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Reproducibility of trace element time-series (Na/Ca, Mg/Ca, Mn/Ca, Sr/Ca, and Ba/Ca) within and between specimens of the bivalve *Arctica islandica* – A LA-ICP-MS line scan study

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ABSTRACT

Trace element time-series in bivalve mollusk shells and other (biogenic) materials can potentially serve as environmental proxies. Yet, the applicability of element-to-calcium ratios is often challenging, because non-environmental factors such as vital effects distort or mask environmental signals. If a trace element time-series is driven by an environmental factor, it should be reproducible within and between coeval specimens of the same species. In the present study, we tested whether time-series of trace element-to-calcium ratios can be reproduced within and between coeval specimens of the bivalve *Arctica islandica* and thus whether an external signal is encoded in the temporal variations of trace elements along the shells. We determined the concentration of sodium, magnesium, manganese, strontium and barium by means of LA-ICP-MS in line scan mode in the hinge area of seven specimens from the Isle of Man, the Gulf of Maine and Iceland. In each specimen, the element composition was determined along two replicate line scans to gauge intra-specimen reproducibility. The degree to which trace element time-series can be reproduced was inferred from linear regression analysis and equaled on average 95 ± 4% for Ba/Ca, 82 ± 27% for Mg/Ca, 83 ± 18% for Sr/Ca, 74 ± 23% for Mn/Ca, and 22 ± 4% for Na/Ca ratios (values correspond to coefficients of determination of the linear regression analysis expressed in percent).
The synchrony of Ba/Ca time-series between contemporaneous specimens from the same habitat has already been demonstrated in previous studies. Here, we observed common high-frequency variations (i.e., peaks) among coeval *A. islandica* from the same site for Mg/Ca, Sr/Ca, Mn/Ca and Na/Ca ratios, especially among specimens of similar ontogenetic age and with similar shell growth patterns. The results of the present study should be considered in interpretations of trace element time-series in bivalve shells as they can help to improve environmental and climate reconstructions.

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1. Introduction

The bivalve mollusk *Arctica islandica* is a powerful marine paleoclimate archive, being exceptionally long-lived (Butler et al., 2013) and widely distributed in the North Atlantic Ocean (Nicol, 1951; Merrill and Ropes, 1969; Dahlgren et al., 2000). Furthermore, shells of *A. islandica* contain precisely dated records of environmental change in the form of variable increment widths that are synchronous between individuals (Witbaard, 1996; Wanamaker et al., 2009a; Butler et al., 2013; Marali and Schöne, 2015), and geochemical properties such as isotopes and, potentially, trace and minor elements (Schöne et al., 2004; Wanamaker et al., 2008, 2012; Mette et al., 2016; Marali et al., 2017).

To determine the trace element record of bivalve shells, a precise analytical technique is required that offers a high spatial (and hence, for the proxy, temporal) resolution such as laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS). This technique has been successfully applied to bivalve shells (e.g., Gillikin et al., 2006; Schöne et al., 2010; Holland et al., 2014a; Füllenbach et al., 2015) and various biominerals (e.g., Sinclair et al., 1998; Jochum et al., 2012; Wit et al., 2013; Montagna et al., 2014), speleothems (e.g., Treble et al., 2003; Desmarchelier et al., 2006; Jochum et al., 2012) and sediments (e.g., Baker et al., 1999; Hennekam et al., 2015). When operated in line scan mode, i.e., in a succession of overlapping LA spots generated by moving the sample under the laser beam at a constant

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