Available online at www.sciencedirect.com
ScienceDirect
Geochimica et Cosmochimica Acta 308 (2021) 326–352
Geochimica et Cosmochimica Acta
www.elsevier.com/locate/gca

Multi-isotopic and trace element evidence against different formation pathways for oyster microstructures

Niels J. de Winter [a,b,*], Linda K. Dämmer [c,d], Michaela Falkenroth [c,d,e], Gert-Jan Reichart [a,c], Simone Moretti [f], Alfredo Martínez-García [f], Nils Höche [g], Bernd R. Schöne [g], Katerina Rodiouchkina [h], Steven Goderis [b], Frank Vanhaecke [h], Sonja M. van Leeuwen [i], Martin Ziegler [a]

[a] *Dept. of Earth Sciences, Utrecht University, Utrecht, the Netherlands*
[b] *AMGC Research Group, Vrije Universiteit Brussel, Brussels, Belgium*
[c] *Ocean Systems Department, Royal Netherlands Institute for Sea Research, Texel, the Netherlands*
[d] *Environmental Geology, Department of Geology, Institute of Geosciences, University of Bonn, Bonn, Germany*
[e] *Neotectonics and Natural Hazards Research Group, Rheinisch-Westfälische Technische Hochschule Aachen, Aachen, Germany*
[f] *Max Planck Institute for Chemistry, Otto Hahn Institute, Mainz, Germany*
[g] *Institute of Geosciences, University of Mainz, Mainz, Germany*
[h] *Atomic and Mass Spectrometry - A&MS Research Group, Department of Chemistry, Ghent University, Ghent, Belgium*
[i] *Coastal Systems Department, Royal Netherlands Institute for Sea Research, Texel, the Netherlands*

Received 10 August 2020; accepted in revised form 7 June 2021; Available online 15 June 2021

Abstract

Shells of oysters (Ostreidae) are predominantly composed of foliated and chalky calcite microstructures. The formation process of the more porous chalky structure is subject to debate, with some studies suggesting that it is not formed directly by the oyster but rather through microbial mineralization within the shell. Here, this hypothesis is tested in modern shells of the Pacific oyster (*Crassostrea gigas*) from coastal regions in France and the Netherlands. We combine measurements of stable carbon, oxygen, nitrogen, sulfur, and clumped isotope ratios with high-resolution spatially resolved element (Na, Mg, Cl, S, Mn and Sr) data and microscopic observations of chalky and foliated microstructures in the oyster shells. Our results show no isotopic differences between the different microstructures, arguing against formation of the chalky calcite by microorganisms. However, we observe a small difference in the oxygen isotope ratio (0.32‰) and clumped isotope composition (0.017‰) between the microstructures, which is likely caused by sampling biases due to seasonal differences in growth rate and the short timespan over which the chalky microstructure forms. We therefore recommend sampling profiles through the foliated microstructure to control for strong seasonal variability recorded in the shell which can bias environmental reconstructions. High-resolution (25–50 μm) Na, Mg, Cl, S, Mn and Sr profiles yield empirical distribution coefficients between seawater and shell calcite for these elements. Significant differences in element concentrations and distribution coefficients were confirmed between the two microstructures, likely reflecting differences in mineralization rates or inclusion of non-lattice-bound elements. Only Mg/Ca ratios in the foliated microstructure vary predictably with growth seasonality, and we show that these can be used to establish accurate oyster shell chronologies. The observed effect of mineralization rate on element incorporation into oyster shells should be considered while developing potential element proxies for paleoclimate reconstructions. Trace element proxies in oyster shells should be interpreted with caution, especially when element chemical properties were measured in different microstructures.

* Corresponding author at: Dept. of Earth Sciences, Utrecht University, Utrecht, the Netherlands.
E-mail addresses: nidewint@vub.be, n.j.dewinter@uu.nl (N.J. de Winter).

https://doi.org/10.1016/j.gca.2021.06.012
0016-7037/