

# Assessment of the mechanism of elemental incorporation into bivalve shells (*Arctica islandica*) based on elemental distribution at the microstructural scale

Kotaro Shirai<sup>a,b,\*</sup>, Bernd R. Schöne<sup>a</sup>, Tsuzumi Miyaji<sup>b,1</sup>, Pascal Radarmacher<sup>a</sup>, Richard A. Krause Jr.<sup>a</sup>, Kazushige Tanabe<sup>b,2</sup>

<sup>a</sup> Institute of Geosciences, Earth System Science Research Center, University of Mainz, Johann-Joachim-Becherweg 21, 55128 Mainz, Germany

<sup>b</sup> Department of Earth and Planetary Science, University of Tokyo, 7-3-1 Hongo, Tokyo 113-0033, Japan

Received 8 February 2013; accepted in revised form 30 October 2013; Available online 12 November 2013

## Abstract

To address the mechanism of elemental incorporation into shells of the bivalve *Arctica islandica*, we performed two-dimensional elemental mapping of Sr, Mg, and S at a  $\sim 3 \mu\text{m}$  spatial resolution using electron microprobe. These elemental distributions were precisely compared to the shell microstructure. The Sr distribution was intimately linked to the S concentration and/or shell microstructure. Sr showed a clear annual pattern with higher values at the annual growth lines and lower values in annual growth increments. The Sr and S concentrations were higher near sub-annual growth lines than in the adjacent regions, which were dominated by acicular microstructure (middle shell layer) or homogeneous microstructure (outer shell layer). Furthermore, the Sr concentration was lower in the middle shell layer than in the outer shell layer, but there was no clear difference in the S concentration between the two layers. The observed elemental distribution in the shell can be reasonably explained by the hypothesis that the organic composition at the calcification site, i.e. in the extrapallial space, can facilitate the preferential elemental incorporation into calcium carbonate. The Sr/Ca ratio shows micrometer scale variation within the shell, suggesting that fine spatial resolution, comparable to the shell microstructure, is required for the analysis of elemental distribution to avoid time-averaging and to correctly evaluate the magnitude of the compositional variation in the shell for past environmental reconstruction.

© 2013 Elsevier Ltd. All rights reserved.

## 1. INTRODUCTION

Bivalve shells are useful for reconstructing past environments because of their broad biogeographic distribution and rich fossil record. The  $\delta^{18}\text{O}$  values of bivalve shells

provide a reliable proxy for temperature and/or  $\delta^{18}\text{O}$  of the ambient water, because the calcium carbonate of both calcitic and aragonitic shells is precipitated near isotopic equilibrium with the ambient environment (e.g. Epstein et al., 1953; Grossman and Ku, 1986). Thus, the  $\delta^{18}\text{O}$  values of bivalve shells have been used in a number of studies for the reconstruction of past water temperature (e.g. Schöne et al., 2004, 2005a; Watanabe et al., 2004; Steuber et al., 2005; Wanamaker et al., 2012). However, distinguishing the salinity signal from the temperature signal obtained from oxygen isotopic ratios of biogenic carbonates can be challenging (e.g. Gillikin et al., 2005a).

Sr/Ca and Mg/Ca ratios of bivalve shells have been explored as potential alternative temperature proxies. Both ratios are much less affected by salinity changes and

\* Corresponding author. Present address: International Coastal Research Center, Atmosphere and Ocean Research Institute, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8564, Japan. Tel./fax: +81 4 7136 6067.

E-mail address: [kshirai@aori.u-tokyo.ac.jp](mailto:kshirai@aori.u-tokyo.ac.jp) (K. Shirai).

<sup>1</sup> Present address: Tomakomai City Museum, Suchiro 3-9-7, Tomakomai, Hokkaido 053-0011, Japan.

<sup>2</sup> Present address: Department of Historical Geology & Paleontology, The University Museum, The University of Tokyo, Hongo 7-3-1, Tokyo 113-0033, Japan.