysis does suggest at least two solutions to the problem that could be compatible with the continental-drift theory.

Figure 1 is taken from the palinspastic map of Bullard *et al.* (*14*), with prominent wrenches and other faults added. Further palinspastic reconstruction can then be made (Fig. 2) by restoration of the Late Paleozoic wrench displacements in one of several ways: First, one may see that the sinistral slips of the British Isles and the opposed dextral slips in Canada could have resulted in the driving together of the Hebrides-Greenland block and the Labrador-Laurentia block, closing out an ancestral Labrador Strait. Such a clo-