

# Evaluating the biomineralization and chemical differentiation of modern brachiopod archives

## 1. General introduction to Brachiopods.

Brachiopods, phylum Brachiopoda, are marine animals that are enclosed by two calcareous "valves" (shells) on the upper and lower surfaces. One of their main characteristics is that they exhibit bilateral symmetry, but the plane of symmetry is parallel to length and passes through the middle of both valves, unlike in bivalve mollusks, where the right valve is a mirror image of the left. The ventral valve is usually larger than the dorsal valve and has a perforation for the pedicle. Most brachiopods are epifaunal except some taxa of lingulids that have adopted an infaunal habit in. The adult is either free-living or attached to the substratum either by a pedicle or by direct cementation of one of the valves. Brachiopods are filter feeders, carried out by their feeding organ, the lophophore. They are exclusively marine, but they are widespread and inhabit a variety of bottom environments at various depths and latitudes.

Modern brachiopods are classified as articulated or inarticulated, but it has been discarded in favour of three subphyla:

- **Linguliformea:** Inarticulated brachiopods with organophosphatic shells.
- **Craniiformea:** articulated brachiopods with high-Mg calcite shells.
- **Rhynchonelliformea:** articulated brachiopods with shells of low-Mg calcite. It includes the groups Rhynchonellida, Thecideidina and Terebratulida.

### 1.2 The Brachiopod shell.

The brachiopod shell is a multi-layered complex of organic and inorganic material. Each valve consists of an outer pericostracum, made of organic compounds (proteins) and up to three layers (Williams et al. 1997):

- **Primary layer** made of acicular calcite.
- **Secondary layer**, underneath the primary layer. It is made of a mixture of proteins and calcite and it is generally thicker. In rhynchonelliformean, this layer is made of low-Mg calcite and it may have fibrous, laminar or cross-bladed laminar shell fabric.
- Tertiary layer, which more often than not is absent.

Many shells are also perforated by small holes, i.e. punctae, in life holding finger-like extensions of the mantle.

## **2. Brachiopods as potential paleoenvironmental proxies. The problem of the vital effect.**

Low-magnesium calcite is the diagenetically more stable polymorph of calcium carbonate and thus, brachiopod shells consisted of low-Mg calcite are resistant to all except the most aggressive diagenetic processes (Brand and Veizer, 1980). For this reason, the isotopic composition (with special emphasis on  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) of fossil brachiopods has been extensively used to reconstruct physicochemical conditions and secular chemical variations of ancient oceans (Lowenstam, 1961; Veizer et al., 1986; Wenzel and Joachimski, 1996). This, assuming that brachiopods incorporate stable isotopes into shell calcite in or near equilibrium with the ambient seawater.

However, the use of brachiopod shells as paleoenvironmental archives is problematic due to the biological processes of the organism, which cause their chemical and isotopic compositions to be significantly different from calcite precipitated in isotopic equilibrium with ambient seawater. These differences are commonly known as the “vital effect”. In this respect, it has been shown that due to the vital effects of the organism  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of some parts of the brachiopod shell are generally out of equilibrium [e.g., Carpenter and Lohmann, 1995; Auclair et al., 2003; Parkinson et al., 2005; Yamamoto et al., 2010; Takayanagi et al. 2015]. Recently, it has also been shown for Mg/Ca ratios and  $\delta^{11}\text{B}$  (Perez-Huerta et al. 2008; Penman et al., 2013), but no data on the vital effects on other relevant isotopes and elemental ratios, such as  $\delta^7\text{Li}$ ,  $\delta^{26}\text{Mg}$ , Li/Ca and Sr/Ca, has been published so far.

Moreover, there are many publications trying to unravel which portions of the shell and brachiopod taxa are most reliable as proxies of paleoenvironment and paleoceanography (Auclair et al., 2003; Perez-Huerta et al. 2008; Von Allmen et al. 2010; Yamamoto et al. 2010, 2013; Takayanagi et al. 2012, 2013, 2015; Penman et al., 2013). Even though, further research on the brachiopod biomineralization processes is required to better understand the mechanisms responsible for such chemical and isotopic fractionations and to reconstruct reliable physicochemical conditions of past oceans.

### **2.1. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ composition of brachiopod shells. Vital effects.**

Generally, the innermost part of the secondary layer is in equilibrium with calcite precipitated in ambient seawater, i.e. the most reliable part, while the primary layer is depleted in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , as well as the outer part of the secondary layer (see references above). The vital effects of the organism predominantly influence these portions out of equilibrium, commonly explained by kinetic fractionation processes or metabolic effects.

Kinetic isotope fractionation is linked to high growth rates and metabolic activity of the outlining mantle, thus is most prominent in rapidly calcifying organisms and in rapidly growing parts of the skeleton. Occurs because precipitation is faster than equilibration during  $\text{CO}_2$  hydration and hydroxylation in the extrapallial fluid, resulting in a depletion

of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  (McConnaughey, 1989a,b; McConnaughey et al., 1997). Is typically characterized by a positive correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values.

Metabolic effects are characterized by a depletion of  $\delta^{13}\text{C}$  in zones of higher metabolic activity, like the marginal mantle, which is involved in the secretion of the shell margin (Auclair et al. 2003). These zones incorporate a larger fraction of  $^{12}\text{C}$ -carbon derived from respiration, leading to a depletion of  $\delta^{13}\text{C}$  (McConnaughey, 1989a; McConnaughey et al., 1997)

Recent studies have shown that the degree of biological isotope fractionation can vary among species, as well as within a single species (Yamamoto *et al.* 2013; Takayanagi et al. 2015), suggesting that knowledge of the nature of inter- and intraspecific variations is still needed.

Yamamoto et al. (2010b) and Takayanagi et al. (2012, 2013, 2015) also reported an increase of  $\delta^{18}\text{O}$  values in shell portions formed at the slowest growth rates. It is known that other calcifying organisms, such as corals and foraminifers, change the pH of their internal fluids, thus, changing  $^{18}\text{O}$  compositions as compared to ambient seawater (Spero et al., 1997; Adkins et al., 2003; Rollion-Bard et al., 2003). Unfortunately, we cannot conclude that the same mechanism holds for brachiopods, since any study have investigated this effect on them yet.

## **2.2. Other isotopes and element ratio. Vital effects.**

There is only one study addressing the vital effects on other isotopes ( $\delta^{11}\text{B}$ ). It is the study of Penman et al. (2013), where they analyzed the vital effects on  $\delta^{11}\text{B}$  compositions in modern brachiopods. They reported an intrashell variability, and suggested that the best area of sampling is center of 2° layer. They also found a depletion of  $\delta^{11}\text{B}$  in the primary layer and innermost part of the secondary layer. It has been demonstrated that foraminifera and corals have the potential to increase the pH at the site of calcification prior to precipitation up to 9, and therefore, having higher  $\delta^{11}\text{B}$  values (Erez 2003; Rollion-Bard and Erez 2010; Rollion-Bard et al. 2011). However, Penman et al. (2013) found the opposite trend, and even they explained that this depletion is due to physiological processes, there is no explanation for such decrease yet.

Regarding the vital effects on other isotopes and element ratios, to date, very little has been done. Von Allmen et al. (2010) reported a homogeneous  $\delta^{44/40}\text{Ca}$  distribution along the shell, but suggesting an interspecific variability. Perez-Huerta et al. (2008) also suggested a biological control on Mg/Ca ratio. Any of these studies didn't report any explanation for the biological processes that may control these effects, though.

### 3. Relevant literature for the topic

- Adkins, J.F., E.A. Boyle, W.B. Curry, and A. Lutring. 2003. Stable isotopes in deep-sea corals and a new mechanism for "vital effect". *Geochim. Cosmochim. Acta.* 67: 1129–1143.
- Auclair A., M.M. Joachimski, and C. Lécuyer. 2003. Deciphering kinetic, metabolic and environmental controls on stable isotope fractionations between seawater and the shell of *Terebratalia transversa* (Brachiopoda). *Chem. Geol.* 202: 59–78.
- Brand U., A. Logan, N. Hiller, and J. Richardson. 2003. Geochemistry of modern brachiopods: applications and implications for oceanography and paleoceanography. *Chem. Geol.* 198: 305–334.
- Brand U., K. Azmy, M.A. Bitner, A. Logan, M. Zuschin, R. Came, and E. Ruggiero. 2013. Oxygen isotopes and MgCO<sub>3</sub> in brachiopod calcite and a new paleotemperature equation. *Chem. Geol.* 359: 23–31.
- Brand, U. and J. Veizer. 1981. Chemical diagenesis of a multi-component carbonate system. Stable isotopes. *J. Sediment. Petrol.* 51: 987–997.
- Brand, U., K. Azmy, E. Griesshaber, M.A. Bitner, A. Logan, M. Zuschin, E. Ruggiero, and P.L. Colin. 2015. Carbon isotope composition in modern brachiopod calcite: A case of equilibrium with seawater? *Chem. Geol.* 411: 81–96.
- Carpenter, S.J. and K.C. Lohmann. 1995. Delta-O-18 and delta-C-13 values of modern brachiopod shells. *Geochim. Cosmochim. Acta.* 59 (18): 3749–3764.
- Cusack M. and A.P. Huerta. 2012. Brachiopods recording seawater temperature—A matter of class or maturation?. *Chem. Geol.* 334: 139–143.
- Cusack, M., Y. Dauphin, J.P. Cuif, M. Salomé, A. Freer, H. Yin. 2008b. Micro-XANES mapping of sulphur and its association with magnesium and phosphorus in the shell of the brachiopod, *Terebratulina retusa*. *Chem. Geol.* 253: 172–179
- Delaney, M.L., B.N. Popp, C.G. Lepzelter, and T.F. Anderson. 1989. Lithium-to-calcium ratios in modern, Cenozoic and Paleozoic articulate brachiopod shells. *Paleoceanography.* 4: 681–691.
- Erez, J. 2003. The source of ions for biomineralization in foraminifera and their implication for paleoceanographic proxies. *Rev. Mineral. Geochem.* 54: 115–149.
- Harper, D.A.T. 2005. Brachiopods, p. 301–310. In *Fossil Invertebrates*. Elsevier.
- James, M. A., A. D. Ansell, M. J. Collins, G. B. Curry, L. S. Peck and M. C. Rhodes. 1992. Biology of living brachiopods, p. 175–387. In J.H.S. Blaxter & A.J. Southward [eds.], *Advances in Marine Biology*. Academic Press.
- Joachimski, M.M., L. Simon, R. van Geldern and C. Lecuyer. 2005. Boron isotope geochemistry of Paleozoic brachiopod calcite: implications for a secular change in the boron isotope geochemistry of seawater over the Phanerozoic. *Geochim. Cosmochim. Acta.* 69 (16): 4035–4044.
- Lécuyer, C., P. Grandjean, B. Reynard, F. Albarède and P. Telouk. 2002. 11B/10B analysis of geological materials by ICP-MS Plasma 54: application to the boron fractionation between brachiopod calcite and seawater. *Chem. Geol.* 186 (1–2): 45–55.
- Lowenstam, H.A. 1961. Mineralogy, O18/O16 ratios and strontium and magnesium contents of recent and fossil brachiopods and their bearing on the history of the oceans. *J. Geol.* 69: 241 – 260.
- Marriott, C.S., G.M. Henderson, N.S. Belshaw, and A.W., Tudhope. 2004. Temperature dependence of d<sup>7</sup>Li, d<sup>44</sup>Ca and Li/Ca during growth of calcium carbonate. *Earth Planet. Sci. Lett.* 222: 615–624.
- Penman, D.E., B. Hönisch, E.T. Rasbury, N.G. Hemming, and H.J. Spero. 2013. Boron, carbon, and oxygen isotopic composition of brachiopod shells: Intra-shell variability, controls, and potential as a paleo-pH recorder. *Chem. Geol.* 340: 32–39.

- Pérez-Huerta, A., M. Cusack, S. McDonald, F. Marone, M. Stampanoni and S. MacKay. 2009. Brachiopod punctae: a complexity in shell biomineralisation. *J. Struct. Biol.* 167:62–67.
- Rollion-Bard C., M. Chaussidon, C. and France-Lanord. 2003. pH control on oxygen isotopic composition of symbiotic corals. *Earth Planet. Sci. Lett.* 215: 275–288.
- Rollion-Bard, C., M. Chaussidon, and C. France-Lanord 2011. Biological control of internal pH in scleractinian corals: Implications on paleo-pH and paleo-temperature reconstructions. *C. R. Geosc.* 343: 397–405
- Rollion-Bard, C. and J. Erez. 2010. Intra-shell boron isotope ratios in the symbiont-bearing benthic foraminiferan *Amphistegina lobifera*: implications for  $\delta^{11}\text{B}$  vital effects and paleo-pH reconstructions. *Geochim. Cosmochim. Acta.* 74: 1530–1536.
- Spero, H.J., J. Bijma, D.W. Lea, and B.E. Bemis. 1997. Effect of seawater carbonate concentration on foraminiferal carbon and oxygen isotopes. *Natur.* 390: 497-500.
- Steuber, T. and D Buhl. 2006. Calcium-isotope fractionation in selected modern and ancient marine carbonates. *Geochim. Cosmochim. Acta.* 70: 5507-5521.
- Takayanagi H., R. Asami, O. Abe, T. Miyajima, H. Kitagawa, and Y. Iryu. 2012. Carbon- and oxygen-isotope compositions of a deep-water modern brachiopod *Campagea japonica* collected off Aguni-jima, Central Ryukyu Islands, southwestern Japan. *Geochem. J.* 46: 77–87.
- Takayanagi H., R. Asami, O. Abe, T. Miyajima, H. Kitagawa, K. Sasaki, and Y. Iryu. 2013. Intraspecific variations in carbon- and oxygen-isotope compositions of a brachiopod *Basiliola lucida* collected off Okinawa-jima, southwestern Japan. *Geochim. Cosmochim. Acta* .115: 115–136.
- Takayanagi H., R. Asami, T. Otake, O. Abe, T. Miyajima, H. Kitagawa, K. Sasaki, and Y. Iryu. 2015. Quantitative analysis of intraspecific variations in the carbon and oxygen isotope compositions of the modern cool-temperate brachiopod *Terebratulina crossei*. *Geochim. Cosmochim. Acta.* 170: 301-320.
- Veizer, J., P. Fritz and B. Jones. 1986. Geochemistry of brachiopods: oxygen and carbon isotopic records of Paleozoic oceans. *Geochim. Cosmochim. Acta.* 50: 1679–1696.
- Von Allmen, K., T.F. Nägler., T. Pettke, D. Hippler, E. Griesshaber, A. Logan, A. Eisenhauer and E. Samankassou . 2010. Stable isotope profiles (Ca, O, C) through modern brachiopod shells of *T. septentrionalis* and *G. vitreus*: Implications for calcium isotope paleo-ocean chemistry. *Chem. Geol.* 269: 210–219.
- Wenzel, B. and M. M. Joachimski. 1996. Carbon and oxygen isotopic composition of Silurian brachiopods (Gotland/Sweden): palaeoceanographic implications. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 122: 143–166.
- Williams, A. 1997. Shell Structure, p. 267–320. In: Kaesler, R. [Ed.], *Treatise on Invertebrate Paleontology*, pt. H. Brachiopoda (revised). Geol. Soc. Am. and Univ. Kansas.
- Williams, A., S. J. Carlson , C. H. C. Brunton, L. E. Holmer and L. A. Popov. 1996. Supra-Ordinal Classification of the Brachiopoda. *Philos. Trans. R. Soc. Lond. B Biol. Sci.* 351: 1171–1193.
- Yamamoto K., R. Asami, and Y. Iryu. 2010a. Carbon and oxygen isotopic compositions of modern brachiopod shells from a warm-temperate shelf environment, Sagami Bay, central Japan. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 291: 348–359.
- Yamamoto K., R. Asami, and Y. Iryu. 2010b. Within-shell variations in carbon and oxygen isotope compositions of two modern brachiopods from a subtropical shelf environment off Amami-o-shima, southwestern Japan. *Geochem. Geophys. Geosyst.* 11: Q10009.
- Yamamoto K., R. Asami, and Y. Iryu. 2011. Brachiopod taxa and shell portions reliably recording past ocean environments: Toward establishing a robust paleoceanographic proxy. *Geophys. Res. Lett.* 38: L13601.
- Yamamoto K., R. Asami, and Y. Iryu. 2013. Correlative relationships between carbon- and oxygen-isotope records in two cool-temperate brachiopod species off Otsuchi Bay, northeastern Japan. *Paleontol. Res.* 16: 12–26.