

From warm to cold: High resolution trace element and isotope ratios during the late Miocene and the Pliocene/Pleistocene transition from ancient warm to modern cold climates

Abstract

A literature study was done on brachiopoda, as one of the most abundant species in the Phanerozoic record. The biology and shell structure of brachiopods is briefly described. Furthermore, the usefulness of brachiopods for palaeoenvironmental studies is explored and the state of the art of Sr and Ca isotope systems as potential target proxies is described. An investigation on potential sampling areas (Pliocene-Pleistocene transition in Italy and Israel, recent Red Sea) is included.

Introduction

Brachiopods are lophophorates and as such related to the bryozoans and phoronides. Molluscs are also debated as sister taxa. From the vast diversity during the Paleozoic only five groups that belong to three different subphyla have survived until recent times: Those are the Lingulida and the Craniida of the Linguliformea and Craniiformea respectively and the Rhynchonellida, Thecideidina and Terebratulida of Rhynchonelliformea. Of these three subphyla, Linguliformea are the only ones to produce an organophosphatic shell¹, all other subphyla precipitate Low-Mg calcite. Brachiopod shells can be distinguished from other CaCO₃-precipitating organisms by their two bilaterally symmetric valves that usually differ in size (the ventral valve that hosts the pedicle is usually larger than the dorsal valve and has a better developed interarea/palintrope; Figure 1). Recent brachiopods are suspension feeders that usually live epifaunally either free or attaching themselves to the substrate with a pedicle or by cementation of one of the valves. An exception to this rule is represented by some taxa of Linguliformea (e.g. species of *Lingula*) that live infaunal. Filtering is done by the lophophore.

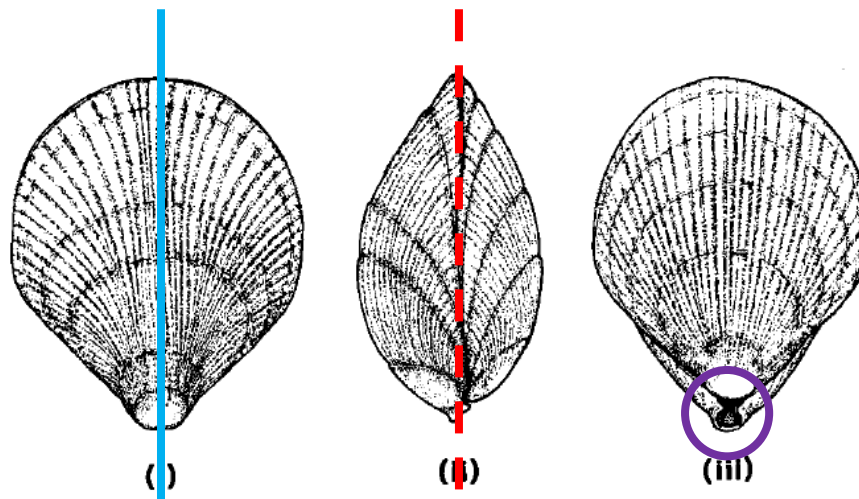


Figure 1: Characteristics of brachiopod shell (i,ii,iii). In brachiopods the single valve is bilaterally symmetrical and the two valves are not (red line) as the plan of symmetry (blue line) is perpendicular to the commissural plane. The ventral valve typically shows a perforation for the pedicle (violet circle)², at least at the juvenile stage.

The general organization is shown in Figure 2².

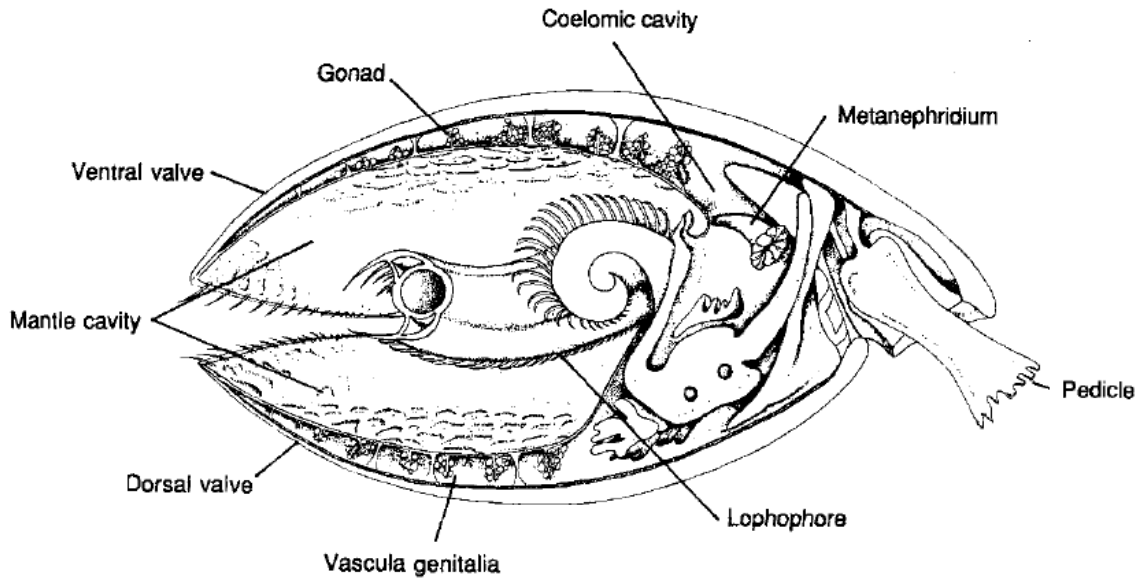


Figure 2: Principal organs of the brachiopod *Terebratulina retusa* (Linnaeus 1758)²

The Brachiopod Shell

The brachiopod shell consists of Low-Magnesium calcite. The boundary between Low- and High-Magnesium calcite is 4% $MgCO_3$, where the solubility of magnesian calcite ($Ca_xMg_{(1-x)}CO_3$) is lowest, even lower than for pure calcite³. For this reason, brachiopods are generally assumed to be more resistant than other species to chemical alteration via diagenesis and have been extensively used for reconstructing various environmental proxies⁴⁻⁶.

The brachiopod shell consists of up to three layers (Figure 3). The thickness of the individual layers varies between the taxa. Generally, most brachiopods precipitate a primary microgranular and a secondary laminar or fibrous layer. A tertiary columnar layer can be present or absent. The primary layer is normally thinner than the secondary layer, though there are brachiopods whose shell is made up almost entirely of primary layer (e.g. *Thecidellina baretii* (Davidson 1864))⁷.

The chemical and isotopical composition varies between the layers. Currently most studies agree that the primary layer and outer parts of the secondary layer show a vital effect in carbon and oxygen isotopes⁷⁻¹⁵ and Mg/Ca ratio¹⁰. These studies recommend only the innermost part of the secondary layer for palaeoenvironmental analysis. A successfully applied approach for this is to dissolve the primary layer and outermost part of the secondary layer via HCl. The rest is then cleaned, grinded and subsequently used for analysis¹⁶⁻¹⁸.

For Sr and Ca isotopes no vital effect has been described so far^{4,16,19}.

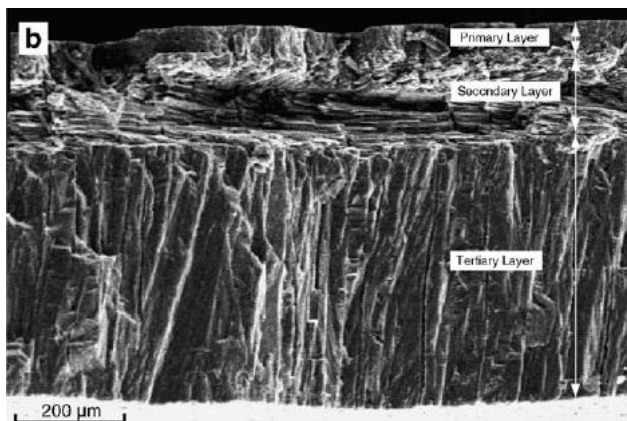


Figure 3: Shell structure of *Liothyrella uva* (Broderip 1833)⁷

The Sr Isotope System

The Sr isotope system is characterized by two reservoirs that show differing isotopical compositions: i) the continental reservoir that is enriched in radiogenic ^{87}Sr and brought into the ocean via weathering fluxes and ii) Sr from the alteration of MORB basalts. The ratios of $^{87}Sr/^{86}Sr$ are ~ 0.7136 and ~ 0.703 for continental crust and MORB respectively²⁰. The $^{87}Sr/^{86}Sr$ ratio was initially used to calculate the Sr flux from MORBs to the ocean assuming a steady state condition²¹. However later studies showed that in today's oceans Sr input from MORB alteration is much lower than the continental input from rivers^{22,23}. The Sr ratios are

recorded in carbonates when they precipitate from seawater. The Sr isotope ratios can thus be used to assess changes in both continental weathering fluxes and MORB alteration driven by spreading rates²⁰.

Recently it has been suggested to also use $^{88/86}\text{Sr}$ to reconstruct changes in Sr output flux via carbonate precipitation. The approach is similar to the one for calcium isotopes described below⁴.

The Calcium Isotope System

The calcium isotope system is still under discussion. Early studies suggest no fractionation at all for abiotic carbonates²⁴. Accordingly there is also no significant difference in calcium isotope composition between different sources like terrestrial weathering or hydrothermal vents and MORB alteration^{25,26}. However according to later studies, organisms do fractionate calcium²⁵. Some studies also describe a temperature dependence for this effect, which varies between species though^{27,28}. This gives two possible applications for calcium isotopes: i) the estimation of marine productivity via the enrichment of heavy calcium isotopes in seawater^{25,26,29} and ii) as a possible palaeotemperature proxy^{27,28}.

The fractionation mechanism has been strongly discussed, however there seems to be an influence of the rate³⁰ and the temperature^{27,28}. The latest approach to explain $^{44/40}\text{Ca}$ fractionation behavior is by surface entrapment model (SEMO)³¹.

The Pliocene/Pleistocene Transition and its occurrences in Israel and Northern Italy

The Pliocene-Pleistocene transition is marked by a significant change in climate. During the Zanclean, both northern and southern hemisphere are free of ice. Glaciation starts in the Piacenzian – early Gelasian and is marked by 41ky cycles between cold and warm times. This is called the Pliocene-Pleistocene transition. Further cooling occurs during the late Gelasian – early Calabrian and cyclicity changes to 100ky. This is called the MPT (Middle-Pleistocene Transition). Together these two events mark the onset of the ice ages³²⁻³⁴.

There are not many occurrences of Pliocene-Pleistocene marine sediments in Israel. Literature mentions two marine formations of this age: The Pleshet formation and the Upper Be'er Sheva formation³⁵. Names are not used consistently, however. The Pleshet formation occurs within the entire coastal area³⁵, but can be limited to small pockets in carstic sinkholes of older sedimentary rocks³⁶. Often they are concealed by younger sediments and the time interval is studied in boreholes³⁷. So far published records of marine fauna were only found for two localities: Neshet quarry close to Haifa and outcrops close to Be'er Sheva³⁸. The Neshet quarry is part of marine section that was uplifted by tectonics³⁹. The Be'er Sheva outcrops are part of an Oligocene submarine canyon that experienced further erosion during the middle Miocene and was filled by sediment during later Miocene, Pliocene and early Pleistocene marine cycles⁴⁰⁻⁴².

The Pliocene-Pleistocene sequences were defined in Italy due to excellent outcrop conditions and only scarce occurrences of hiatuses⁴³. The outcrops of the Castell'Arquato Formation along the Arda and Stirone rivers have been intensively studied in the past⁴⁴⁻⁴⁸.

Modern Brachiopods in the Red Sea

Modern brachiopods from tropical and subtropical environments are typically small (<1 cm) and occur in cryptic habitats, where grazing pressure is low⁴⁹. In total 14 taxa are currently known from the Red Sea, most of which are <0.5 cm. Only one of them, *Frenulina* sp. indet., is 2 cm in size^{50,51}. The related species *Frenulina sanguinolenta* (Gmelin 1791) is described to occur between 30 and 1100 meters depth within the southwestern Pacific^{52,53}. The most abundant brachiopod in the Red Sea is *Argyrotheca jacksoni* (Cooper 1973), which occurs in depths of <10 to 90 m⁵¹. Living *Argyrotheca jacksoni* are 1.4-1.9 mm in size⁵⁰.

Recognized target areas for sampling of tropic brachiopods from earlier studies are i) cryptic habitats such as the underside of tabular corals or ii) caves⁵⁴ and iii) overgrown and encrusted branches of dead coral⁴⁹.

Sampling of planktonic brachiopod larvae is expected to be strongly biased towards lingulids. This is because articulated brachiopods and craniids are normally lecithotrophic and/or brooders². Up to date no articulated brachiopods have been described from planktonic hauls⁵⁵.

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