

$\delta^{18}\text{O}$ of carbonate, quartz and phosphate from belemnite guards: implications for the isotopic record of old fossils and the isotopic composition of ancient seawater

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Abstract

Belemnite guards of Cretaceous and Jurassic age were found to contain varying amounts of quartz deposited both on the external surface and inside the rostrum. The oxygen isotopic composition of coexisting carbonate, quartz and phosphate from the same rostrum was measured according to well-established techniques. None of these compounds showed isotopic values in equilibrium with one another. Assuming $\delta^{18}\text{O}$ values of the diagenetic water within the range of meteoric waters, the $\delta^{18}\text{O}(\text{SiO}_2)$ yield temperatures in agreement with the apparent secondary origin of this phase. The $\delta^{18}\text{O}(\text{CO}_3^{2-})$ range, with a certain continuity, between -10.8 and $+0.97$ PDB-1 with most of the intermediate values being within the range of the carbonate isotopic values of Mesozoic fossils. The most positive isotopic results obtained from phosphate are close to $+23/+24\%$ (V-SMOW). They can hardly be related to a secondary origin of the phosphate, or to the presence of diagenetic effects, since these results are among the most positive ever measured on phosphate. As far as we know there is no widespread diagenetic process determining an ^{18}O enrichment of phosphate. The very low concentration of phosphate did not allow the determination of its mineralogical composition. All the available $\delta^{18}\text{O}(\text{PO}_4^{3-})$ values from belemnite and non-belemnite fossils of marine origin of Tertiary and Mesozoic age are reported along with the newly measured belemnites. The following conclusions may be drawn from the data reported: (1) the pristine oxygen isotope composition of fossil marine organisms (either carbonate or phosphate) may easily undergo fairly large changes because of oxygen isotope exchange processes with diagenetic water; this process is apparent even in the case of geologically recent fossils; (2) the $\delta^{18}\text{O}(\text{PO}_4^{3-})$ of belemnite rostra seems to be, at least in the case of the most positive results, in isotopic equilibrium with environmental water because of the similarity between the results from Cretaceous belemnites and the results from Cretaceous and Lower Tertiary pelecypods and fish teeth; 3) if so, the only feasible interpretation that can be suggested for the ^{18}O enriched data is the possibility of a relatively large variation of the oxygen isotopic composition of ocean paleowater from Jurassic to recent time.

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1. Introduction

Paleoclimatological and paleoceanographic reconstructions based on the isotopic measurement

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of carbonate and phosphate samples (both biogenic or abiogenic materials) rely on two basic assumptions that are generally accepted by most of the scientists involved in this research. These two assumptions have become the soul of truth. (1) The pristine isotopic composition of both carbonate and (a fortiori) phosphate is generally preserved throughout geologic time. Even Paleozoic fossils (e.g. [1,2]) and sediments (e.g. [3,4]) are often considered to have truly preserved their pristine values despite diagenetic processes affecting them for hundreds of million years. (2) The oxygen isotopic composition of ocean water is considered to have undergone only very minor changes through geologic time (or, at least, throughout Phanerozoic), preserving a mean $\delta^{18}\text{O}$ value equal or very close to the mean modern value (e.g. [5–8]). These ‘*truths of science*’ have lasted through time despite repeated results in contrast to these two assumptions, particularly the former.

Among these results the tendency of fossil carbonate shells, limestones, marine phosphorites, phosphatic fossils and cherts towards lighter $\delta^{18}\text{O}$ values with increasing geologic age is of importance. This tendency has been documented in a number of papers published in the last fifty years for carbonates (e.g. [9–12]), cherts [13–15] and phosphorites [16,17]. Some authors agree on the interpretation of these trends as the effect of a continuous post-depositional oxygen isotope exchange between the pristine material and isotopically light meteoric water. However, there is no general consensus on the possibility that such an exchange may control the isotopic composition of these compounds through geologic time. Some authors believe that the lighter isotopic values exhibited by Mesozoic and Paleozoic fossils or limestones may be related to very high oceanic temperatures that existed in the past. It must be pointed out that very high temperatures are inconsistent with the existence of metazoan life in the oceans, the upper temperature limit for living marine communities being lower than 40°C. Rush and Chafetz [18] concluded that even fabric-retentive, non-luminescent fossils (in this case, brachiopods) can undergo compositional alteration and oxygen isotope exchange. However, isotopic mea-

surements on very old carbonate fossils are still carried out and normally interpreted in terms of paleoclimatological and paleoceanographic conditions despite the opposed conclusions of a few papers [19,20].

Certain authors have shown that phosphate minerals may easily undergo chemical and isotopic alteration during weathering and diagenesis [21–24]. However, completely recrystallized bones of Mesozoic age have been measured in order to draw conclusions on the biology of dinosaurs [25], and microfossils of Paleozoic age have been used to evaluate quantitatively paleoclimatological conditions (e.g. [1,26]).

As regards belemnites, a number of papers was published, particularly in the sixties and seventies, with the purpose of ‘translating’ their oxygen isotope record in terms of paleoclimatological and paleoceanographic variations throughout the Mesozoic (for an almost complete list of these papers see [27,28]). In the case of belemnites the so-called ‘seasonal variations’ exhibited by many specimens when radial spot measurements are made from the apical canal to the external margin have been considered a mark of preservation of the pristine isotopic values. However, Longinelli [29] reported isotopic ‘seasonal variations’ in the case of partially re-crystallized belemnite rostra; these findings contradict the above hypothesis. Veizer and Fritz [30] found that ‘anomalous’ concentrations of trace elements in belemnites could be systematically referred to light oxygen isotope values, and concluded that the pristine oxygen isotope values of belemnites may be controlled by post-depositional alteration processes.

Several different hypotheses have been suggested on the possible evolution of the isotopic composition of ocean water. Silverman [31] suggested an initial $\delta^{18}\text{O}$ of primordial ocean close to +7‰, today’s $\delta^{18}\text{O}$ of ocean water being the result of various processes that have caused a progressive removal of heavy oxygen. In partial agreement with the hypothesis of a progressive removal of heavy oxygen, Longinelli and Nuti [32] suggested the possibility of heavier isotopic values for Mesozoic ocean water. On the contrary, several authors suggested a possible evolution of the oxygen isotopic composition of sea-

water towards heavier oxygen isotope values with decreasing geologic ages [12,33–35]. Other authors, on the basis of ophiolite studies [6,7] and by model considerations [5,35], argued that the $\delta^{18}\text{O}$ value of ocean water is mainly buffered by hydrothermal and weathering processes at mid-ocean ridges to an almost constant value of about 0‰. The latter hypothesis seems to be generally accepted by most of the scientists involved in paleoceanographic and paleoclimatological studies.

The set of isotope data obtained from seawater fossils of Tertiary and Mesozoic age and reported in this paper seems to contradict either the assumption of a long-lasting good preservation of the isotopic composition of phosphate (and, *a fortiori*, of carbonate) or the assumption of a quasi constant isotopic composition of ocean water through geologic time.

2. Materials and methods

Forty-two belemnites (or groups of belemnites coming from the same level of the same formation) of Jurassic and Cretaceous age were measured for the oxygen isotopic composition of their quartz (when present), carbonate and phosphate (all but two of the specimens studied had measurable amounts of phosphate). These specimens come from different stratigraphic positions and different continents (Europe, North America and Greenland) (Table 1). A set of 16 belemnites of Toarcian age comes from the same formation in UK. During the chemical treatment for the measurement of the phosphate isotopic composition some belemnite rostra were found to contain fairly large amounts of quartz of secondary origin (X-ray diffraction patterns confirmed that we were dealing with quartz, not with hydrated silica). The quartz was apparently deposited on the external surface (Fig. 1) or inside the rostrum by solutions percolating through micro-fractures (Fig. 2) and/or along the apical canal (Fig. 3). In some cases the rostrum carbonate was almost completely replaced by quartz (Fig. 4).

Isotopic measurements of quartz, carbonate and phosphate were carried out according to well-established techniques. The quartz was ob-

tained by dissolution of the carbonate rostra in 0.5 M HNO_3 . The residual quartz skeleton was washed repeatedly with double-distilled water and dried overnight in an oven at 50°C. After grinding in an agate mortar, aliquots of about 7–8 mg of the fine-grained powder were reacted with BrF_5 *in vacuo* for at least 12 h at $600 \pm 10^\circ\text{C}$. The O_2 obtained from the reaction was converted to CO_2 and then measured by means of a Finnigan Delta S mass spectrometer. The standard deviation of these measurements is equal to or better than $\pm 0.3\text{‰}$ (2σ).

About 10 mg of fine-grained carbonate powder were roasted for about 45 min *in vacuo* at $350 \pm 10^\circ\text{C}$ to pyrolyze the trace amounts of organic matter still present in all fossils, no matter what their age. The powder was then reacted with 100% phosphoric acid at 25°C for 12 h, and the evolved CO_2 measured by means of a Finnigan Delta S mass spectrometer after cryogenic purification. The standard deviation of these measurements was close to $\pm 0.1\text{‰}$ (2σ).

The chemical preparation for the phosphate measurements was carried out according to well-established techniques. The belemnite rostra were dissolved in 10 M nitric acid and the organic matter oxidized by the addition of 0.3 M KMnO_4 . The phosphate was precipitated twice as ammonium phosphomolybdate, dissolved again and reprecipitated as ammonium magnesium phosphate. The sample was rinsed in double-distilled water and dried at 50°C and the protocol outlined by Crowson et al. [36] and Lécuyer et al. [37] was then used till the precipitation of Ag_3PO_4 . The final product of the chemical treatment was reacted overnight (≥ 15 h) at about 600°C with BrF_5 . The O_2 obtained from this reaction was converted to CO_2 by cycling over hot graphite in the presence of a platinum catalyst, and the CO_2 measured by means of a Finnigan Delta S mass spectrometer. The standard deviation of these measurements was close to $\pm 0.3\text{‰}$ (2σ).

3. Isotopic results and discussion

The isotopic results are reported in Table 1. None of the three compounds shows oxygen iso-

Table 1

Oxygen isotopic composition of phosphate, carbonate and quartz, and phosphate content of belemnite rostra of Jurassic and Cretaceous age

Sample no.	Species	Location	Stratigraphic position	% PO ₄ ³⁻	δ ¹⁸ O _p (V-SMOW)	δ ¹⁸ O _c (PDB-1)	δ ¹³ C _c (PDB-1)	δ ¹⁸ O _q (V-SMOW)	δ ¹⁸ O _c (V-SMOW)
1	Belemnitella sp.	Denmark	L. Maastrichtian	0.00		0.42	1.83	29.2	31.34
2	Belemnitella mucronata	Sweden	U. Campanian	0.06	20.4	-0.58	2.15	31.0	30.31
3	Belemnitella mucronata	Sweden	U. Campanian	0.05	16.8	0.41	1.20		31.33
4	Belemnitella mucronata	The Netherlands	U. Senonian	0.05	21.5	0.37	0.87	29.1	31.29
5	Actinocamax mammilatus	Sweden	L. Campanian	0.00		-0.23	0.42	28.9	30.67
6	Actinocamax mammilatus	Sweden	L. Campanian	0.02	18.5	-0.39	-0.66		30.50
7	Actinocamax mammilatus	Sweden	L. Campanian	0.02	19.5	-0.37	-0.52	29.9	30.52
8	Belemnitella mucronata	Sweden	Senonian	0.02	14.9	0.19	1.75		31.10
9	Actinocamax sp.	Denmark	Albian	0.02	18.8	0.38	1.12	29.9	31.30
10	Acroteuthis impressa	Canada	Barremian	0.04	20.9	-5.50	-1.96	26.9	25.24
11	Oxyteuthis sp.	Canada	Barremian	0.08	23.4	0.97	0.49	27.7	31.90
12	Belemnitella americana	NJ, USA	Maastrichtian	0.15	20.7	0.15	1.01		31.06
13	Acroteuthis impressa	Canada	Valanginian	0.05	20.2	-5.65	-2.01	27.1	25.08
14	Belemnitella mucronata	Breteuil, France	Senonian	0.01	16.3	-0.55	2.43		30.34
15	Dimitobelus sp.	Hughenden, Australia	L. Cretaceous	0.01	16.9	0.57	1.51		31.50
16	Acroteuthis sp.	Ottensen, Germany	Valanginian	0.01	24.3	0.38	0.38		31.30
17	Belemnitella mucronata	Saratov, Russia	Senonian	0.03	16.5	0.71	0.58		31.64
18	Belemnites lensus	Hullet, UK	Cretaceous	0.04	22.2	-1.60	2.70		29.25
19	Belemnitella americana	MT, USA	Cretaceous	0.02	21.5	0.30	0.98		30.60
20	Belemnites sp.	Pescara, Italy	Kimmeridgian	0.03	23.5	-0.07	0.94	31.9	30.83
21	Cylindroteuthis puzosiana	UK	Oxfordian	0.06	23.9	-0.75	0.79	31.9	30.13
22	Cylindroteuthis puzosiana	UK	Callovian	0.08	24.3	-0.95	0.68	31.1	29.93
23	Megateuthis giganteus	Germany	Bajocian	0.08	21.5	-1.02	1.02	29.8	29.85
24	Acrocoelites sp.	Cosenza, Italy	Bajocian Alalen.	0.05	23.7	-0.59	0.76	32.7	30.30
25	Belemnites sp.	P. Mulgrave, UK	Toarcian	0.09	17.5	-10.72	2.92		19.86
26	Belemnites sp.	Yorkshire, UK	Toarcian	0.09	20.4	-4.66	2.83		26.10
27	Belemnites sp.	Yorkshire, UK	Toarcian	0.18	17.1	-10.98	2.68		19.59

Table 1 (Continued).

Sample no.	Species	Location	Stratigraphic position	% PO ₄ ³⁻	δ ¹⁸ O _p (V-SMOW)	δ ¹⁸ O _c (PDB-1)	δ ¹³ C _c (PDB-1)	δ ¹⁸ O _d (V-SMOW)	δ ¹⁸ O _c (V-SMOW)
28	Belemnites sp.	Yorkshire, UK	Toarcian	0.09	20.9	-3.40	3.92		27.40
29	Belemnites sp.	Saltwich, UK	Toarcian	0.09	21.5	-3.59	3.88		27.20
30	Belemnites sp.	Saltwich, UK	Toarcian	0.10	19.8	-4.47	3.93		26.30
31	Belemnites sp.	Saltwich, UK	Toarcian	0.08	21.1	-4.76	3.03		26.00
32	Belemnites sp.	Runswick, UK	Toarcian	0.07	20.0	-5.92	3.60		24.80
33	Belemnites sp.	P. Mulgrave, UK	Toarcian	0.08	19.6	-10.72	-0.03		19.85
34	Belemnites sp.	P. Mulgrave, UK	Toarcian	0.01	15.8	-10.10	1.17		20.50
35	Belemnites sp.	Saltwich, UK	Toarcian	0.07	20.1	-8.15	0.14		22.50
36	Belemnites sp.	Saltwich, UK	Toarcian	0.08	20.5	-4.59	3.69		25.80
37	Belemnites sp.	Runswick, UK	Toarcian	0.06	19.2	-5.34	1.58		25.40
38	Belemnites sp.	Runswick, UK	Toarcian	0.04	18.2	-3.79	2.27		27.00
39	Belemnites sp.	Saltwich, UK	Toarcian	0.04	18.4	-4.56	1.58		26.20
40	Belemnites sp.	Saltwich, UK	Toarcian	0.05	19.0	-4.98	1.90	29.0	25.77
41	Cylindroteuthis sp.	Greenland	U. Kimmeridgian	0.08	22.3	-1.85	1.03	26.8	29.00
42	Cylindroteuthis sp.	Greenland	Kimmeridgian	0.06	20.3	-2.05	0.80		28.79

tope values in equilibrium with one another at a given temperature.

3.1. Quartz

The oxygen isotope values obtained range from +26.8 to +32.7‰ (V-SMOW). According to the apparent secondary origin of quartz, if we assume for the fluid solution percolating through the fossil oxygen isotope values within the range of mean meteoric-water values (e.g. -7.5‰ ± 2.5‰), the temperatures calculated by extrapolation of the Clayton et al. equation [38] to low temperatures are in the range of about 20 ± 20°C. These values are acceptable for the apparent secondary origin of this phase, particularly if we take into account the errors that can be caused by the extrapolation of the Clayton et al. equation [38] to low temperatures.

If a secondary origin of quartz is accepted, one should take into account the effects that the large amount of diagenetic water that percolated through each rostrum may have caused. This

water dissolved considerable amounts of the pristine carbonate, replacing it with equal amounts of quartz. Under these conditions it seems improbable that no isotopic exchange took place between this water and the remaining material in the belemnite rostra. However, the carbonate and phosphate oxygen isotope values exhibited by the quartz-bearing belemnites are not far from those of the specimens that do not contain quartz. On this basis one should conclude that isotope exchange processes affect all belemnite rostra, even though at different rates according to the different minerals considered, to different local conditions such as different water fluxes, different pH values, different chemical composition of diagenetic water, different permeability of the embedding sediments, different diagenetic temperatures and pressures, different age, etc.

3.2. Carbonate

The δ¹⁸O_c obtained (Table 1) range from -10.98‰ (sample no. 27) to +0.97 (sample no.

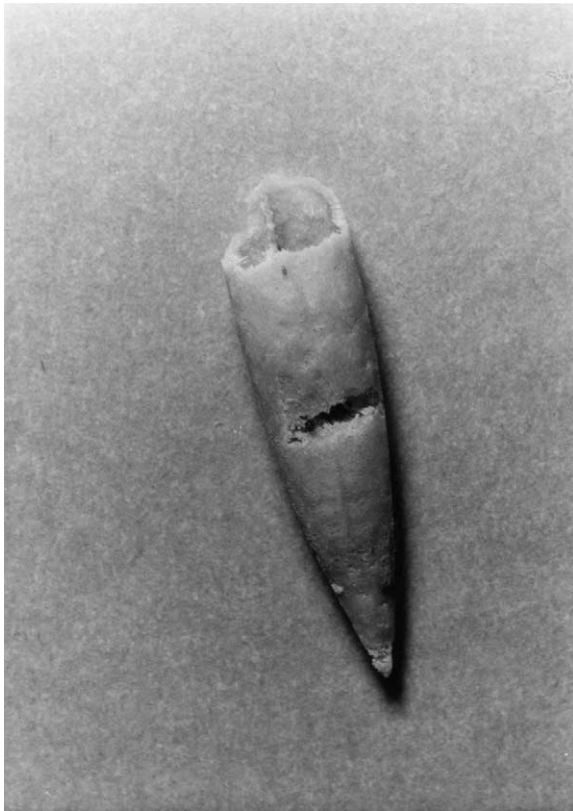


Fig. 1. External quartz shell of a belemnite rostrum.

11) vs. PDB-1. The most negative results are undoubtedly due to the effect of a marked diagenetic alteration affecting the single specimens. In fact, the sea-water temperatures that can be calculated by means of the Craig's equation [39] for $\delta^{18}\text{O}_c$ values lower than -6‰ , and assuming a $\delta^{18}\text{O}$ of ocean water equal to -1‰ (Shackleton and Kennett [40]), are higher than 40°C . These values are inconsistent with the existence of metazoan life in the oceans.

Let us calculate the environmental temperature corresponding to the heaviest carbonate isotopic composition (an *Oxyteuthis* of Barremian age from Canada), again by means of the Craig's equation [39] and assuming an oxygen isotopic composition of ocean water equal to -1‰ (Shackleton and Kennett [40]). The calculated temperature is close to 9°C , which seems a rather 'improbable' temperature for that period. Moreover, there would be an approximation to even

lower temperatures if an isotopic shift towards negative values of even a small magnitude was determined by diagenetic effects. This is not the only 'improbable' temperature value obtained from carbonate fossils (not only Belemnites) of Mesozoic and Paleozoic age. According to the brachiopod data listed in Brand [11], a few specimens of Paleozoic and Mesozoic age yield temperatures as low as about $2\text{--}10^\circ\text{C}$ (it must be pointed out that the shell structure of Brachiopods favors diagenetic alteration when compared to the more compact structure of fossils such as Belemnites). Temperatures lower than 10°C or close to this value have been reported in several papers, e.g. Dorman and Gill [41], Teis et al. [42], Bowen [43], Bowen and Fritz [44], Pirrie and Marshall [45,46], Lowenstam and Epstein [47], Ditchfield [48], etc. It is important to note that these temperatures were calculated assuming the $\delta^{18}\text{O}$ of ocean

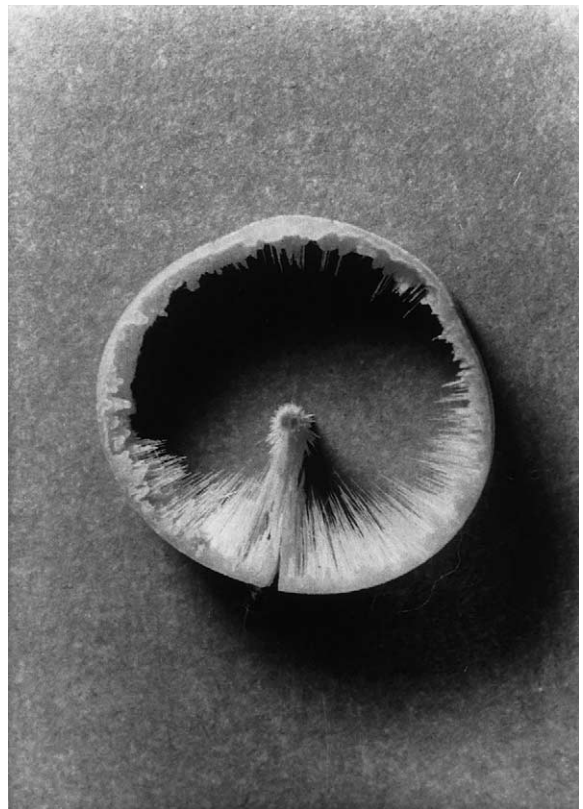


Fig. 2. Quartz skeleton in a section of a belemnite rostrum at right angle with the apical canal.



Fig. 3. Quartz skeleton in a longitudinal section of a belemnite rostrum.

water equal to 0‰ (vs. SMOW). If the temperatures are calculated assuming a $\delta^{18}\text{O}_w$ of -1‰ , values about 5°C lower are obtained. These temperatures are definitely unreliable for the Mesozoic, and particularly for the Jurassic, no matter what stratigraphic position or paleolatitude is taken into account.

The exceptionally positive isotopic values obtained by various authors were explained by means of different hypotheses. For example, Naidin et al. [49] suggested the possibility of belemnites spending most of their life in very deep waters, approaching shallow waters (shelf areas) only at the very last period of their life. Railsback [50] suggested the hypothesis of an isotopic stratification of the oceans having ^{18}O enriched heavily saline waters in deeper layers. Ditchfield [48] considers the calculated very low paleotemperatures (down to 5°C) compatible with high latitude pa-

leoceanographic conditions: the negative oxygen isotope values (down to -13‰) are considered to represent ‘anomalously warm periods’. These assumptions, or at least most of them, are at least debatable and sometimes completely unacceptable.

These data are strongly contradicted by what Hallam ([51] and enclosed references) defines as ‘overwhelming evidence’ that the Mesozoic climate had temperatures characteristic of the tropics extending into mid-latitudes, while polar regions experienced temperate conditions. The striking contradiction between the very low ‘paleotemperature’ values reported previously and the paleontological and paleobotanical evidence should be explained despite the apparent difficulty of reconciling completely different paleoclimatological considerations.



Fig. 4. Section of a belemnite rostrum at right angle with the apical canal. The carbonate is almost entirely replaced by quartz.

Several authors suggested various hypotheses to explain the evolution through time of the oxygen isotopic composition of carbonate fossils and a similar evolution of cherts. According to Knauth and Epstein [14], Kolodny and Epstein [52] and Karhu and Epstein [15], the average temperature of the ocean water declined in the course of geologic time. On the contrary, Weber [33], Perry et al. [34] and Walker and Lohmann [35] suggested the possibility of an ocean becoming progressively enriched in ^{18}O over geologic time. It is rather difficult to reconcile these and other different hypotheses.

3.3. Phosphate

If we now consider the $\delta^{18}\text{O}_p$ reported in Table 1 (the overall range of values is from +14.9 to +24.3‰) it should be pointed out that the lowest isotope values are strongly in favour of a marked diagenetic effect. The possibility of an isotopic alteration of phosphatic material and of a shift towards light isotope values during weathering and diagenesis has already been demonstrated by several authors [21–24]. However, the most striking feature is the ^{18}O enriched value exhibited by some of the specimens studied, namely nos. 11, 16, 18, 20, 21, 22, 24 and 41. It can be seen that they come from completely different areas (Canada, Germany, UK, Italy and Greenland) and completely different stratigraphic positions (Barremian, Valanginian, Kimmeridgian, Oxfordian, Callovian and Bajocian–Aalenian). If in this case we are dealing with isotopic values originally in equilibrium with environmental conditions, the temperatures that can be calculated from the heavy $\delta^{18}\text{O}_p$ values according to the Longinelli and Nuti equation [53] and assuming the mean isotopic composition of ocean water as equal to -1 (Shackleton and Kennett [40]) are of only a few degrees centigrade above 0°C . Obviously, these are unacceptable temperatures regardless of stratigraphic or latitudinal position during the Mesozoic.

As previously stated, the ‘heavy’ $\delta^{18}\text{O}_p$ values can hardly be related to diagenetic processes or to a secondary origin of the phosphate, since they are among the most positive ever measured on

phosphate, and as far as we know there is no widespread diagenetic process which can cause an ^{18}O enrichment of phosphate. On the other hand, it must be clearly stated that the low concentration of phosphate in belemnite rostra (Table 1) did not allow the determination of its mineralogical composition.

Similar PO_4^{3-} concentrations are found nowadays in the case of the modern belemnite counterpart, *Sepia officinalis*. In the case of *Sepia* cuttlebones, carbonate (Bettencourt and Guerra [54], Longinelli and Nuti [53]) and phosphate (Longinelli and Nuti [53]) are in isotopic equilibrium with ocean water at environmental conditions.

If the isotopically heavy data cannot be related to diagenetic processes, the only remaining choices are the possibility of phosphate ions bound to organic matter or the possibility of vital effects. Very positive $\delta^{18}\text{O}$ values were measured, e.g. in the flesh of modern fish and of other marine organisms [55]. However, the amount of organic matter which may have been directly included in belemnite rostra is insufficient by far to support this hypothesis. The same consideration holds in the case of the amount of organic matter present in the sedimentary formations in which fossil belemnites rostra are normally found. Very little is known on the biological behavior of these organisms, so that the possibility of vital effects cannot be discarded ‘a priori’. To have an overall picture of the $\delta^{18}\text{O}$ values obtained so far from marine fossils, we report here (Fig. 5 and Table 2) all the $\delta^{18}\text{O}_p$ obtained from marine organisms of Tertiary and Mesozoic age (pelecypods and fish teeth whose phosphate should be precipitated under isotopic equilibrium conditions with seawater according to the results reported by several papers on this subject, e.g. [26,56–58]) plus all the $\delta^{18}\text{O}_p$ from belemnites of Jurassic and Cretaceous age. The values reported in Fig. 5 include all the samples in Table 1 plus the results published long ago by Longinelli and Nuti [32]. According to the distribution of these results the following considerations can be made. (1) The phosphate of shells and teeth of marine fossils can easily undergo an isotopic shift towards lighter values because of diagenetic processes as clearly shown by the most negative phosphate values of

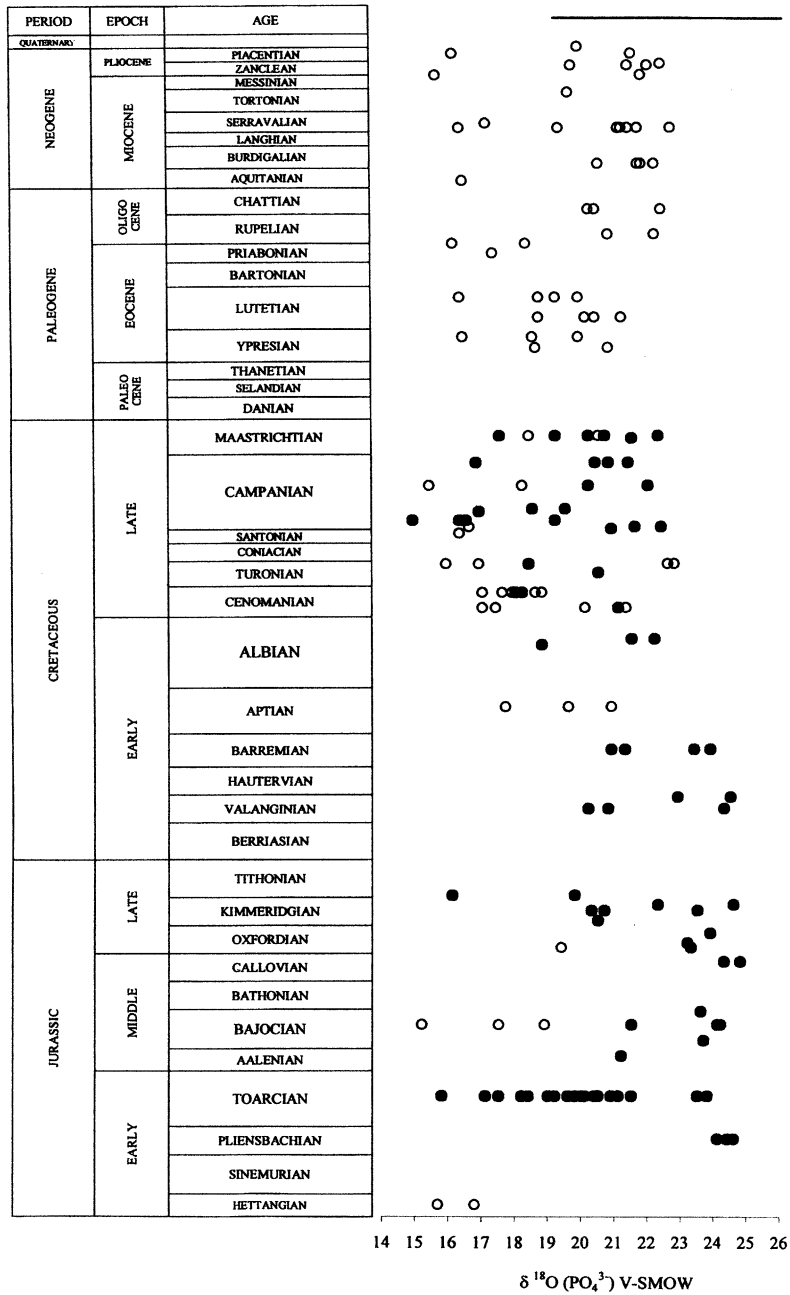


Fig. 5. Oxygen isotopic composition of phosphate from marine fossils of Mesozoic and Cenozoic age. Open circles are pelecypods, brachiopods and fish teeth; black dots are belemnites. The results reported refer to all the marine fossils measured up to now, including the belemnites in Table 1 and the results already published [32]. The segment on top of the figure is the range of $\delta^{18}\text{O}(\text{PO}_4^{3-})$ values measured on modern pelecypods, brachiopods and fish teeth from tropical to polar waters.

Table 2

Oxygen isotopic composition of phosphate and carbonate from fossil shells and skeletons of marine organisms of Jurassic, Cretaceous and Tertiary age from all over the world: results from Table 1 and from [32].

Sample No.	Species	Age and location	$\delta^{18}\text{O}(\text{PO}_4^{3-})$ vs. V-SMOW	$\delta^{18}\text{O}(\text{CO}_3^{2-})$ vs. PDB-1
1	<i>Disciniscus cumingii</i>	U. Quaternary, CA, Mexico	19.9	−1.90
2	<i>Lopha</i> sp.	U. Pliocene, FL, USA	21.5	−0.41
3	<i>Ostrea vespertina</i>	U. Pliocene, CA, USA	16.1	0.43
4	Undetermined fish tooth	Pliocene, Italy	19.7	
5	<i>Pycnodonta</i> sp.	Pliocene, Italy	21.4	0.42
6	<i>Lopha</i> sp.	Pliocene, NC, USA	22.0	0.70
7	<i>Oxyrhina spallanzani</i> (tooth)	L. Pliocene, Italy	22.4	
8	<i>Ostrea hermanni</i>	L. Pliocene/U. Miocene, CA, USA	15.6	−8.80
9	<i>Lopha sculpturata</i>	L. Pliocene/U. Miocene, VA, USA	21.8	0.71
10	<i>Ostrea titan</i>	U. Miocene, CA, USA	19.6	0.15
11	<i>Isurus</i> sp. (tooth)	Miocene, CA, USA	21.1	
12	<i>Crassostrea</i> sp.	Neogene, Israel	17.1	−8.00
13	<i>Disciniscus lugubris</i>	Miocene, CA, USA	21.2	−5.94
14	<i>Disciniscus lugubris</i>	Miocene, VA, USA	22.7	−4.83
15	<i>Ostrea</i> sp.	Miocene, CA, USA	19.3	0.51
16	<i>Ostrea</i> sp.	M. Miocene, Italy	21.7	−3.50
17	<i>Ostrea titan</i>	M. Miocene, CA, USA	16.3	−4.80
18	<i>Ostrea</i> sp.	Miocene, MD, USA	21.4	−1.40
19	<i>Pycnodonta</i> sp.	L. Miocene, Italy	21.8	0.43
20	<i>Ostrea thomasii</i>	L. Miocene, MD, USA	21.7	0.10
21	Undetermined fish tooth	L. Miocene, CA, USA	20.5	
22	<i>Ostrea percrassa</i>	L. Miocene, MD, USA	22.2	0.48
23	<i>Disciniscus</i> sp.	L. Miocene/U. Oligocene, CA, USA	13.4	−5.45
24	<i>Ostrea</i> sp.	L. Miocene/U. Oligocene, CA, USA	16.4	−4.79
25	<i>Lamna cuspidata</i> (tooth)	M. Oligocene, Germany	20.2	
26	<i>Lamna cuspidata</i> (tooth)	M. Oligocene, Germany	20.4	
27	<i>Ostrea</i> sp.	M. Oligocene, Italy	22.4	−0.80
28	<i>Gryphaea gigantea</i>	U. Priabonian, Italy	20.8	−2.15
29	<i>Pycnodonta brognarti</i>	U. Priabonian, Italy	22.2	−0.87
30	<i>Lamna elegans</i> (tooth)	Priabonian, UK	16.1	
31	<i>Lamna elegans</i> (tooth)	Priabonian, UK	18.3	
32	<i>Ostrea bersonensis</i>	L. Priabonian, Italy	17.3	−2.60
33	Undetermined fish tooth	M. Eocene, France	19.2	
34	<i>Ostrea crenulimarginata</i>	M. Eocene, AL, USA	19.9	−3.00
35	<i>Ostrea stewarti</i>	M. Eocene, CA, USA	18.7	−6.32
36	<i>Cucullea gigantea</i>	M. Eocene, VA, USA	16.3	−2.61
37	Undetermined fish tooth	M.-L. Eocene, AL, USA	20.1	
38	Undetermined fish tooth	M.-L. Eocene, AL, USA	21.2	
39	Undetermined fish tooth	M.-L. Eocene, AL, USA	18.7	
40	<i>Ostrea</i> sp.	M.-L. Eocene, AL, USA	20.4	−0.98
41	<i>Lamna obliqua</i> (tooth)	L. Eocene, UK	18.5	
42	<i>Lamna</i> sp. (tooth)	L. Eocene, France	16.4	
43	<i>Lamna</i> sp. (tooth)	L. Eocene, Italy	19.9	
44	<i>Cubitostrea compressirostra</i>	U. Paleocene, DC, USA	18.6	−2.08
45	Undetermined fish tooth	U. Paleocene, DC, USA	20.8	
46	Undetermined fish tooth	U. Paleocene, DC, USA	21.8	
47	<i>Lamna</i> sp.	L. Paleocene, Denmark	21.5	
48	<i>Lamna appendiculata</i> (tooth)	L. Paleocene, Denmark	19.9	
49	<i>Lamna</i> sp.	L. Paleocene, Denmark	18.0	
50	<i>Belemnitella</i> sp.	Maastrichtian, The Netherlands	17.5	0.15
51	<i>Belemnitella mucronata</i>	Maastrichtian, The Netherlands	19.2	0.59
52	<i>Belemnitella americana</i>	Maastrichtian, NJ, USA	20.2	−0.05

Table 2 (Continued).

Sample No.	Species	Age and location	$\delta^{18}\text{O}(\text{PO}_4^{3-})$ vs. V-SMOW	$\delta^{18}\text{O}(\text{CO}_3^{2-})$ vs. PDB-1
53	Biradiolites aquitanicus	Maastrichtian, France	18.4	−4.18
54	Belemnitella americana	Maastrichtian, NJ, USA	22.3	0.22
55	Pycnodonta vesicularis	Maastrichtian, AL, USA	20.5	−1.93
56	Belemnitella americana	Maastrichtian, NJ, USA	20.7	0.15
57	Belemnitella mucronata	U. Senonian, The Netherlands	21.5	0.37
58	Belemnitella americana	U. Campanian, NJ, USA	20.8	0.23
59	Belemnitella americana	U. Campanian, NJ, USA	21.4	−0.23
60	Belemnitella mucronata	U. Campanian, Sweden	20.4	−0.58
61	Belemnitella mucronata	U. Campanian, Sweden	16.8	0.41
62	Belemnitella mucronata	Campanian, Belgium	20.2	0.31
63	Belemnitella quadrata	Campanian, Belgium	22.0	−0.76
64	Lamna sp. (tooth)	Campanian, Belgium	18.2	
65	Crassostrea soleniscus	Campanian, TX, USA	15.4	−6.11
66	Belemnitella mucronata	Senonian, UK	19.2	−0.20
67	Belemnitella mucronata	Senonian, Russia	16.5	0.71
68	Belemnitella mucronata	Senonian, France	16.3	−0.55
69	Belemnitella mucronata	Senonian, Sweden	14.9	0.19
70	Actinocamax mammilatus	L. Campanian, Sweden	18.5	−0.39
71	Actinocamax mammilatus	L. Campanian, Sweden	19.5	−0.37
72	Belemnitella sp.	Santonian, Belgium	21.6	−0.15
73	Belemnitella sp.	L. Senonian, UK	20.9	−1.50
74	Jophia sp.	Santonian, Italy	16.6	−2.96
75	Unknown fish (vertebra)	Santonian–Coniacian, KS, USA	16.3	
76	Actinocamax subventricosus	Coniacian, Sweden	22.4	−0.20
77	Pseudoraneella sp.	Turonian, Greenland	22.6	
78	Pseudoraneella sp.	Turonian, Greenland	22.8	
79	Actinocamax plenus	Turonian, Belgium	18.4	−0.60
80	Undetermined fish tooth	Turonian, SD, USA	16.9	
81	Undetermined fish tooth	Turonian, SD, USA	15.9	
82	Actinocamax sp.	L. Turonian, Belgium	20.5	−0.52
83	Belemnites sp.	Cenomanian, Belgium	18.2	−0.52
84	Alectryonia scyphax	Cenomanian, Italy	17.0	−3.29
85	Alectryonia scyphax	Cenomanian, Italy	18.6	−2.93
86	Exogyra columba	Cenomanian, Israel	17.9	−2.82
87	Exogyra flabellata	Cenomanian, Israel	17.6	−3.75
88	Belemnites sp.	Cenomanian, Belgium	18.0	−0.60
89	Oxyrhina mantelli (tooth)	Cenomanian, UK	18.8	
90	Neohibolites minimus	Cenomanian–Albian, UK	21.1	−0.60
91	Lamna sp. (tooth)	Cenomanian–Albian, UK	21.2	
92	Lamna sp. (tooth)	Cenomanian–Albian, UK	20.1	
93	Exogyra flabellata	Cenomanian–Albian, Somaliland	17.4	−4.80
94	Lamna sp. (tooth)	Cenomanian–Albian, UK	17.0	
95	Isurus sp. (tooth)	Cenomanian–Albian, UK	12.8	
96	Actinocamax sp.	Albian, Denmark	18.8	0.38
97	Belemnites lensus	M. Cretaceous, UK	22.2	−1.60
98	Belemnitella americana	M. Cretaceous, MT, USA	21.5	0.30
99	Exogyra latissima	Aptian, Somaliland	19.6	−2.61
100	Exogyra latissima	Aptian, Somaliland	20.9	−1.98
101	Exogyra latissima	Aptian, Somaliland	17.7	−3.48
102	Oxyteuthis cfr. jaskowi	Barremian, Canada	23.9	0.47
103	Acroteuthis impressa	Barremian, Canada	21.3	−5.35
104	Acrotentis impressa	Barremian, Canada	20.9	−5.50
105	Oxyteuthis sp.	Barremian, Canada	23.4	0.97
106	Belemnites pistilliformis	Neocomian, Germany	24.5	−0.16

Table 2 (Continued).

Sample No.	Species	Age and location	$\delta^{18}\text{O}(\text{PO}_4^{3-})$ vs. V-SMOW	$\delta^{18}\text{O}(\text{CO}_3^{2-})$ vs. PDB-1
107	Belemnites sp.	Neocomian, Madagascar	22.9	0.44
108	Acroteuthis impressa	Valanginian, Canada	20.8	-5.25
109	Acroteuthis sp.	Valanginian, Germany	24.3	0.38
110	Acroteuthis impressa	Valanginian, Canada	20.2	-5.65
111	Dimitobelus sp.	L. Cretaceous, Austria	16.9	0.57
112	Hibolites arkelli	L. Titonian, New Zealand	16.1	-0.88
113	Hibolites m. marwicki	L. Titonian, New Zealand	19.8	-2.21
114	Cylindroteuthis sp.	U. Kimmeridgian, Greenland	22.3	-1.85
115	Belemnites sp.	U. Kimmeridgian, Greenland	24.6	-1.00
116	Cylindroteuthis sp.	Kimmeridgian, Scotland	20.7	-1.73
117	Cylindroteuthis sp.	Kimmeridgian, Greenland	20.3	-2.05
118	Belemnites sp.	Kimmeridgian, Italy	23.5	-0.07
119	Cylindroteuthis puzosiana	Oxfordian, UK	23.9	-0.75
120	Cylindroteuthis puzosiana	L. Oxfordian, UK	23.2	-0.16
121	Belemnites sp.	U. Jurassic, WY, USA	20.5	0.76
122	Gryphaea cfr. arcuata	Oxfordian–Callovian, France	19.4	-0.80
123	Pachyteuthis excentralis	Oxfordian–Callovian, UK	23.3	-0.50
124	Cylindroteuthis puzosiana	Callovian, UK	24.3	-0.95
125	Cylindroteuthis puzosiana	Callovian, UK	24.8	0.75
126	Belemnites sp.	U. Bajocian, Greenland	23.6	-1.46
127	Megateuthis giganteus	Bajocian, Germany	24.2	-0.60
128	Lopha cristagalli	Bajocian, Germany	17.5	-3.08
129	Terebratula digona	Bajocian, France	15.2	-3.26
130	Lopha cristagalli	Bajocian, Germany	18.9	-2.00
131	Megateuthis giganteus	Bajocian, Germany	24.1	-0.05
132	Megateuthis giganteus	Bajocian, Germany	21.5	-1.02
133	Acrocoelites sp.	Bajocian–Aalenian, Italy	23.7	-0.59
134	Acrocoelites triscissus	Aalenian, France	21.2	-1.92
135	Salpingoteuthis sp.	Toarcian, Germany	23.8	-2.54
136	Acrocoelites sp.	Toarcian, Germany	23.5	-1.72
137	Belemnites sp.	Toarcian, UK	17.5	-10.72
138	Belemnites sp.	Toarcian, UK	20.4	-4.66
139	Belemnites sp.	Toarcian, UK	17.1	-10.98
140	Belemnites sp.	Toarcian, UK	20.9	-3.40
141	Belemnites sp.	Toarcian, UK	21.5	-3.59
142	Belemnites sp.	Toarcian, UK	19.8	-4.47
143	Belemnites sp.	Toarcian, UK	21.1	-4.76
144	Belemnites sp.	Toarcian, UK	20.0	-5.92
145	Belemnites sp.	Toarcian, UK	19.6	-10.72
146	Belemnites sp.	Toarcian, UK	15.8	-10.10
147	Belemnites sp.	Toarcian, UK	20.1	-8.15
148	Belemnites sp.	Toarcian, UK	20.5	-4.95
149	Belemnites sp.	Toarcian, UK	19.2	-5.34
150	Belemnites sp.	Toarcian, UK	18.2	-3.79
151	Belemnites sp.	Toarcian, UK	18.4	-4.56
152	Belemnites sp.	Toarcian, UK	19.0	-4.98
153	Passaloteuthis sp.	Pliensbachian, Germany	24.6	-0.81
154	Passaloteuthis sp.	Pliensbachian, Germany	24.1	-0.15
155	Passaloteuthis sp.	Pliensbachian, Germany	24.4	-1.40
156	Gryphaea arcuata	Hettangian, Germany	13.4	-2.80
157	Gryphaea arcuata	Hettangian, Germany	16.8	-2.98
158	Gryphaea arcuata	Hettangian, Germany	15.7	-3.39

fossils of upper- and mid-Tertiary age. In fact, while both pelecypods and fish teeth are considered to precipitate the phosphate of their shell and skeleton under isotopic equilibrium conditions, several fossils of Tertiary age show $\delta^{18}\text{O}_p$ values that are so negative as to definitely exclude the possibility of a good preservation of their pristine isotope values. (2) Pelecypods and fish teeth of mid- and lower-Tertiary age and uppermost Mesozoic age form a continuous set of data with belemnites of Cretaceous and Jurassic age. The most negative belemnite values should obviously be related to diagenetic effects, while equilibrium conditions and good preservation should be seriously considered as explanations for the highest $\delta^{18}\text{O}$ values of belemnite phosphate.

4. Conclusions

From the reported set of data (Table 1) and from the results in Fig. 5, the following conclusions can be drawn: (1) the phosphate isotopic composition of shells and skeletons of fossil marine organisms may easily undergo oxygen isotope exchange with diagenetic water, even in the case of geologically recent fossils; (2) some belemnite rostra of Jurassic and Cretaceous age show such positive $\delta^{18}\text{O}_p$ values that they can hardly be explained by means of diagenetic processes, vital effects or other processes. It follows that the only interpretation of these results that can be suggested is related to $\delta^{18}\text{O}$ values of Mesozoic ocean water that were heavier than those of modern ocean water by, at least, $3 \pm 1\%$.

This hypothesis is rejected 'a priori' by most of the scientists involved in paleoclimatological and paleoceanographic studies. However, so far, we are unable to advance alternative hypotheses to explain the reported set of data. Further measurements on fossil marine organisms are now in progress.

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