The macro-structure of modern and fossil brachiopod archives

Abstract

Brachiopods, are not the dominant element in modern oceans, but were very common in the past. Over 12,000 species and 5,000 genera fossils have found and recognized. As high variation and longtime distribution in the Paleozoic ocean, brachiopods are very important tools for paleontology research. Moreover, owing to the unique features of shells, which may very hard withstanding post-depositional alteration, and be considered the very credible indicators of climate changes in the ancient oceans.

Shells of brachiopods

Brachiopods have two hard "valves" (or shells: ventral valve and dorsal valve) on the upper and lower surfaces, also be called “lamp shells” due to the curved shells of the class Terebratulida look rather like pottery oil-lamps. Based on the hinged tooth and socket arrangement between two valves, there are two major groups of brachiopods are recognized, articulate and inarticulate.

From outside to inside, articulate brachiopod shells are generally composed of following representative shell layers: 1)a thin organic periostracum (rarely preserved in fossils); 2)a thin outer primary layer(rare except in extremely well-preserved fossil shells); 3)a thicker inner secondary layer(always present in fossils); 4)a tertiary layer(always absent except in specific order). (e.g., Armstrong, 1968; Williams, 1968, 1997; Grossman et al., 1993; Azmy et al., 1998, 2006) Different kinds of brachiopods will have very different fabrics and structure of the layers, especially in the secondary layer. (Williams, 1997) Detailed different kinds secondary layer have described in (Williams, 1997): 1) organophosphatic lamination; 2) calcitic fabrics; 3) calcitic fibers; 4) calcitic tabular lamination; 5) calcitic cross-bladed lamination. Moreover, the secondary layer is the most important biomineralization layer for classification and chemistry analyses.

By the way, the columnar epithelial cell, which initially secreted the periostracum, is responsible for the deposition of the calcareous shell of two layers (outer primary and inner secondary) (Williams, 1956)

For a new three-part scheme from 1990s, the Linguliformea have shells of calcium phosphate while the Craniiformea and Rhynchonelliformea have calcite shells. Craniiformean brachiopods have high Mg-calcite semi-nacre shells, and Rhynchonelliform brachiopods have shells comprising low Mg-calcite fibres (e.g. Williams, 1970; England et al., 2007; Pérez-Huerta et al., 2008)

Chemistry proxy for paleo-environment

There are several common proxies for paleo-environment, such as: brachiopods, conodonts, and whole rocks (Brand et al., 2011). Some comparison between different type’s materials for isotopic examination have carried out. (Qing et al., 1998; Wenzel et al., 2000; Brand, 2004). However, of all commonly occurring Paleozoic sedimentary carbonates, the fossil record of brachiopod have the highest probability of having retained their original isotopic composition. (Grossman et al., 1993; Banner and kaufman, 1994; Mii and Grossman, 1994; Mii et al., 2001; Brand et al., 2003)

According to previous studies(Popp B B, et al., 1986; Grossman et al., 1991; Bates and Brand, 1991; Banner and Kaufman., 1994; Azmy et al., 1998; Brand et al., 2003, 2007; Griesshaber et al., 2004; Parkinson et al., 2005; Angiolini et al., 2007; Brand et al., 2011;), the brachiopods are the best choice for “ideal” carbonate reference standard as following characteristic:

1) Very common for fossils record even index fossils; (first appearance from Cambrian, also have the modern representatives for investigating)

2) lived in normal environment;

3) Isotopic equilibrium with ambient environment; (primary layers depleted in $\delta^{18}O$ and $\delta^{13}C$, (Korte et al., 2005) Secondary layers equilibrium (Grossman et al., 1991; Parkinson et al., 2005))

4) Brachiopods shells are low-Mg calcite; (for example: Articulated brachiopods Rhynchonelliform)

5) Textures are well known and crystallites are available;

6) Brachiopods are large enough for analyses. (thick shells are especially resistant to diagenesis. (Grossman et al., 2008))

In order to make sure that the brachiopods are good archive of geochemistry research, many scholar have been starting lab work for comparisons. Some studies have raised interesting and debatable views, such as: Differentiation between data from different samples styles(Brand et al., 2012), species(Grossman et al., 1991), ventral and dorsal valves(Curry and Fallick., 2002) or even within the secondary layer of the shell(Griesshaber et al., 2004) are obviously.

Corresponding, different views as flowing: Parkinson et al. (2005) found no significant difference in $\delta^{18}O$ compositions between ventral and dorsal valves. Small $\delta^{18}O$ and $\delta^{13}C$ variations for different brachiopod orders. (Azmy et al., 1998) Interspecies and interspecies isotope effects are not important factors for isotope variations. (Azmy et al., 1998)

Nevertheless, the important role of brachiopod shells for geochemistry indicators is unshakable. Therefore, we have to using the brachiopod shells proxy to paleo-environment reconstruction more cautiously.

Screening methods and Diagenesis evaluation

For the purpose of obtain better data, the sample for examination should meet following requirements (e.g., Brand et al., 2011): 1) passed the most screening tests, 2) stratigraphically well constrained, 3) reflecting ambient oceanographic environment. In addition, we prefer the impunctate shells to examine in order to avoid any post-depositional contamination by secondary calcite filling punctae. (Azmy et al., 1998; Cusack et al., 2012)

Despite their resistance to diagenesis, brachiopod shells can be subject to oxygen and carbon exchange. $\delta^{18}O$ and $\delta^{13}C$ shifts can be caused by diagenesis dramatically. (Grossman et al., 1991; Mii et al., 1997) And we must therefore be carefully scrutinized for preservation of original microtexture and chemistry.

Following the work of Williams, it became obvious that SEM is an appropriate tool to study brachiopod biomineralisation processes. (Gaspard et al. 2007) And traditionally, microstructure preservation, cathodoluminescence and trace-element characterization are the main tools (criterion) for shell-preservation evaluation. (e.g., Popp et al., 1986; Grossman et al., 1991, 1993, 1996, 2008; Mii and Grossman, 1994; Banner and Kaufman. 1994; Angiolini et al., 2007, 2009; Gaspard et al., 2007)

There are some indexes (references/indicators) for sample evaluation:

1) Clear and well-oriented microstructure is the first evidence of shell preservation. (Grossman et al., 1991)

2) Nonluminescent (NL) calcite are preferred (Grossman et al.,1993; Banner and Kaufman, 1994) Isotopic values of NL shells are equal to (unanimous) for the same stratigraphic interval. (Mii et al., 1997)

3) Prismatic tertiary layer shell is the material most resistant to diagenesis, and probably the best biogenic material for developing a detailed isotope stratigraphy for the Paleozoic. (Grossman et al., 1996; Griesshaber et al., 2004; Garbelli et al., 2012)

4) Shell fabric and its relative organic matter content influencing factor in geochemical data (Garbelli et al., 2014)

5) Shells growth rates will affect δ13C compositions (Garbelli et al. 2014)

6) Shell size also is important. Large specimens tend to be better preserved than smaller ones (Grossman et al., 1993)

With the improvement of technology and depth research, more and more advanced means have applied in screening methods and diagenesis evaluation.

Electron backscatter diffraction (EBSD) analyses (Schmahl et al., 2004; Griesshaber et al., 2007; Cusack et al., 2008a; England et al., 2007; Cusack et al., 2008b; Pérez-Huerta and Cusack, 2008; Goetz et al., 2011; Griesshaber et al., 2012)

laser-ablation inductively coupled plasma mass-spectrometry (LA-ICP-MS) (Griesshaber et al., 2007)

Vickers microhardness indentation (VMHI). (Griesshaber et al., 2007)

Atomic force microscopy (AFM) (Cusack et al., 2008a; Pérez-Huerta et al., 2013)

Synchrotron-radiation X-ray tomographic microscopy (SRXTM) (Pérez-Huerta A et al., 2009)

Backscattered electron z-contrast (BSE-Z) (Zabini et al., 2012) energy dispersive X-ray spectroscopic (EDS) (Zabini et al., 2012)

Polarizing microscope (Garbelli et al., 2015)

Additionally, based on the fabric of the layer and the morphology of their microstructural units, brachiopods shells microstructures can be classified into different micromorphological types. (Samtleben et al., 2001. 9 types) (Garbelli et al., 2012. 8 types) (Garbelli et al., 2015. 7 types)

Application

In recent years, the examination of shells microstructure became more and more important on brachiopod research. Types of shell structure can help for classification and an important factor in establishing evolutionary kinship. (e.g., four types in late Ordovician-early Silurian. (Dewing, 2004)) Shell microstructure help to understand the biomineralization under biological control (Cusack et al. 2008b) Texture of brachiopods shells and the process of brachiopod shell formation are more clarify with EBSD application. (Goetz et al., 2009; Griesshaber et al., 2009), AFM methods also can reveal the nanostructure of biomineral structures, which SEM images cannot demonstrate. (Pérez-Huerta A et al., 2013)

To sum up, after careful assessments for the brachiopod sample, it is therefore suitable as proxy of original chemistry of paleo-ocean. And their shells has widely been used for paleo-environment and paleo-climate reconstruction.

For example:

Isotopic data from brachiopod shells were able to unravel the seawater geochemistry, temperature change, and geologic event during the prehistoric time. (e.g., Bates and Brand, 1991; Grossman et al., 1991, 1993, 2008; Banner and Kaufman, 1994; Azmy et al., 1998; Korte et al., 2005; Brand et al., 2012; Nielsen et al., 2013; Roark et al., 2015; Veizer and Prokoph, 2015; Garbelli et al., 2015) reflecting regional differences in salinity, circulation, and productivity.(Grossman et al., 1993)

For smaller time scales, $\delta^{18}O$ can reflect paleo-seasonality change. (Mii and Grossman, 1994); $\delta^{13}C$ and $\delta^{18}O$ data can also reflect E1 Nifio events (Buening and Spero, 1996). Furthermore, just one single shell, can also reveal the information about ancient seasonal climate. (Angiolini et al., 2012)

Problem and Purpose

In addition to the evolution of taxonomy, the musculature, microstructure and the composition of brachiopod shells may also change a lot. (e.g. baculation in fabric, Cusack et al., 1999). Up to date, our knowledge of how biomineral structures are related to material properties is still limited. (Pérez-Huerta et al., 2007)

Apart from this, it is still controversial whether the data from brachiopod fossil represent the original ocean information. Some people believe that, before Cenozoic, isotopic analyses of older samples are more problematic. (Wenzel et al., 2000)

The interpretation of the isotopic signals of the shells in paleo-climatic research relies heavily on knowledge of biological fractionation between the shells and ambient sea water and of effects of diagenetic overprint processes. (Brand et al., 2003; Schmahl et al., 2004) Palaeozoic shells suffered further recrystallization. (Cusack and Williams, 2001) And the $\square^{18}O$ should normalized for paleo-depth, (Bates and Brand, 1991) paleo-temperature calculate may adjustment for shell $MgCO_3$ contents. (Brand et al., 2013). As the result of comparison of trends of the seawater $\delta^{18}O$ and shell-$MgCO_3$, the new equation were proposed: $T°C = 16.192-3.468(_C-\square_{SW}-Mg_C)$ (Brand et al., 2013)

In summary, based on the outstanding characteristic of their shells, brachiopod maybe the best choice for “ideal” proxy reference in research. Thus, for ensure the representativeness of the brachiopod sample and for a better understanding of the relationship between shell fabric and climate change, and it is of immense importance to examine micro/nano-structure more meticulous. Furthermore, test their veracity in withstanding post-depositional alteration with new methods. The aim of this study will be to uncover following questions:

1) Examine the macro-and chemico-structure of brachiopod shells, reconstruct evolutionary changes and fabric differentiation of the main brachiopod classes during the Phanerozoic (e.g., two brachiopod classes dominated the late Paleozoic seas; the Rhynchonellata and the Strophomenata)

2) With new methods come from modern biology, engineering and materials science, appraise their reliability and validity within the influence of diagenesis.

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