Publication I

Introduction for the wider audience

The significance of the long lived (> 400 years) bivalve *Arctica islandica* as a high-resolution bioarchive

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Abstract

Information about past environmental conditions is preserved in the elemental signature of biogenic marine carbonates. Thus, trace element to calcium ratios (Me/Ca) of biogenic calcium carbonates, such as bivalve shells, are often used to reconstruct past environmental conditions at the time of carbonate formation (Foster et al., 2008). In this study, we examine the suitability of the long-lived (> 400 years) bivalve *Arctica islandica* as a high-resolution bioarchive by measuring Me/Ca ratios in the shell carbonate. Pb/Ca concentrations in *A. islandica* shells reflect anthropogenic gasoline lead consumption and further provide a centennial record of lead pollution for the collection site off the coast of Virginia, USA. With *A. islandica* shells from the North Sea we test the hypothesis that Ba/Ca and Mn/Ca ratios are indicators of the diatom abundance. Our results indicate that statistically both ratios correlate well with the diatom abundance, and yet, on a year-to-year base, there is no consistent reflection of diatom abundance patterns in the Ba/Ca and Mn/Ca annual profiles. These findings indicate that primary production affects Ba/Ca and Mn/Ca shell ratios, though we suggest that both elements are coupled to primary production through different processes and are affected by further, yet unknown processes.

Keywords: *Arctica islandica*, bivalve, bioarchive, biogenic carbonate, trace elements, lead, barium, manganese, gasoline lead pollution, ocean production

1. Introduction

"Bioarchives" are organisms that grow permanent hard body parts by periodic accretion of biogenic material. These hard parts, e.g., bivalve shells, record the ambient environmental conditions throughout the organism's life-span. In the terrestrial system trees (dendrochronology) and in the marine environment calcium carbonate parts of corals, bivalves, and finfish are used as such archives (sclerochronology). This section focuses on the long-lived (> 400 years) bivalve *Arctica islandica* as a high-resolution bioarchive. In several studies we analyze the biogeochemistry in terms of trace element to calcium ratios (Me/Ca) of *A. islandica* shells to reconstruct environmental parameters of the marine ecosystem over time scales of decades to centuries (Figure 1).

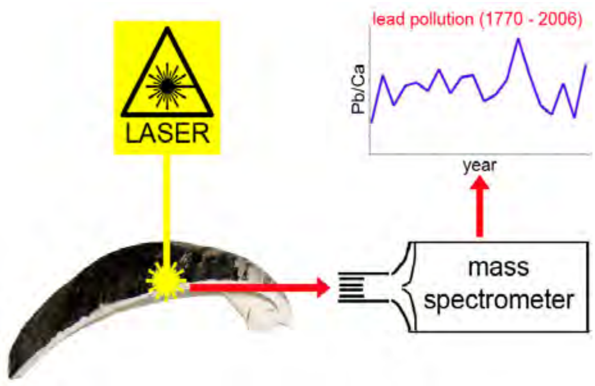

Figure 1 Schematic illustration of the technique to analyze trace elements in bivalve shells. A laser is used to ablate sample material at specific locations within the shell (here: *Arctica islandica*). Next, the ablated material is transported into a mass spectrometer for trace element analyses. Finally, trace element to calcium (here: Pb/Ca) ratios are plotted against time (here: time period between 1770 and 2006).

Sample treatment prior to Me/Ca analysis often includes chemical removal of organic matter from the biogenic calcium carbonate (Gaffey and Bronnimann, 1993). The efficiency of this approach, however, remains questionable and chemical treatment itself may alter the outcome of subsequent Me/Ca analysis (Love and Woronow, 1991). Thus, we first examine the efficiency of eight chemical treatments and their impact on the carbonate composition (for further details see Krause-Nehring et al. (2011)) (Effect of sample preparation).

Next, we aim at reconstructing environmental history by measuring trace elements along the growth trajectory of *A. islandica* shells. We determine Pb/Ca ratios in an *A. islandica* shell to examine influxes of lead into the seawater and to establish a centennial record of anthropogenic lead pollution at the collection site off the coast of Virginia, USA (Krause-Nehring et al., accepted) (Lead as a pollution tracer). In addition, we measure Ba/Ca and Mn/Ca ratios in three *A. islandica* shells collected off the island of Helgoland and correlate our results with the diatom abundance in the North Sea to evaluate both ratios as potential indicators of ocean primary production (Krause-Nehring et al., submitted) (Barium and manganese as indicators of primary production).

2. Methods

2.1. Effect of sample preparation

To examine the efficiency and side effects of eight chemical treatments, we conducted a systematic study on inorganic calcium carbonate and *A. islandica* shell powder. We combined different analytical techniques, such as

(I) inductively coupled plasma mass spectrometry (ICP-MS),
(II) nitrogen (N) analyses, and
(III) X-ray diffractometry (XRD) to analyze the impact of each treatment on
(I) Me/Ca ratios,
(II) organic matter content (using N as a proxy), and
(III) the composition of the carbonate and of newly formed phases (Figure 2).

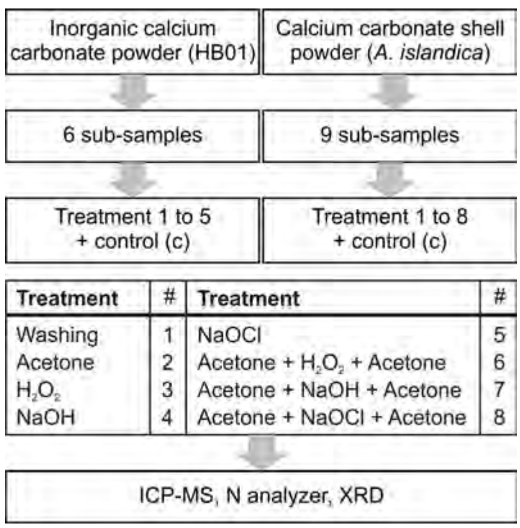

Figure 2 Preparation, treatment (control "c"; treatment 1 to 8), and subsequent analyses (ICP-MS, N analyzer, XRD) of inorganic (HB01) and organic (*Arctica islandica*) calcium carbonate powder samples.

2.2. Lead, barium, and manganese measurements

Prior to Me/Ca analyses, we embedded each shell in epoxy resin and cut a narrow section along the (red) line of strongest growth (Figure 3A). Next, we ground the section with sandpaper until the annual growth lines were clearly visible (Figure 3B). Finally, we used a laser ablation system connected to an inductively coupled plasma mass spectrometer (LA-ICP-MS) for element analyses (Pb/Ca, Ba/Ca, Mn/Ca) of the shell carbonate (Figure 3C). In the end, we either assigned each laser spot a specific year using the growth lines as year markers (inter-annual Pb/Ca variations) or converted the location of each laser spot between two adjacent growth lines into a point in time during the year (Ba/Ca and Mn/Ca intra-annual variations).

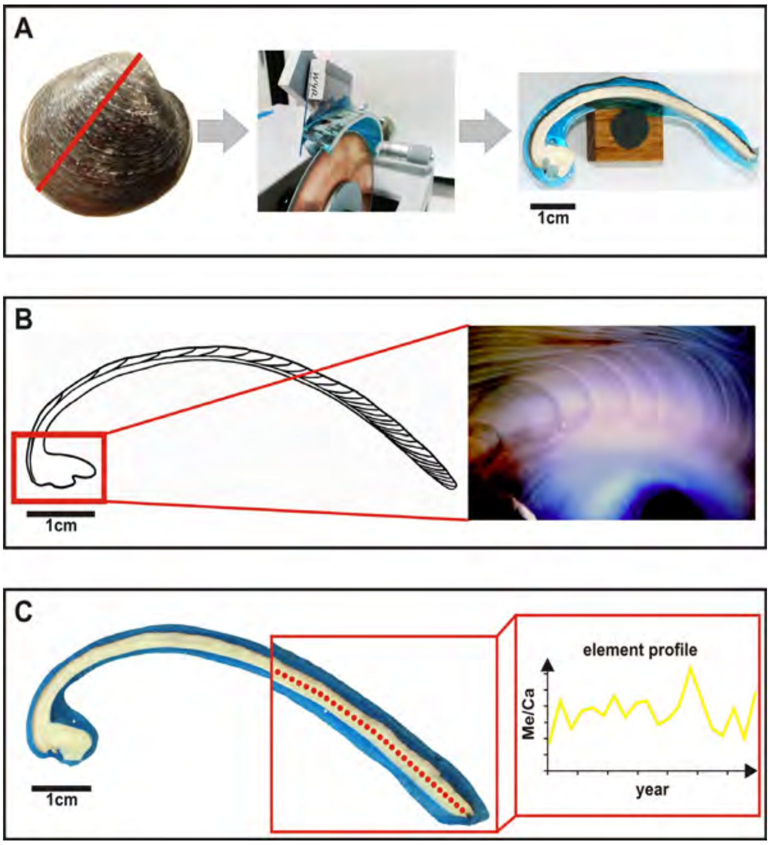

Figure 3 (A and B) Preparation of an *Arctica islandica* shell for subsequent element analyses of the shell carbonate (C) using a laser ablation-inductively coupled plasma-mass spectrometer (LA-ICP-MS). The red line in (A) indicates the line of strongest growth.

3. Results and discussion

3.1. Effect of sample preparation

Our results indicate that the different treatments

(I) alter the Me/Ca ratios (Figure 4),

(II) vary in their ability to remove organic matter (with NaOCl being the most efficient), and

(III) can alter the phase composition of the sample (e.g., $Ca(OH)_2$ formation during treatment 4).

Thus, chemical removal of organic matter prior to Me/Ca analyses has to be applied with extreme caution (for further details see Krause-Nehring et al. (2011)).

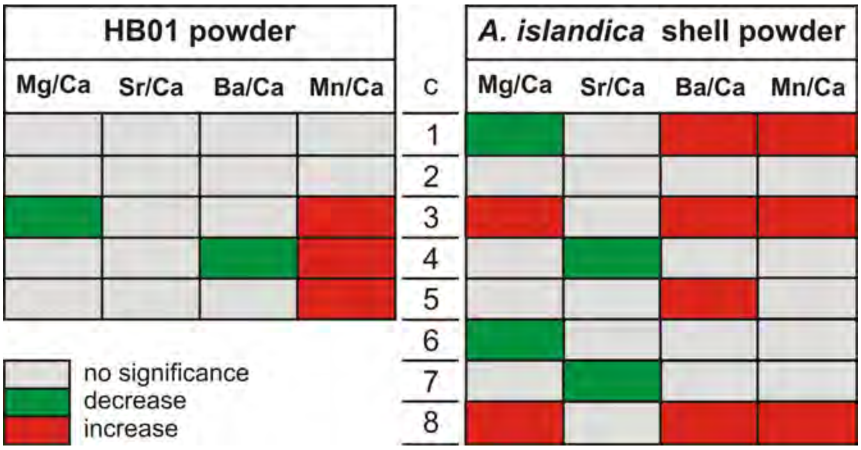

Figure 4 Effects of treatments (control "c"; treatments 1 to 8) on the Me/Ca ratios of the (left) HB01 and of the (right) *Arctica islandica* shell powder samples. (grey: no significant difference between the treated sample and the control, red: significant increase, green: significant decrease).

3.2. Lead as a pollution tracer

Our results indicate that the lead profiles we obtain from *A. islandica* shells reflect local influxes of lead into the seawater. The Pb/Ca profile we measure between 1770 and 2006 in an *A. islandica* shell collected off the coast of Virginia, USA, is clearly driven by anthropogenic lead emissions due to gasoline lead combustion which are transported eastwards from the North American continent to the Atlantic Ocean by westerly surface winds (Figure 5). Depending on the prevalent sources of lead at certain locations, the lead profiles of *A. islandica* shells may as well be driven by random natural influxes of lead into the water or various other sources of lead (e.g., dumping of sewage sludge or munitions; see Krause-Nehring et al., accepted). Our findings support the applicability of Pb/Ca analyses in *A. islandica* shells to reconstruct anthropogenic lead pollution at specific locations. In addition, we provide a centennial record of lead pollution for the collection site off the coast of Virginia, USA. For comparison of *A. islandica* lead profiles from different boreal sites (Iceland, USA, and Europe) see Krause-Nehring et al. (accepted).

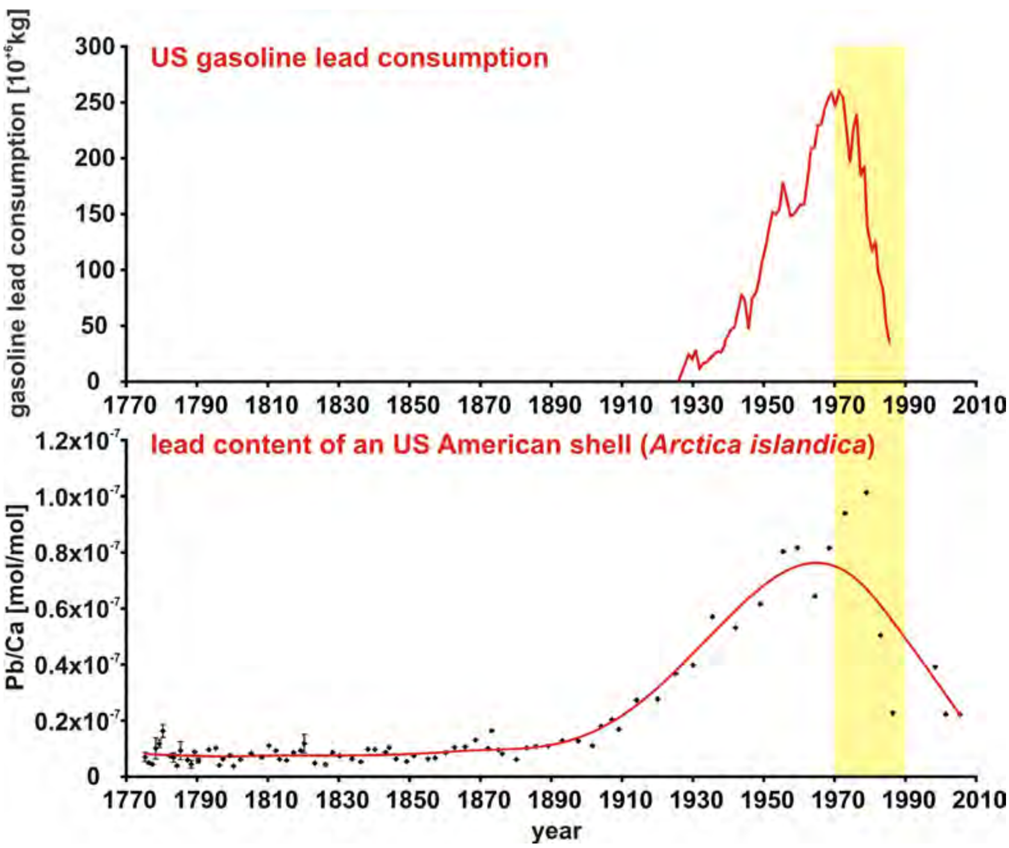

Figure 5 Top graph: US gasoline lead consumption (in 10^{+6} kg) (modified after Nriagu (1990)). Bottom graph: Pb/Ca profile (in mol/mol) between 1770 and 2010 determined in an *Arctica islandica* shell collected off the coast of Virginia, USA, with the black dots indicating the annual Pb/Ca ratios (± 1 standard error for years with > 1 sample spot) and the red line being a cubic spline trendline (λ = 8000). The yellow bar indicates the time of maximum gasoline lead emissions (1980 ± 10 years).

3.3. Barium and manganese as indicators of primary production

Over several decades, we find a significant correlation between the Mn/Ca and Ba/Ca ratios of three *A. islandica* specimens collected off the island of Helgoland and the diatom abundance in the North Sea (Krause–Nehring et al., submitted).

Nevertheless, the annual Ba/Ca (summer peak) and Mn/Ca profile (spring and summer peak) do not resemble the annual diatom profile (spring and summer peak) in a consistent manner (Figure 6). Thus, we conclude that primary production does affect Ba/Ca and Mn/Ca shell ratios, though we suggest that both elements are coupled to primary production through different processes. We suggest that peak concentrations of barium in bivalve shells result from sudden fluxes of barite to the sediment water interface as a consequence of phytoplankton blooms (Stecher et al., 1996), and that this mechanism involves an extended time delay between diatom blooms and Ba/Ca peaks in *A. islandica* shells, as observed in our study (Figure 6: ~ 3.5 months time lag between the spring bloom and subsequent Ba/Ca summer peak). The second diatom bloom in summer would cause another increase in barite in winter which coincides with the winter growth inhibition (mid-December to mid-February) (Schöne et al., 2005) of *A. islandica*, and is thus, not recorded by the shell. Mn/Ca ratios, on the other hand, seem to be coupled to diatom abundance both through direct influx of manganese to the sediment water interface or through remobilization of manganese from sediments during post-bloom reductive conditions, and thus, instantly record any phytoplankton debris reaching the ocean floor (Krause-Nehring et al., submitted).

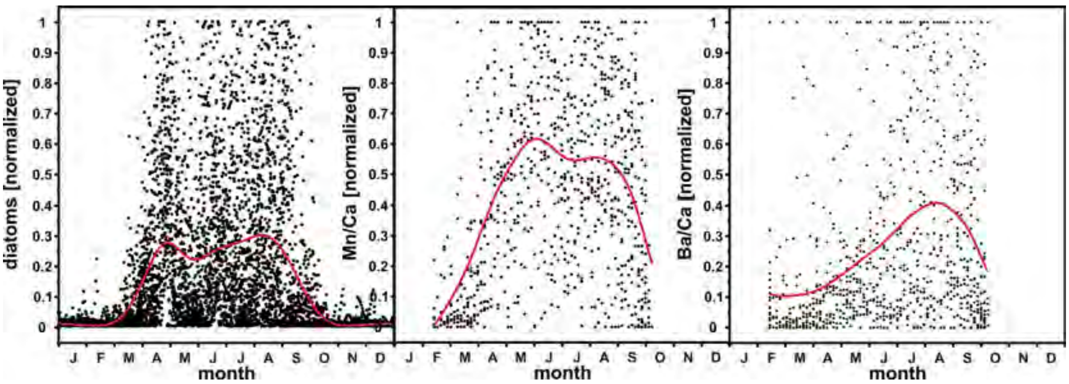

Figure 6 Left: Typical annual profile of the diatom abundance measured off the coast of Helgoland as part of the Helgoland Roads time series (Wiltshire and Dürselen, 2004). All data points are plotted over the course of one calendar year (J = January to D = December) after filtering (removal of the upper 5% and lower 10% of the data) and normalization (minimum = 0; maximum = 1) of the data. Superimposed is the corresponding cubic spline trendline (λ = 0.025). Centre and right: Typical annual (centre) Mn/Ca and (right) Ba/Ca profile obtained from three *Arctica islandica* shells collected off the coast of Helgoland. All data points are plotted over the course of one calendar year (J = January to D = December) after detrending (removal of linear trends, where necessary), filtering (removal of the upper 5% and lower 10% of the data), and normalization (minimum = 0; maximum = 1) of the data. Superimposed are the corresponding cubic spline trendlines (λ = 0.0045).

4. Conclusion

Since environmental data is often limited in time and space, bioarchives provide valuable information to reconstruct past environmental conditions. The bivalve *A. islandica* is an important bioarchive due to its longevity, wide distribution, and long-term occurrence throughout earth history. Our results demonstrate that both long-term and high-resolution records of environmental history can be extracted from *A. islandica* shells. They further illustrate, however, that it is crucial to understand the mechanistic links between bivalve shell chemistry and environmental parameters in order to extract valuable information from bivalve shells. Future studies on the biogeochemistry and growth morphology of *A. islandica* shells will facilitate our understanding of environmental processes within the field of earth system science.

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