Palaeogeography, Palaeoclimatology, Palaeoecology 373 (2013) 50–59

Contents lists available at SciVerse ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

Crystal fabrics and element impurities (Sr/Ca, Mg/Ca, and Ba/Ca) in shells of *Arctica islandica*—Implications for paleoclimate reconstructions

Bernd R. Schöne [a,*], Pascal Radermacher [a], Zengjie Zhang [b], Dorrit E. Jacob [a]

[a] 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
[b] Institute of Mineral Resources, Chinese Academy of Geological Sciences, Baiwanzhuang Road 26, Beijing 100037, China

ARTICLE INFO

Article history:
Received 28 February 2011
Received in revised form 20 April 2011
Accepted 6 May 2011
Available online 15 May 2011

Keywords:
Element-to-calcium ratio
Bivalve shell
Crystal fabrics
Biomineralization
Climate proxy

ABSTRACT

Sr/Ca, Mg/Ca and Ba/Ca values are heterogeneously distributed in shells of *Arctica islandica*. These patterns are largely associated with crystal fabrics (size, habit and orientation of crystals) or the processes controlling them. The outer sublayer of the outer shell layer (oOSL; homogenous and irregular simple prismatic crystal fabrics,) contained element/Ca values up to 62% higher than the inner sublayer (iOSL; crossed-acicular, crossed-lamellar, fine crossed-lamellar and irregular simple prismatic crystal fabrics). A gradual decrease in Sr/Ca and Mg/Ca values was observed from the outer portions of the oOSL toward the oOSL/iOSL transition zone. This chemical shift was accompanied by a gradual transition from homogenous crystal fabrics into crossed-lamellar/acicular crystal fabrics. Near annual growth lines (irregular simple prisms), i.e., during periods of slow growth, Sr and Mg seemed to be deposited in equilibrium with the ambient environment because the Sr/Ca and Mg/Ca values approached values typical for seawater. During the remainder of the growing season, Sr/Ca and Mg/Ca remained far below values expected for thermodynamic equilibrium. Ba/Ca peaks, however, occurred erratically at different times of the year without any noticeable changes in crystal fabrics. Likely, the environmental information contained in these peaks was less severely filtered by vital effects than in Sr and Mg. The findings of the present study can help to develop new techniques with which extract environmental signals from the metal-to-calcium ratios of bivalve shells.

1. Introduction

Element-to-calcium ratios of biogenic aragonite can be used to reconstruct past environmental conditions. This has been demonstrated for several trace and minor elements including strontium (Sr), magnesium (Mg) and barium (Ba). Water temperatures have been inferred from Sr/Ca and Mg/Ca ratios of a large number of taxonomic groups such as brachiopods (Lowenstam, 1961; Mii and Grossman, 1994; Powell et al., 2009), corals (Weber, 1973; Smith et al., 1979; Beck et al., 1992), sclerosponges (Rosenheim et al., 2004), ostracods (Corrége, 1993) and foraminifera (Nürnberg et al., 1996). In many organisms, the empirical relationship between temperature and Sr/Ca or Mg/Ca ratios is in close agreement with the results obtained by inorganic precipitation experiments (Kinsman and Holland, 1969; Gaetani and Cohen, 2006). With increasing temperature, fewer strontium and magnesium ions substitute calcium in the crystal lattice. The Ba/Ca ratios of many biogenic carbonates, however, closely reflect past variations of seawater Ba/Ca. This ratio has therefore been used to reconstruct upwelling events or variable influxes of terrigenous sediments into coastal areas from corals (Alibert et al., 2003; Montaggioni et al., 2006; Lewis et al., 2007), coccoliths (Langer et al., 2009), foraminifera (Lea et al., 1989; Lea and Boyle, 1990) etc. Likewise, Ba/Ca values of bivalve shells provide useful environmental records (Lazareth et al., 2003; Thébault et al., 2009; but see Gillikin et al., 2008). For example, Stecher et al. (1996) used Ba/Ca values of *Mercenaria* sp. and *Spisula* sp. as a proxy for productivity, and Torres et al. (2001) reconstructed the fluid flow at cold seeps from Ba/Ca profiles of *Calyptogena kilmeri*.

However, Sr/Ca and Mg/Ca variations in shells of bivalve mollusks are far more difficult to interpret. In most species, both ratios remain far below that of the ambient environment suggesting non-equilibrium fractionation and an active control by the animal ("vital effects" sensu Urey et al., 1951) of how many trace and minor element impurities are incorporated into the shells. For example, in specimens of the ocean quahog, *Arctica islandica*, from the Northeast Atlantic, shell Sr/Ca values range between ca. 1 and 5 mmol/mol (e.g., Foster et al., 2009; Schöne et al., 2010, 2011), whereas the value of average seawater is up to ca. nine times as high (8.9 mmol/mol; Elderfield, 2006). Mg/Ca values fluctuated between ca. 0.2 and 1 mmol/mol in this species (Schöne et al., 2010, 2011) and were therefore up to ca. 26 times lower than expected for thermodynamic equilibrium deposition with seawater (5.2 mmol/mol; Elderfield, 2006). Furthermore, the

* Corresponding author.
E-mail address: schoeneb@uni-mainz.de (B.R. Schöne).

0031-0182/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.palaeo.2011.05.013