Assessing the potential of brachiopod shell geochemistry as a recorder of past sea-water temperatures and oxygen isotope composition.

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Most of our knowledge of past ocean temperature history is based on the $\delta^{18}O$ measurements of calcium carbonate fossil shells. However, the determination of past temperature using this proxy requires the knowledge of past ocean $\delta^{18}O$, which is generally poorly constrained. Other carbonate-based paleothermometers, such as Mg/Ca ratios, and clumped isotopes ($\Delta47$), have hence been developed to estimate independently paleotemperatures, and to calculate past ocean $\delta^{18}O$ using various groups of calcifying organisms. Articulated brachiopods are some of the most commonly used in studies of past oceans geochemistry and temperature. They are abundant in the fossil record since the Cambrian, and their low Mg-calcite shell is relatively resistant to diagenetic alteration. Here we investigate the potential of brachiopod shells as recorders of growing temperature and sea-water $\delta^{18}O$ via multiple carbonate based paleothermometers.

Modern articulated brachiopod shells from different locations were analyzed for their stable isotopes composition ($\delta^{13}C$ and $\delta^{18}O$), $\Delta47$ and Mg/Ca ratios. They cover a wide range of temperatures (-1.8 to 25.5°C), depths (5 to 3431m) and salinities (33.4 to 37.0 PSU). A broad sampling was performed so that the different analyses can be achieved on the same sampled powder, but care was taken to avoid shell areas that are considered in chemical disequilibrium with sea-water. Our results and the calculated $\delta^{18}O_{sw}$ allow us to propose a revised oxygen fractionation equation between sea-water and modern brachiopod shell calcite:

$$1000\ln\alpha_{(CaCO_3\text{-}H_2O)} = -4.99T + 169.57 \qquad R^2 = 0.95$$

Where $\alpha_{(CaCO_3\text{-}H_2O)}$ is the oxygen fractionation factor, T is in °C. Measured $\Delta47$ imply growing temperatures that are in excellent agreement with those estimated from oceanographic data. This supports the use of clumped isotopes as an alternative temperature proxy which can be used with $\delta^{18}O$ to estimate past $\delta^{18}O_{sw}$ with a precision of about 1‰ VSMOW. The application of Mg/Ca paleothermometry to brachiopod shells will also be discussed. Our results will be compared to published relationships between brachiopod shell geochemistry and growing temperature. Such multi-proxy studies of modern brachiopod shell geochemistry are critical for studying the fossil record and resolve challenging questions regarding the Phanerozoic climate record.

Keywords: Paleotemperature, Brachiopod calcite, Sea-water $\delta^{18}O$, Clumped isotopes

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