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Trace and minor element records in aragonitic bivalve shells as environmental proxies

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ABSTRACT

Investigation of the geochemical composition of bivalve shells can provide information on changes in the marine environment occurring during the lifespan of an organism. Three species, locally abundant in the Adriatic Sea, were chosen in this study, namely *Glycymeris pilosa*, *Callista chione*, and *Venus verrucosa*. Of these, *G. pilosa* has the longest lifespan, exceeding 50 years, and therefore presents a potential archive of decadal climate variability. The other two species, *C. chione* and *V. verrucosa*, are commercially important. Samples were collected alive by SCUBA diving in the North Adriatic Sea, near Barbariga, Istria. Major growth increments in these shells form on an annual basis and are clearly visible in shell cross-sections enabling correct temporal positioning of geochemical data obtained from different shell parts. In this study, we applied laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS) in line scan mode to determine the trace and minor element composition along the major growth axis in the hinge area of the shells. Objectives of this study were to compare signals within and between species, and to relate results to available environmental parameters. High resolution time-series of Na/Ca_{shell}, Mg/Ca_{shell} and Sr/Ca_{shell} display characteristic cyclic variations. Na/Ca_{shell} minima and Mg/Ca_{shell} and Sr/Ca_{shell} maxima occur near shell annual growth lines in all three studied species. Results indicate that seawater temperature is not a main driver for incorporation of these elements. Ba/Ca_{shell} data vary between years and species and have noncyclic sharp peaks. *Callista chione* and *V. verrucosa* specimens show higher peaks and background Ba/Ca_{shell} values than *G. pilosa*. Most pronounced peaks in Ba/Ca_{shell} occurred at the beginning of the growing season corresponding to the end of year 2011 and beginning of year 2012 and coincided with unusual dense water formation and subsequent changes in the plankton communities in the Adriatic Sea. Implications of our study suggest that synchronous peaks in studied specimens are caused by external forcing which could occur on larger, regional scales, encouraging future studies covering wider area in the Adriatic Sea and other parts of the Mediterranean.

1. Introduction

Bivalve shells contain growth patterns reflected as growth lines and increments on the outer shell surface and in cross-sections (Richardson, 2001). These growth patterns are deposited periodically and enable to assign calendar years to each shell portion. Furthermore, the geochemical properties of the shells provide a potential archive of climate variability covering years, decades and even centuries (e.g., Schöne et al., 2011; Füllenbach et al., 2015; Reynolds et al., 2016; Marali et al., 2017a). High spatial and temporal resolution trace and minor element records can be obtained through laser ablation - inductively coupled

plasma - mass spectrometry (LA-ICP-MS). Over the last years, this approach has been applied to different bivalve species from tropical (Thébault et al., 2009a) to polar regions (Vihtakari et al., 2017). Examples of target species include long-lived ocean quahog, *Arctica islandica* (e.g., Foster et al., 2009; Thébault et al., 2009b; Schöne et al., 2010, 2011; Marali et al., 2017a, 2017b; Wanamaker and Gillikin, 2018), the commercially important great scallop, *Pecten maximus* (e.g., Lorrain et al., 2005; Gillikin et al., 2008; Barats et al., 2009, 2010; Tabouret et al., 2012; Thébault and Chauvaud, 2013), the common cockle, *Cerastoderma edule* (e.g., Füllenbach et al., 2015, 2017; Ricardo et al., 2015), and giant bivalve shell *Tridacna gigas* (e.g., Elliot et al.,

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