Brachiopods recording seawater temperature – grow up and be a good proxy

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Brachiopods are attractive proxies

The stable, low- magnesium shells of brachiopods and their long geological record means that they are an attractive source of past seawater temperature data. Although brachiopod shells appear simple, analysis of their crystallography e.g. [1-2] or shell punctae (perforations) [3], reveals the extent of the biological control that is exerted as these shells form. This biological control makes it all the more impressive that the calcite fibres of the secondary (inner) layer of low magnesium-calcite brachiopod shells are in oxygen isotope equilibrium with ambient seawater [4-5].

Maturation or class?

In *Terebratalia transversa*, micromilling and conventional mass spectrometry revealed that oxygen isotope equilibrium is not achieved instantly with the abrupt switch from primary (outer) to secondary (inner) layer secretion but rather that oxygen isotope equilibrium is attained towards the innermost shell [6]. Thus, the first formed calcite fibres of the secondary layer of *T. transversa* are not in isotopic equilibrium while the later fibres of mature valves are in oxygen isotope equilibrium with seawater.

This study exploits the high spatial resolution of secondary ion mass spectrometry (SIMS) to investigate this oxygen isotope trend in *Terebratalia transversa* as investigated by Auclair [6] as well as *Terebratulina retusa* and *Notosaria nigricans*. Thus, three species of brachiopod from two Orders and two sub-orders are investigated by high resolution SIMS. This will help us understand whether only mature valves can be relied upon in proxy measurements or whether this caveat is restricited to *T. transversa*.

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Arsenic and phosphate cycling in surface waters of the North Atlantic

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Introduction

It is well known that As(V), arsenate, is toxic to marine phytoplankton when phosphate concentrations drop to the 10-15 nM levels of arsenate found in oligotrophic surface waters. This toxicity is due to the chemical and biochemical similarities of the two. Interestingly, many phytoplankton have evolved arsenic detoxification mechanisms that include reducing arsenate to arsenite (AsIII) and/or methylating it to monomethyl (MMAs) and dimethyl arsenic (DMAs); these species are not taken up by phytoplankton. Thus, phytoplankton in oligotrophic, low P waters have a two-fold problem: first phosphate stress and then arsenate toxicity. Existing methods to assay phosphate stress via measurements of the enzyme alkaline phosphatase's activity (APA) have no associated time clock to establish how long the stress has occurred. Depending on their residence times, the As detoxification products could provide this missing temporal information.

The coupled biogeochemistries of As and P were examined on the US GEOTRACES cruises from Lisbon, Portugal to Cape Verde and then Charleston, South Carolina USA in 2010, and Woods Hole, Massachusetts USA to Cape Verde in 2011. Surface samples were acquired with a trace metal-clean towed "fish" at two hour intervals, 0.2 μm filtered, immediately refrigerated, and analyzed within 24 hours. Additional samples for APA were unfiltered and passed through an 80 μm mesh to remove zooplankton; assays were begun within 4 hours. Nanomolar reactive phosphate was determined using a modified molybdenum blue method and liquid core waveguides. Arsenic speciation was determined using selective hydride generation coupled to gas chromatography with photoionization detection.

Results and Discussion

On the two transects, phosphate varied from 3-20 nM (except near the coasts). AP activities were highest in the oligotrophic central gyre with the lowest phosphate concentrations. Arsenite varied between 0.2-5 nM, the highest values in the gyre. Arsenite has an surface residence time of ca. 3d and showed a significant correlation with APA (r=0.6), suggesting it may be a good short term indicator of P-stress. MMAs was relatively uniform in its distribution, while DMAs varied more, 0-4 nM. Neither methyl species correlated with APA, but if their residence times (to be determined) are longer, then no direct relationship would be expected. Overall, it does appear that As speciation may be a useful integrator of P-stress.