Seasonal seawater pH variations in the late Paleozoic – boron isotopes from brachiopod shells as a paleo-proxy

Dr. Marco Viaretti
Dipartimento di Scienze della Terra "Ardito Desio", Università degli Studi di Milano

Introduction

Brachiopods are widely recognized as one of the best archives for geochemical proxies, particularly their secondary (fibrous or laminar) and tertiary (columnar) layers, which are mostly secreted in near-equilibrium with seawater (e.g. Brand et al., 2011, 2019; Garbelli et al., 2022). The growth of the shell is episodic, with periods of slowest shell production coinciding with the formation of growth lines and growth lamellae. For this reason, a recent challenge arisen in the study of the brachiopod shell geochemistry is the application of sclerochronology, particularly on upper Paleozoic shells (e.g. Angiolini et al., 2012; Garbelli et al., 2022), which are the most diversified and abundant. The method consists in collecting a series of samples along the growth axis of the shell, to be able to measure the seasonal changes experienced by the brachiopods during their lives and recorded by the isotopic signature of the shell (e.g. Crippa et al., 2016). Another recent developement in the study of shell geochemistry is the analysis of boron isotopes ($\delta^{11}B$) to reconstruct past pH seawater conditions (e.g. Legett et al., 2020; Jurikova et al., 2020). The project funded with the scholarship of the Società Paleontologica Italiana to the writer aimed to analyse the $\delta^{11}B$ of upper Paleozoic brachiopod shells for two main purposes: to test the seasonal boron signal recorded by the shells to detect past past pH seasonal changes, and to use $\delta^{11}B$ to assess the preservation of microstructure in partially silicified shells.

Material and methods

Brachiopod shells were selected from different localities around the Neo-Tethys. The sclerochronological method was applied to two specimens of *Pachycyrtella omanensis* Angiolini, 2001 from the Saiwan Formation (Sakmarian, Early Permian) of Interior of Oman (Angiolini, 2007). The secondary layer of *P. omanensis* is fibrous and the tertiary layer is not present. The partially silicified shells were selected from the Mobarak Formation (Visean, Mississippian) of North Iran (Bahrammanesh et al., 2011) and the Qarari Unit (Kungurian, Lower Permian) of Oman (Viaretti et al., 2022). The selected material counts twelve specimens, belonging to the following taxa: *Aequalicosta* sp., *Callytharrella websteri* Viaretti et al., 2022, *Marginatia vaughani* (Muir-Wood, 1928), *Martinia* sp., *Parallelora* sp., *Retimarginifera auricolata* Viaretti et al., 2022, *Spiriferella posterosulcata* Viaretti et al., 2022, *Suqamularia marcouxi* Verna & Angiolini in Verna et al., 2011, *Stenoscisma qararensis* Viaretti et al., 2022, *Tomiproductus elegantulus* (Tolmatchoff, 1924) and *Unispirifer striatoconvolutus* (Benson & Dun in Benson, Dun & Browne, 1920), having fibrous or laminar secondary layer. The brachiopod shells from these localities were previously analyzed at the SEM to assess the morphological preservation of their microstructural units. They showed varied silicification patterns involving different regions and microstructures of the shells with very different morphological and spatial distribution of the silica replacements, but always leaving some relics of morphologically well preserved shell microstructure. In the case of these specimens, the measurements were made in the form of transects along the growth axis of the shell, from the umbo to the anterior commissure, to measure both the silicified shell and the preserved portions of shell microstructure.

The boron measurement were performed with a LA-MC-ICPMS (RESOlution-SE 193nm ArF laser ablation system (Applied Spectra) connected to a Neptune Plus (Thermo-Fisher Scientific) (Fig. 1), at the University of St Andrews, Scotland. With this technique series of samples are programmed prior to the measurement session, and the machine works overnight. The samples are taken in the form of data points, which are the result of a laser beam hitting a spot 8 µm wide for six times, and the resulting powder is then collected and analyzed. The hole created by the laser beam is about 4 µm deep. The resulting data are spatially characterized on the sample, and pictures of every data point are provided along with the analytical results. In total, more than 1500 measurements were made through four measurement sessions of 18 to 22 hours.

Preliminary results and future developements

Preliminary analyses of the $\delta^{11}B$ measurements made on the partially silicified shells show that the resulting expected values for boron isotopes ($\delta^{11}B$ ~15‰) are found in the data point placed on portions of shell microstructure not affected by silicification. The laser ablation analysis provides images of each measured data point, which show the correspondence between stable $\delta^{11}B$ results and shell microstructure unaffected by silicification (Fig. 2). These data, along with SEM results, are a good indication of the preservation of the microstructure unaffected by the process of silicification. These preliminary data however showed how the silicification could either alter or preserve the shell microstructure, depending on the completeness of the process. For instance, a big portion of shell enclosed by silica can be a good target for geochemical analyses since the silicification process shielded the microstucture from the alteration from other diagenetic processes. The subsequent tests to completely assess wether the partially silicified shells are a good geochemical archive are cathodoluminescence and EBSD analyses, presently in progress. Another information gained though the laser ablation technique is the fact that silicification patterns are not uniform is space inside the shells. In particular, SEM images showed that silicification patterns are morphologically variable in different parts of the shell, depending also on the stage of the process which has been reached through diagenesis. The SEM information, however, is limited to the plain of the longitudinal section, showing the morphological variation of silicification from the umbo to the anterior commissure. In some instances instead, the holes left by the laser beam revealed morphologically well preserved shell microstructure hidden by the silica. This means that the silicification is not spatially uniform not only longitudinally, but also transversally, and different longitudinal sections of the same shell could show different amount of well-preserved microstructure.

The $\delta^{11}B$ sclerochronological data from the two specimens *P. omanensis* will be coupled with $\delta^{13}C$ and $\delta^{18}O$ measured from powders collected from the same specimens (analyses currently in progress) in order to compare the different isotopic signatures along the same longitudinal transect. In this way the interpretation of the potential seasonal signal will be based on three paleo-proxies and will provide additional data on the climate change at temperate southern palaeolatitudes at the end of the Gondwana glaciation (Angiolini 2007).

Acknowledgements

I want to deeply thank the Società Paleontologica Italiana for supporting my project with this scolarship, as well as continuing to create opportunities for young paleontologists like me to develop a career in this fascinating field of research. I also want to thank Dr. H. Jurikova for hosting me and providing help and support during my stay at the St Andrews University.

References

Angiolini L. (2001). New Syringothyridid genus (Spiriferida, Brachiopoda) from the Early Permian of Interior Oman. *Rivista Italiana di Paleontologia e Stratigrafia*, 107(1), 125-130.

Angiolini L. (2007). Quantitative palaeoecology in the Pachycyrtella bed, Early Permian of interior Oman. *Palaeoworld*, 16(1-3), 233-245.

Angiolini L., Stephenson M., Leng M.J., Jadoul F., Millward D., Aldridge A., Andrews J., Chenery S. & Williams G. (2012). Heterogeneity, cyclicity and diagenesis in a Mississippian brachiopod shell of palaeoequatorial Britain. *Terra Nova*, 24(1), 16-26.

Bahrammanesh M., Angiolini L., Antonelli A.A., Aghababalou B. & Gaetani M. (2011). Tournaisian (Mississippian) brachiopods from the Mobarak Formation, North Iran. *GeoArabia*, 16(3), 129-192.

Brand U., Logan A., Bitner M.A., Griesshaber E., Azmy K. & Buhl D. (2011). What is the ideal proxy of Palaeozoic seawater chemistry? *Memoirs of the Association of Australasian Palaeontologists*, (41), 9-24.

Brand U., Bitner M.A., Logan A., Azmy K., Crippa G., Angiolini L., Colin P., Griesshaber E., Harper E.M., Ruggiero E.T. & Haussermann V. (2019). Brachiopod-based oxygen-isotope thermometer: update and review. *Rivista Italiana di Paleontologia e Stratigrafia*, 125(3), 775-778.

Crippa G., Angiolini L., Bottini C., Erba E., Felletti F., Frigerio C., Hennissen J.A.C., Leng M.J., Petrizzo M.R., Raffi I., Raineri G. & Stephenson M.H. (2016). Seasonality fluctuations recorded in fossil bivalves during the early Pleistocene: Implications for climate change. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 446, 234-251.

Garbelli C., Angiolini L., Posenato R., Harper E.M., Lamare M.D., Shi G.R. & Shen S.Z. (2022). Isotopic time-series ($\delta^{13}C$ and $\delta^{18}O$) obtained from the columnar layer of Permian brachiopod shells are a reliable archive of seasonal variations. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 607, 111264.

Ghaderi A., Garbelli C., Angiolini L., Ashouri A.R., Korn D., Rettori R. & Gharaie,M.H.M. (2014). Faunal change near the end-Permian extinction: the brachiopods of the Ali Bashi Mountains, NW Iran. *Rivista Italiana di Paleontologia e Stratigrafia*, 120(1), 27-59.

Jurikova H., Gutjahr M., Wallmann K., Flögel S., Liebetrau V., Posenato R., Angiolini L., Garbelli C., Brand U., Wiedenbeck M. & Eisenhauer A. (2020). Permian–Triassic mass extinction pulses driven by major marine carbon cycle perturbations. *Nature Geoscience*, 13(11), 745-750.

Legett S.A., Rasbury E.T., Grossman E.L., Hemming N.G. & Penman D.E. (2020). The brachiopod $\delta^{11}B$ record across the Carboniferous-Permian climate transition. *Paleoceanography and Paleoclimatology*, 35(10), e2019PA003838.

Viaretti M., Heward A.P., Gementi A. & Angiolini L. (2022). Upper Cisuralian-lower Guadalupian brachiopods from the Qarari Unit, Batain plain, northeast Oman: systematics, palaeoecology and correlation. *Rivista Italiana di Paleontologia e Stratigrafia*, 128(3), 643-694.

Figures

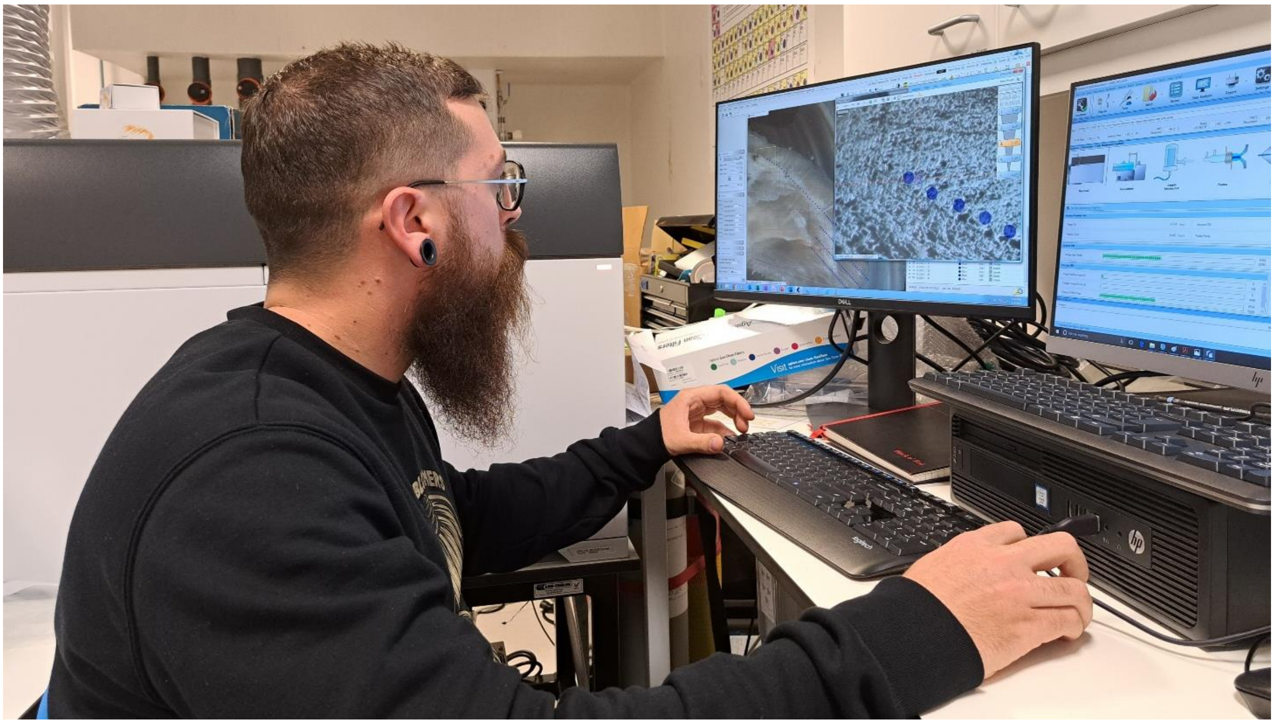

Fig. 1. Programmation of a transect for the laser ablation analysis with the Neptune Plus software.

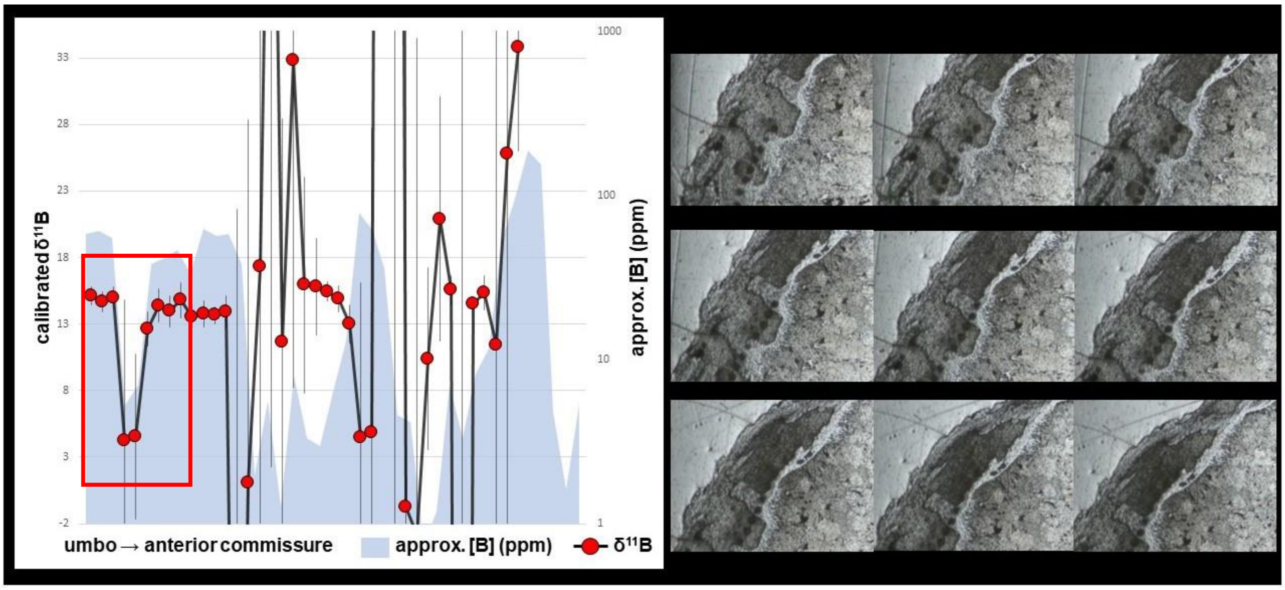

Fig. 2. Transect of $\delta^{11}B$ values with their corresponding sampling site images measured on a *Callytharrella websteri* shell.