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journal homepage: [www.elsevier.com/locate/palaeo](http://www.elsevier.com/locate/palaeo)Sr/Ca and Mg/Ca ratios of ontogenetically old, long-lived bivalve shells (*Arctica islandica*) and their function as paleotemperature proxiesBernd R. Schöne<sup>a,\*</sup>, Zengjie Zhang<sup>a,b</sup>, Pascal Radermacher<sup>a</sup>, Julien Thébault<sup>a,c</sup>, Dorrit E. Jacob<sup>a</sup>, Elizabeth V. Nunn<sup>a</sup>, Anne-France Maurer<sup>a</sup><sup>a</sup> Department of Applied and Analytical Paleontology and INCREMENTS Research Group, Earth System Science Research Center, Institute of Geosciences, University of Mainz, Johann-Joachim-Becher-Weg 21, 55128 Mainz, Germany<sup>b</sup> Institute of Mineral Resources, Chinese Academy of Geological Sciences, Baiwanzhuang Road 26, Beijing 100037, China<sup>c</sup> Université de Bretagne Occidentale, Institut Universitaire Européen de la Mer, Laboratoire des Sciences de l'Environnement Marin (UMR6539 UBO/IRD/CNRS), Technopôle Brest-Iroise, Place Nicolas Copernic, 29280 Plouzané, France

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## ABSTRACT

The Sr/Ca and Mg/Ca ratios of many biogenic skeletons provide useful paleotemperature estimates. As yet however, it has remained largely impossible to obtain such information from bivalve shells. In the present study, metal-to-calcium values in the hinge plate (aragonite, outer shell layer) of four ontogenetically old (85 to 374 year-old) specimens of the long-lived bivalve, *Arctica islandica*, were measured on a LA-ICP-MS. The shells were collected alive in 1868, 1986 and 2003 from three different localities around Iceland. With increasing ontogenetic age and decreasing growth rate, a distinct trend toward increasing Sr/Ca (max. 5.17 mmol/mol) and Mg/Ca values (max. 0.89 mmol/mol) and greater variance were observed. Three potential explanations for these trends include a reduced capacity for element selection due to cell ageing, changing metabolism and/or a relative increase in the number of organic-rich (= Mg-rich) and organic-poor (= Sr-rich) shell portions through ontogeny. Partition coefficients however, remained far below 1, indicating that physiology exerted a strong control over the element partitioning between the shells and the ambient water. After mathematical elimination of these vital effects, residuals exhibited a highly significant negative correlation (e.g., age-detrended Sr/Ca data:  $R = -0.64$ ,  $R^2 = 0.41$ ,  $p < 0.0001$ , growth rate-detrended Mg/Ca data:  $R = -0.52$ ,  $R^2 = 0.27$ ,  $p < 0.0001$ ) with sea surface temperature. These results are in good agreement with results obtained from the precipitation of abiogenic aragonite. The results of the present study can help to develop new techniques to extract environmental signals from the metal-to-calcium ratios of bivalve shells.

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## 1. Introduction

Metal-to-calcium ratios (Me/Ca) of biogenic carbonates likely contain a broad array of paleoenvironmental information. Without doubt, strontium (Sr) and magnesium (Mg) are the most studied trace elements. For example, past water temperatures have been reconstructed from Sr/Ca and Mg/Ca ratios of many different taxonomic groups, such as brachiopods (Lowenstam, 1961; Powell et al., 2009), corals (Beck et al., 1992; Mitsuguchi et al., 1996; Goodkin et al., 2007), foraminifera (Nürnberg et al., 1996), ostracods (Corrège, 1993), echinoids (Pilkey and Hower, 1960), sclerosponges (Rosenheim et al., 2004), belemnites (McArthur et al., 2007), gastropods (Sosdian et al., 2006) and bivalves (Dodd, 1965, 1967; Hart and Blusztajn, 1998). In general, temperature reconstructions based on Sr/Ca and Mg/Ca ratios are considered superior to oxygen isotope based

reconstructions because, unlike  $\delta^{18}\text{O}$  values, the concentration of these elements in seawater above 10 PSU (Dodd and Crisp, 1982) remains relatively constant over time.

However, the empirically determined relationship between Me/Ca ratios of biogenic carbonates—especially bivalve shells—and environmental parameters often depart significantly from results obtained by abiogenic precipitation experiments<sup>1</sup>. At equilibrium, the distribution coefficient

$$K_{D(\text{Me})} = \left( \frac{\text{Me}}{\text{Ca}} \right)_{\text{CaCO}_3} / \left( \frac{\text{Me}}{\text{Ca}} \right)_{\text{solution}} \quad (1)$$

<sup>1</sup> It is worth noting that thermodynamic equilibrium is difficult to maintain even during abiogenic precipitation experiments (Gaetani and Cohen, 2006), i.e. kinetic effects are likely always present. In fact, the mechanisms for producing impurities in artificially grown carbonate crystals—much less complex systems because of the lack of biologically controlled reaction compartments, e.g., semipermeable membranes—are still strongly debated (e.g., Tiller et al., 1953; Albarede and Bottinga, 1972; Watson and Liang, 1995; Watson, 1996, 2004).

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