

# THE NATURE OF THE ARAGONITE AND CALCITE IN THE ROSTRA OF UPPER CRETACEOUS BELEMNITES OF WESTERN TAYMYR: INFORMATION ON THE OXYGEN AND CARBON STABLE ISOTOPE COMPOSITION

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**ABSTRACT:** The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  isotopic values in aragonite and calcite were determined from rostra of the belemnite *Goniacamax* sp. from the Turonian concretions of western Taymyr. The differences in isotopic composition between the different parts of the rostra and the carbonate of the concretions imply a massive calcite composition for belemnite rostra in life.

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## INTRODUCTION

The composition of the oxygen stable isotope of calcitic belemnite rostra has been widely used until recently for determining the paleotemperatures of Mesozoic seas [6, 8, 13, et al.]. Practically no traditional isotopic paleoecological investigations on belemnites have been conducted in recent years, due in great measure to doubts about the existence of massive calcite in the rostra in life [1, 2, 12] and thus to doubts about the preservation of the original isotopic values. However, the very question of the *in vivo* internal structure and material composition of belemnite rostra has remained open until now.

In the present work the isotopic composition of carbon and oxygen is studied in uniquely preserved belemnite rostra, different parts of which have different mineral composition. A comparative study of the isotopic composition of minerals in fossils and in their rocky matrices can provide an understanding of the processes of biomineralization in life and postdepositional changes in mineral skeletons.

## MATERIALS AND METHODS

Five fragments of different rostra of the belemnite *Goniacamax* sp. were studied from concretions in Turonian deposits of western Taymyr (the numbers are of fragments in the collection of the authors; collected by D. P. Naydin). A complete description of the geological setting of the concretions and of the invertebrates enclosed in them was published earlier by Teys, Kiselevskiy and Naydin [9]. The massive part of the rostrum (*rostrum solidum*) in all fragments is, as usual for belemnite rostra, composed of dark brown, translucent calcite. The alveolar part (*rostrum cavum*) consists of a less dense, light pale yellow, opaque substance that splits easily along the growth lines. The contact of this substance with the massive calcite makes a sharp boundary perpendicular to the axis of the rostrum.

Determination of the mineral composition of the different parts of the rostrum was done by x-ray diffraction analysis in a DRON-2 apparatus.

Carbonate samples from different parts of the rostra were taken with a dental burr. Two fragments provided a series of samples that corresponded with the rostrum's growth lines (Fig. 1).  $\text{CO}_2$  for mass spectrometry was obtained by placing the carbonate samples in 100% orthophosphoric acid at 25°C with no previous thermal treatment

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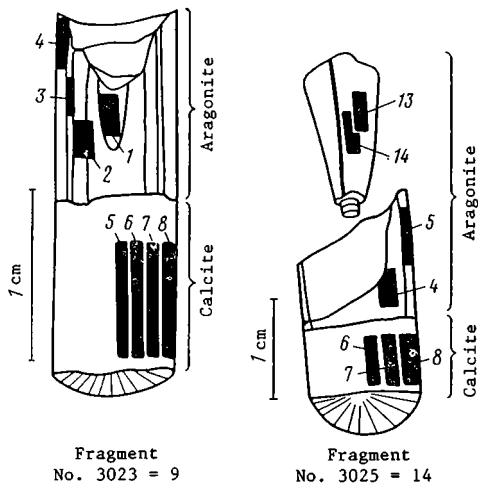


Fig. 1. Diagrams of the carbonate samples from belemnite rostra for isotopic analysis. The numerals signify the sample numbers.

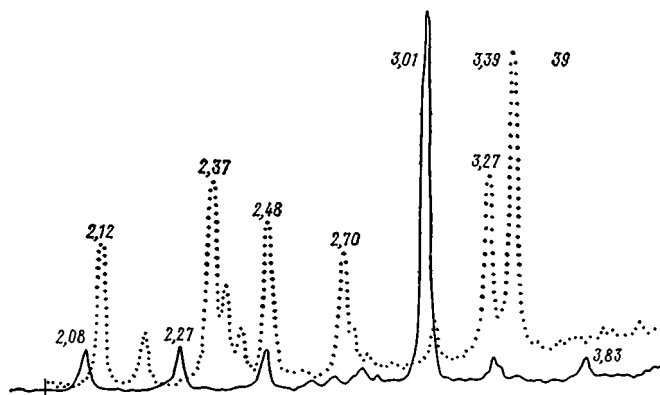


Fig. 2. Spectrograms of material from the alveolar (dots) and postalveolar (solid line) parts of the rostrum. The numerals indicate the characteristic peaks. Fragment No. 3023-1.

of the carbonate samples. The ratios  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  were determined in an MI-1201 mass spectrometer equipped with a three-slot ion receiver and were recorded as the generally accepted quantities  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , respectively, with a precision of better than  $\pm 0.2\%$ . All the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values are expressed as compared to the PDB standard.

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## RESULTS

The x-ray structural analysis showed that in all the fragments the light pale yellow substance making up the alveolar part of the rostrum is aragonite. The massive part of the rostrum consists of calcite. Spectrograms with the characteristic peaks are presented in Fig. 2.

Table 1

Oxygen and Carbon Stable Isotope Composition of Belemnite Rostra and  
Secondary Calcite from Upper Cretaceous Concretions of Western  
Taymyr

No. of fragment	No. of samples	Sample characteristics	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)	Remarks
		Belemnites			
3023-9	1*	Aragonite	-3.3	0.0	Author's data
	2	"	-2.9	-1.3	
	3	"	-3.0	-2.4	
	4	"	-2.8	-3.2	
	5	Calcite	-2.6	+3.5	
	6	"	-2.5	+3.5	
	7	"	-2.6	+3.7	
	8	"	-2.6	+3.5	
3025-14	14*	Aragonite	-2.6	-0.1	
	13	"	-3.2	-0.3	
	4	"	-3.3	+2.8	
	5	"	-3.6	+1.2	
	6	Calcite	-2.7	+3.6	
	7	"	-2.9	+4.0	
	8	"	-3.4	+3.2	
3025-8	1	Aragonite	-3.5	+1.7	
	2	Calcite	-2.9	+3.5	
3030-2	1	Aragonite	-3.5	-1.0	
	2	Calcite	-2.9	+3.2	
3023-1	1	Aragonite	-3.0	-8.3	
	2	Calcite	-2.7	+3.7	
		Secondary calcite			
3025-14	2	Calcite filling the	-4.2	-19.2	
	3	chambers of ammonite shells	-3.8	-19.7	
3025-12/1	12	"	-3.9	-18.8	Data of Teys et al. [9]
		Carbonate cement of the inner part of the concretion	-4.4	-18.1	
3025-2/1		"	-3.7	-31.8	
3025-3/2		"	-4.3	-18.4	
3023-9/1		"	-5.6	-20.5	

\*Sample numbers correspond to the diagrams in Fig. 1.

The determinations of the isotopic composition of oxygen and carbon from the aragonitic and calcitic parts of the rostra are presented in Table 1. Also given there are the isotopic ratios for the carbonate cement of the concretions and for the calcitic infilling of the shell chambers of ammonoids that originated in the same concretions.

The massive and alveolar parts of the rostra have similar isotopic compositions of oxygen, but are sharply different in  $^{13}\text{C}$  content. The variation of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of the aragonite of the alveolar parts ranged from -2.6 to -3.6‰ and from +2.8 to -8.3‰ respectively. For the calcite, the  $\delta^{18}\text{O}$  values vary from -2.5 to -3.4‰ whereas the more stable  $\delta^{13}\text{C}$  values vary from +3.2 to +4.0‰ and do not overlap the range of  $\delta^{13}\text{C}$  values of the aragonite in the alveolar part. The secondary calcite filling the ammonite shell chambers is amber-colored and translucent, resembling at first glance the rostral calcite. It is considerably impoverished in the heavy isotopes  $^{18}\text{O}$  and, especially,  $^{13}\text{C}$  in comparison with the belemnite rostra:  $\delta^{18}\text{O}$  ranges from -3.8 to -4.2‰,  $\delta^{13}\text{C}$  from -18.8 to -19.7‰. These values coincide completely with the ranges of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  determined earlier [9] from the carbonate cement of the concretions in which the belemnite rostra were found.

#### DISCUSSION

Previous works on the isotopes of the present carbonates from Turonian concretions

from western Taymyr and from the enclosed fossils [7, 8] have conclusively shown that the isotopic composition of the concretions, in contrast to the surrounding sandstone, underwent no alteration or exchanges with meteoric water. The skeletal remains of organisms within the concretions, including aragonitic ammonite and gastropod shells and the pearly layer of inoceramid shells, have regularly differing isotopic compositions. This fact testifies to the absence of secondary redistribution of the oxygen and carbon isotopes in the originally mineralized elements of the skeletons either through diagenesis or by meteoric water. In the opposite case one would expect a levelling of the differences in isotopic composition among the fossils contained in a single concretion.

The oxygen and carbon isotope ratios of the concretions from which the rostra came are characteristic of the Cretaceous early diagenetic concretions [10] formed in sediments that did not undergo considerable compaction. The fact that the  $\delta^{18}\text{O}$  values fall into the range typical of marine carbonates points to a shallow burial depth of the fossils at the time of concretion formation. Pore water  $\text{CO}_2$ , produced by the anaerobic decomposition of buried marine organic substances with a typical  $\delta^{13}\text{C}$  value of about  $-20\%$ , served as the source of the isotopically light carbon [8].

The identical isotopic composition of the secondary calcite filling the shells and of the carbonate cement of the concretions is evidence for the common genesis of these minerals (Table 1). In view of the substantial impoverishment of secondary calcite in the isotope  $^{13}\text{C}$  when compared with equilibrated marine carbonate, secondary changes in the *in vivo* isotope composition of the carbonate invertebrate skeletons in the concretions must have led to a reduction in the  $\delta^{13}\text{C}$  values. We propose that most skeletons, including their aragonitic parts, have retained their original isotopic composition. Only the anomalously low reduction in  $\delta^{13}\text{C}$  of some fragments ( $-8.3\%$  for the aragonite of rostrum No. 3023-1) could be ascribed to a secondary redistribution of isotopes between the carbonate in the concretion and the minerals in the skeleton.

Calcite from belemnite rostra and from the prismatic outer layer of inoceramid shell from the same concretions [9] show the highest  $\delta^{13}\text{C}$  values and are clearly different from the secondary calcite fillings and the carbonate cement of the concretions. This can be taken as evidence that the rostral calcite was formed in a normal marine environment up and until the time of the concretion formation and the beginning of the secondary calcite infilling: that is, up and until the rostra were buried in the sediment.

We propose that belemnite rostra were formed in a shell sac: that is, they were positioned as an internal skeleton. Available data on the isotopic composition of internal shells of modern molluscs show the impoverishment of their carbonate in the isotope  $^{13}\text{C}$  in comparison with equilibrated marine carbonate ( $\delta^{13}\text{C}$  about  $+2.0\%$ ) as a result of the participation of  $\text{CO}_2$  of metabolic origin in the process of biomineralization: the skeleton of the cuttlefish *Sepia* sp. is impoverished 5-7% [14]; *Spirula* sp. (of the Fiji Sea) has a phragmocone  $\delta^{13}\text{C}$  value of  $-1.0\%$  [3], and the armor plates of the gumboot chiton *Crypthochiton stelleri* from the Sea of Japan, which form beneath the fused perinota, have a  $\delta^{13}\text{C}$  of  $-6.5\%$  [5].

The aragonite of the alveolar parts of the rostra of our belemnites has a  $\delta^{13}\text{C}$  value (Table 1), close to the mineral skeletons of modern molluscs with internal shells. Spaeth et al. [12] also reported a low  $\delta^{13}\text{C}$  value in aragonite from the skeleton (phragmocone) of the belemnite *Megateuthis giganteus* (Bayoskiy stage of the Jurassic, FRG), and a regular impoverishment was noted in the heavy isotope in the aragonite of the phragmocone septa during their growth.

A positive  $\delta^{13}\text{C}$  value of the massive calcite in the rostrum, characteristic not only of the studied *Goniacamax* sp. but also of other Jurassic and Cretaceous belemnites [12], testifies in favor of a nonbiogenic origin of these mineral formations, in contrast to the aragonite of the alveolar part of the rostrum. However, the tendency noted in the differences in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  between the alveolar (aragonite in our case) and massive parts of belemnite rostra is also present in those belemnite species in which the entire rostrum is solid calcite [12] (Fig. 3A, B).

Hence it is possible that the formation of both aragonite and calcite in the rostrum of *Goniacamax* sp. occurred biogenically, by the secretory activity of the mantle. The mantle covering the massive, postalveolar part of the rostrum was of an insignificant thickness and consisted of two layers of epithelia; these allowed the transport of bicarbonate ions, enriched in the heavy carbon isotope from the external aquatic medium, into the extrapallial fluid of the shell sac, where secretion of the rostrum's carbonate occurred. Formation of the alveolar part of the rostrum and phragmocone took place under a more complexly structured and more massive soft tissue that, supplying the isotopically lighter metabolic  $\text{CO}_2$  to the mineralization site caused an impoverishment of the heavy isotope in the skeletal carbonate (Fig. 3).

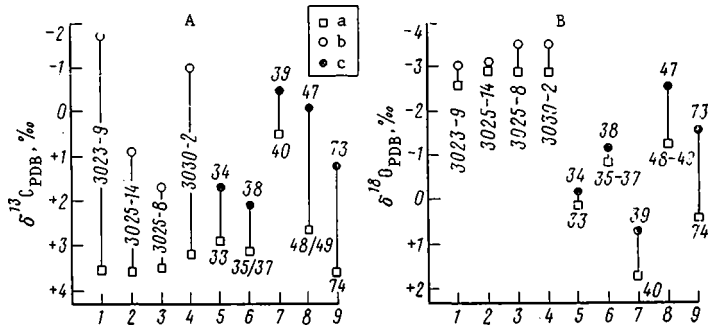


Fig. 3. Isotopic composition of carbon (A) and oxygen (B) of different parts of belemnite rostra: a) calcite from the massive part of the rostrum; b) aragonite from the alveolar part of the rostrum; c) calcite from the alveolar part of the rostrum; 1-4) *Goniacamax* sp., Turonian stage, Taymyr; 5-8) *Megateuthis giganteus*, Bayoskiy stage, Western Europe; 9) *Belemnitella occidentalis*, Maastrichtian stage, Western Europe; 5-9) according to the data of [12] with an indication of the original fragment numbers. The lower  $\delta^{18}O$  values of the Turonian belemnites from the Taymyr are explained as a peculiarity of the isotopic composition of the water in Mesozoic basins [6, 9].

However, a different interpretation is possible, i.e., that the calcite part of the rostrum has an intermediate  $\delta^{13}C$  between the admittedly biogenic aragonite of the rostra and the secondary calcite infilling of the belemnite chambers and the calcite of the concretion. It is well known that calcitic fossilized belemnite rostra originally were primarily organic and were only insignificantly mineralized in thin growth bands. Indirect arguments in favor of this are based on finds of "crushed" rostra, on analogies with the rostral formations of the Recent squid *Moroteuthis* [4], and also on interpretations of the microstructural peculiarities of the rostra, which consist of alternating primary lamellae (predominantly aragonite) of the calcified layers and prismatic, supposedly secondary mineralizations of the original organic substrate [1] (see also [11]).

The light carbon isotope from the organic material together with isotopically heavy carbon from the surrounding medium can be utilized in secondary, posthumous mineralization of the originally organic parts of the rostrum. As a result, the  $\delta^{13}C$  indices of the calcite in the massive part of the rostrum have intermediate values between the admittedly lighter biogenic aragonite and the admittedly heavier secondary calcite of the concretion.

#### SUMMARY

1. The alveolar part of the rostrum of the belemnite *Goniacamax* is represented by aragonite, the postalveolar part by calcite.

2. Sharp differences in the isotopic composition of carbon in the calcite of the rostrum and the admittedly secondary calcite of the concretion is evidence of *in vivo* secretion of the postalveolar part of the rostrum in the form of calcite. However, it cannot be excluded that the reduction of the  $\delta^{13}C$  values in the rostral calcite, in contrast to the admittedly diagenetic calcite, is associated with the utilization, during diagenetic calcification, of isotopically light carbon from the primary organic matter of this part of the rostrum.

3. Regular differences in the isotopic composition of oxygen and carbon of the alveolar and massive parts of belemnite rostra were discovered: The alveolar part is richer in light isotopes. This agrees with earlier published data [11] in which, however, both the alveolar and massive parts of the rostra were composed of calcite.

4. If we accept the original calcite composition of the massive part of the rostrum, its enrichment in heavy isotopes, compared with modern internally shelled molluscs, is probably due to a greater ease in bringing bicarbonate ions from the aquatic medium to the biomineralization site than metabolic  $CO_2$ , which is evidence for having a very thin, soft covering over this part of the skeleton.

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