



Modification of Ca isotope and trace metal composition of the major matrices involved in shell formation of *Mytilus edulis*

Agnes Heinemann, Jan Fietzke, Anton Eisenhauer, and Karsten Zumholz

*Leibniz-Institute for Marine Sciences (IFM-GEOMAR), Wischhofstrasse 1-3, D-24148 Kiel, Germany
(abeinemann@ifm-geomar.de)*

[1] In this study we present the first combined investigation into the composition of the major matrices involved in calcification processes (surrounding water, extrapallial fluid, aragonite, and calcite) of *Mytilus edulis* with respect to their calcium isotope ($\delta^{44/40}\text{Ca}$) and elemental compositions (Sr/Ca and Mg/Ca). Our aim was to examine the suitability of *Mytilus edulis* as a proxy archive and to contribute to the understanding of the process of biomineralization. *Mytilus edulis* specimens were live collected from the Schwentine Estuary, Kiel Fjord, and North Sea (Sylt). $\delta^{44/40}\text{Ca}$ was determined by thermal ionization mass spectrometry (TIMS) accompanied by measurements of Mg/Ca and Sr/Ca using inductively coupled plasma–optical emission spectroscopy (ICP-OES). The elemental and isotopic compositions of the investigated matrices showed systematic offsets. The carbonates are strongly depleted in their magnesium and strontium concentrations and fractionated toward lighter calcium isotope compositions relative to the surrounding Schwentine Estuary water. The opposite is observed for the extrapallial fluid (EPF). Our findings extend the results of previous studies reporting a strong biological control and the interaction of different environmental conditions influencing biomineralization. Future studies should focus on the temporal development of the interrelation between the different matrices.

Components: 4025 words, 4 figures, 2 tables.

Keywords: calcium isotopes; trace elements; *Mytilus edulis*; proxy; biomineralization.

Index Terms: 0419 Biogeosciences: Biomineralization; 0424 Biogeosciences: Biosignatures and proxies; 0454 Biogeosciences: Isotopic composition and chemistry (1041, 4870).

Received 3 August 2007; **Revised** 19 August 2007; **Accepted** 19 November 2007; **Published** 26 January 2008.

Heinemann, A., J. Fietzke, A. Eisenhauer, and K. Zumholz (2008), Modification of Ca isotope and trace metal composition of the major matrices involved in shell formation of *Mytilus edulis*, *Geochem. Geophys. Geosyst.*, 9, Q01006, doi:10.1029/2007GC001777.

1. Introduction

[2] Different environmental parameters like temperature and salinity are reported to have significant impacts on the composition of the shells of calcifying marine organisms [Henderson, 2002]. The degree of these impacts can be investigated by

established proxies. Proxies such as elemental ratios or stable isotopes [e.g., Beck *et al.*, 1992; Nürnberg *et al.*, 1996; Epstein *et al.*, 1953] are used in geochemistry to reconstruct (paleo)environmental conditions and thus serve to construct and improve models of the recent and past climate.

[3] Bivalves have the potential to provide high-resolution records of a large variety of environments because of their high longitudinal growth rate, a wide geographic distribution [Gossling, 1992], and tolerance to a broad range of environmental conditions [Seed and Suchanek, 1992].

[4] A problem of the use of mussels as a proxy archive consists in the strong biological control and the complexity of the calcification process. The environmental control on minor and trace elements in molluscs seems often too weak to develop suitable proxies. Even the mechanisms controlling the trace element incorporation in mollusc shells remain largely unknown [Carré *et al.*, 2006].

[5] In molluscs, shell material is precipitated from the extrapallial fluid which is physically separated from the external solution by the old shell, the mantle membrane and the periostracum [Wilbur, 1972]. Wilbur [1972] indicates that the mantle mediates the transfer of ions from the seawater to the extrapallial fluid.

[6] Different internal and external parameters (chemical, physical and physiological) are influencing the exchange between the extrapallial fluid (EPF) and surrounding seawater.

[7] Lorens and Bender [1980] found that when Mg content of seawater solution with varying Na/Ca, Sr/Ca and Mg/Ca ratios is raised above the normal Mg content of seawater, the biological Mg exclusion mechanism becomes saturated, and is no longer able to effectively control EPF Mg concentrations.

[8] Crenshaw [1972] showed that the pH of the EPF of a mollusc decreased when the animal closed its valves and rose again when the valves were opened. The calcium concentration also changed with the opening and closing of the valves. It decreased with increasing pH while the valves were open and rose with decreasing pH when the valves were closed.

[9] During precipitation different proteins are involved in the biological control which was found in the EPF [Kobayashi, 1964; Misogianes and Chasteen, 1979]. Misogianes and Chasteen [1979] determined that almost 85% of the calcium in native fluid is bound to other molecules compared to seawater, where less than 10% is complexed. They suggested that CaCO₃ deposition may be controlled by complexation of Ca²⁺ by small chelates produced by the animal.

[10] Our aim was to examine the suitability of *Mytilus edulis* as a proxy archive. For this purpose we present the first investigation into the composition of the major matrices involved in calcification process (surrounding water, extrapallial fluid, aragonite and calcite) with respect to their Ca isotope and elemental compositions in *Mytilus edulis* specimen.

2. Materials and Methods

2.1. Samples

[11] A number of blue mussels were live collected from three different sites with different salinities around half a meter below water surface. Two specimens were collected from the Schwentine Estuary (brackish water) and one from the Kiel Fjord (brackish water) on 16 June 2006, five on 28 August 2006 from the Schwentine Estuary and one on 11 August 2006 from the beach of Sylt (seawater). An overview of all samples is given in Table 1. After collection some of the mussels (1a, 1c, 1d, 2a, and 3a) were frozen for three days at −20 °C, opened and the soft tissue removed. The shells were cleaned with water, dried at 60 °C and stored in plastic vials (100 ml, Nunc). For one of the mussels collected in the Schwentine Estuary (1a), another one collected in Kiel Fjord on 16 June (2a) and the one from Sylt beach (3a) the $\delta^{44/40}\text{Ca}$ was measured by thermal ionization mass spectrometry (TIMS) in the aragonite as well as in the calcite. In addition for a second specimen from the Schwentine Estuary Mg/Ca and Sr/Ca ratios were determined in the calcite with inductively coupled plasma–optical emission spectroscopy (ICP-OES).

[12] 50–100 μL extrapallial fluid (EPF) per individual was taken from the living animal before they were frozen using a sterile needle (diameter 0.9 mm). The unfiltered EPF was filled in pre-cleaned vials (4 ml) and stored in a fridge. Because of the extremely small amount of EPF the $\delta^{44/40}\text{Ca}$ determination by TIMS could be carried out just once for three individuals from 28 August 2006 (1e, f, g). For the elemental concentration measurements by ICP-OES, the small amount was sufficient, and thus samples could be processed individually (1c, d).

[13] Simultaneously, water samples were taken at all sites from the same positions where the mussels were collected and stored in a fridge in pre-cleaned

Table 1. All Samples^a

Site Reference/Sample	Site of Sampling	Date of Sampling	Kind of Sample	Method	Measured
1a	Schwentine Estuary	16.06.2006	aragonite	TIMS, ICP-OES	$\delta^{44/40}\text{Ca}$, Mg, Sr, Ca
1b			calcite	TIMS, ICP-OES	$\delta^{44/40}\text{Ca}$, Mg, Sr, Ca
1c	Kiel Fjord	28.08.2006	water	TIMS, ICP-OES	$\delta^{44/40}\text{Ca}$, Mg, Sr, Ca
1d			aragonite	ICP-OES	Mg, Sr, Ca
			calcite	ICP-OES	Mg, Sr, Ca
1e, f, g			EPF	ICP-OES	Mg, Sr, Ca
	aragonite	ICP-OES	Mg, Sr, Ca		
1h	Sylt, North Sea	11.08.2006	calcite	ICP-OES	Mg, Sr, Ca
			EPF	ICP-OES	Mg, Sr, Ca
2a	Kiel Fjord	16.06.2006	water	TIMS	$\delta^{44/40}\text{Ca}$
2b			aragonite	TIMS	$\delta^{44/40}\text{Ca}$
3a	Sylt, North Sea	11.08.2006	calcite	TIMS	$\delta^{44/40}\text{Ca}$
3b			aragonite	TIMS	$\delta^{44/40}\text{Ca}$
			water	TIMS	$\delta^{44/40}\text{Ca}$

^aEPF, extrapallial fluid.

closed vials (4 ml). $\delta^{44/40}\text{Ca}$, Mg/Ca and Sr/Ca ratios were determined.

2.2. Analytical Methods

[14] Prior to analysis the calcium carbonate from the two regions of the shell, the nacre (aragonite) and the prismatic (calcite) of the shell material was drilled using a dental drill. To confirm that there was no overlap between the materials the samples were analyzed by XRD. The obtained powder was transferred in pre-cleaned screw-top Savillex PFA vials.

[15] Ca isotopic compositions were analyzed by thermal ionization mass spectrometry (ThermoFinnigan Triton TI) in the laboratories of the Leibniz-Institute of Marine Sciences IFM-GEOMAR, Kiel using a routine method close to that described by Heuser *et al.* [2002]. The external reproducibility was typically better than 0.2‰.

[16] The data are normalized to IAPSO as a reference for seawater, measured within each analytical run. The Ca isotope data are presented in the notation suggested by Eisenhauer *et al.* [2004].

[17] The fluids were processed through a chemical separation in order to isolate Ca from potentially interfering elements such as K, Sr and Mg. A commonly used chromatographic clean-up for seawater, which is based on cation exchange and HCl elution, was applied [Amini, 2007].

[18] The elemental ratios were measured by ICP-OES (JY 170 ULTRACE (Jobin Yvon)) at IFM-GEOMAR in Kiel, Germany.

3. Results

[19] TIMS and ICP-OES results for the Ca isotopic composition of the samples investigated in this study are shown in Table 2.

[20] The carbonates are strongly depleted in their magnesium and strontium concentrations and fractionated toward lighter calcium isotope compositions relative to the surrounding Schwentine Estuary water. The opposite is observed for the EPF.

[21] The isotopic composition ($\delta^{44/40}\text{Ca}$) of the extrapallial fluid (samples 1c, d, e, f and g) correspond approximately to that of the seawater and not to the Schwentine water (samples 1b and 1h) even though the mussels came from the Schwentine Estuary. The $\delta^{44/40}\text{Ca}$ of the surrounding estuary water is 0.31‰ lower than that of the EPF. Paired analysis of calcite and aragonite showed a consistent offset, with aragonite featuring 0.15 to 0.31‰ lower $\delta^{44/40}\text{Ca}$ values. In general the two polymorphs of calcium carbonate of all analyzed shells differ by 0.84 to 1.32‰ from the isotopic composition of the seawater standard and hence from that of the sampled EPF. The aragonite and the calcite show only slight differences between the mussels from different sites. The heaviest $\delta^{44/40}\text{Ca}$ values for both aragonite and calcite

Table 2. Results for TIMS and ICP-OES Measurements^a

Site Reference/ Sample	Site of Sampling	Date of Sampling	Kind of Sample	$\delta^{44/40}\text{Ca} \pm 2\text{sem}$ (Number of Replicates)	Sr/Ca, mmol/mol, $\pm 2\text{sd}$	Mg/Ca, mmol/mol, $\pm 2\text{sd}$
1a	Schwentine Estuary	16.06.2006	aragonite	-1.33 ± 0.10 (15)	1.59 ± 0.05	9.05 ± 0.17
			calcite	-1.09 ± 0.08 (15)	1.64 ± 0.01	7.39 ± 0.27
1b			water	-0.32 ± 0.06 (8)	5.45 ± 0.05	2929 ± 25
1c		28.08.2006	aragonite		3.63 ± 0.09	9.54 ± 0.27
	calcite			1.56 ± 0.74	9.96 ± 1.10	
	EPF			7.59 ± 1.25	4465 ± 141	
1d	aragonite			1.66 ± 0.02	4.00 ± 0.25	
	calcite		1.55 ± 0.01	12.05 ± 0.08		
	EPF		7.79 ± 0.47	4935 ± 75		
1e, f, g			EPF	-0.01 ± 0.07 (3 but different individuals)		
1h			water		6.22 ± 0.02	3485 ± 22
2a	Kiel Fjord	16.06.2006	aragonite	-1.16 ± 0.08 (15)		
			calcite	-0.85 ± 0.06 (13)		
2b			water	-0.02 ± 0.10 (8)		
3a	Sylt, North Sea	11.08.2006	aragonite	-1.25 ± 0.15 (4)		
			calcite	-1.10 ± 0.11 (4)		
3b			water	-0.01 ± 0.07 (2)		
IAPSO				0.00 ± 0.06 (16)	8.45 ± 0.02	5077 ± 23

^aUncertainties quoted as external errors; sem, standard error of the mean; sd, standard deviation.

were found in the specimens taken from the Kiel Fjord.

[22] The elemental ratios of the calcite and aragonite samples (1a, c, and d) show considerably lower concentrations than found in either the water samples or the EPF (a factor of 4 to 7 for Sr/Ca and a factor of about 200 to 400 for Mg/Ca). There is less variability in Sr/Ca than in Mg/Ca. Furthermore the elemental ratios of the EPF are about a factor of 1.5 higher than in the surrounding water. Figures 1 and 2 summarize the elemental/Ca and the calcium-isotope ratios, respectively, for the four different matrices of the samples of the Schwentine Estuary.

4. Discussion

[23] The different areas of the mussel and the surrounding water from the Schwentine Estuary clearly show the varied composition of the different materials (shown in Figure 3). In comparison with the Schwentine water (the ambient water) all values show a considerable deviation of the EPF. Our data show that calcium in mussels from Schwentine Estuary becomes isotopically heavier in the EPF compared to the surrounding water and Sr as well as Mg is enriched. In the shell calcium is

isotopically lighter than in the EPF and even lighter than in the surrounding water. Sr and considerably Mg are also depleted in the shell in comparison with the water and the EPF. Our results agree with previous studies [Crenshaw, 1972; Wada and Fujinuki, 1976]. Similar observations were made for freshwater mussels [Wada and Fujinuki, 1976].

[24] The pronounced differences between the values of the Schwentine water and the EPF exclude a contamination of the fluid with the surrounding water during preparation.

[25] An evidence for a biological control mechanism is the high magnesium concentration in the EPF which would hinder the precipitation of calcite. Berner [1975] shows that the Mg/Ca ratios in modern seawater inhibit the inorganic formation of calcite. Magnesium appears to be extensively regulated by *Mytilus edulis* so as to minimize the Mg concentration of the extrapallial fluid [Lorens and Bender, 1980].

[26] Because of our findings we assume the EPF to be modified while the shell is precipitated. The calcium is attached in the shell and in the EPF the other elements become relatively enriched (see Figure 1). These elements must be actively removed from the EPF; otherwise the high concen-

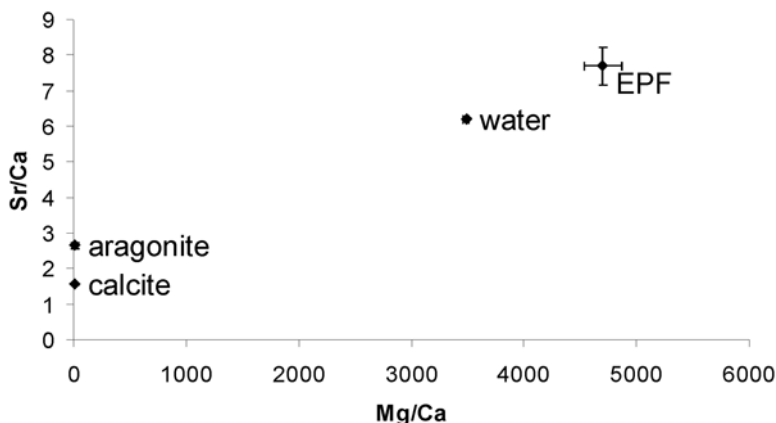


Figure 1. The Sr/Ca ratio of water from the Schwentine Estuary, together with EPF and shell (both aragonite and calcite) taken from the same location relative to the Mg/Ca ratio. Errors are given as 2sd (standard deviation; $n = 3$).

trations would not permit a further calcite precipitation. Because of energy consumption of such an active mechanism the exclusion of Mg eventually does not exceed a physiologically necessary value and Mg concentration is just kept below a certain level (perhaps the open ocean Mg/Ca as suggested by our EPF data).

[27] This may also account for the different isotopic Ca compositions in water, EPF and shell (see Figure 2).

[28] Previous studies stated that calcium becomes isotopically lighter as it moves through the food chain [Skulan *et al.*, 1997; Zhu and Macdougall, 1998; DePaolo, 2004]. Our data indicate that the calcium becomes isotopically heavier as it is transported through the mantle (surrounding water →

EPF). During the following precipitation step the lighter Ca isotopes are preferentially incorporated into the shell. Because of this mechanism, that is also described for Mg/Ca, the heavier isotopes are enriched in the EPF. It is shown by several studies that heavier Ca isotopes are depleted in the solid phase relative to the fluid [e.g., Skulan *et al.*, 1997; Zhu and Macdougall, 1998; DePaolo, 2004].

[29] For inorganically precipitated calcium carbonate, there is an offset between aragonite and calcite of about 0.9‰ for $\delta^{44/40}\text{Ca}$ [Gussone *et al.*, 2005]. On skeletal aragonite and calcite from different marine biota they also found an offset in $\delta^{44/40}\text{Ca}$ of about 0.6‰. In our study a much lower offset of 0.15 to 0.31‰ between the aragonite and the calcite of *Mytilus edulis* was found. It could be that the precipitation of aragonite and calcite influ-

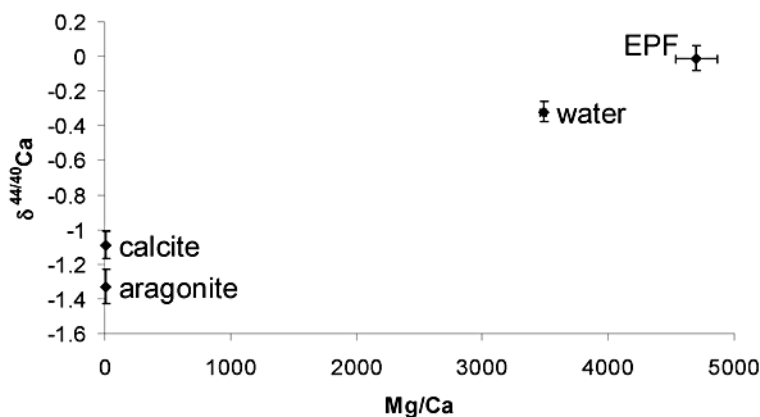


Figure 2. The $\delta^{44/40}\text{Ca}$ composition of water from the Schwentine Estuary, together with EPF and shell (both aragonite and calcite) taken from the same location relative to the Mg/Ca ratio. The $\delta^{44/40}\text{Ca}$ error is given as 2sem (standard error of the mean); Mg/Ca error is given as 2sd (standard deviation).

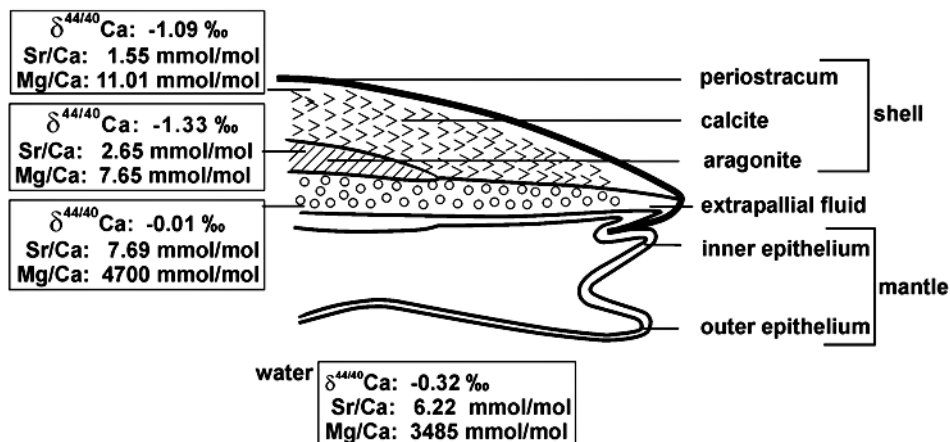


Figure 3. An abstract of all data from the mussel out of the Schwentine Estuary (schematic picture modified after Vander Putten *et al.* [2000]).

ence each other when both polymorphs are formed in the same specimen.

[30] All these results lead the conclusion that there must be a biological control mechanism which already was suggested from different authors [e.g., *Lorens and Bender, 1980; Vander Putten et al., 2000; Carré et al., 2006*].

[31] A number of different environmental conditions are influencing the biological activity and thus the behavior of individual mussels. The inter-

actions of these conditions (see Figure 4) cause an individual integration of elements into the shell and make it complicated to use the isotopic or elemental composition as a proxy for only one parameter, e.g., temperature.

5. Outlook

[32] More information needs to be obtained about the precipitation rate/growth rate and the possibil-

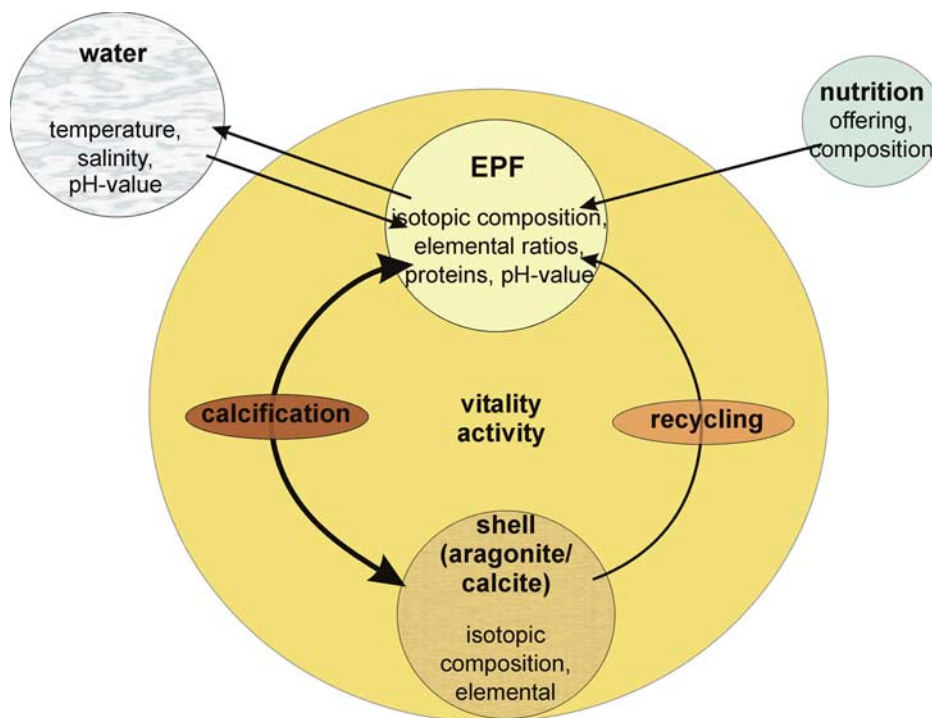


Figure 4. Main factors influencing the EPF and therefore the shell composition of *Mytilus edulis*.

ity of identifying single growth increments in the shell. There is insufficient knowledge about the correlation between such increments and the time required for their formation.

[33] Future studies should focus on the temporal development of the interrelation between the different matrices.

[34] Measurements of the EPF of the same specimen over longer periods in both the field and culturing under controlled and logged conditions would enable us to get more information about temporal variations in the chemical composition of the EPF and the interaction between EPF and the precipitation.

[35] More groundwork into basic biology of the mantle epithelium and the EPF is required, in particular the question of how different isotopes are transported and arranged.

[36] The calcium concentration in the EPF is influenced by the pH value [Crenshaw, 1972]. This implies that the shell may be recycled when pH decreases and the composition of the EPF alters in support of the isotopically lighter calcium. Thus the pH value of the EPF should be a field of further studies because this also is a biological controlled factor influencing the composition of the EPF and the shell. It probably depends on different environmental conditions like nutrition supply, temperature, salinity or the presence of predators.

[37] There are also some indications that there is a correlation between salinity, growth rate and the isotopic composition of the shell. Kossak [2006] shows optimum salinity for growing of *Mytilus edulis* is about 20 and with a tolerance range of 17–34. We found the highest $\delta^{44/40}\text{Ca}$ values in both carbonate polymorphes of the shell at a salinity of about 20 (Kiel Fjord) too and systematically lower $\delta^{44/40}\text{Ca}$ values for the salinities of about 17 (Schwentine Estuary) and 34 (North Sea) respectively. This is therefore an interesting finding and requires further studies at a range of conditions.

6. Conclusions

[38] Our results about the isotopic composition in different areas of the blue mussel in comparison with the surrounding water show that the mechanisms of precipitation in *Mytilus edulis* are largely unknown. The biological control seems to be more considerable for the composition of the shell than the environmental influence.

[39] The precipitation influences the composition of the EPF and vice versa the latter influences the composition of the subsequently formed shell in a complex feedback mechanism.

[40] The influence of a number of different environmental conditions and their interaction complicate the determining of a proxy.

[41] There is variability in the composition within the similar materials that shows the impact of physiology too.

[42] The wide geographic distribution of *M. edulis* [Gossling, 1992] also indicates the high tolerance to a broad range of environmental conditions [Seed and Suchanek, 1992] and reveals the intensive biological control.

[43] The mechanisms controlling biomineralization, shell precipitation and consequently the incorporation of isotopes and minor/trace elements are poorly understood and thus the suitability of *Mytilus edulis* as a proxy archive. Maybe the system of biomineralization is too complex to use *Mytilus edulis* as a proxy archive. This question should be subject of further investigation.

Acknowledgments

[44] This study is a contribution to the CASIOPEIA project funded by the ESF. A.H. gratefully acknowledges financial support from the LASSO project group, funded internally by the IFM-GEOMAR. We gratefully acknowledge the continuous support and constant interest of Marghaleray Amini. A.H. wishes to thank Reinhard Kozdon for the introduction into calcium isotope lab procedures and TIMS measurements. This study benefited from interesting discussions with Martin Wahl. Finally, we thank Florian Böhm for his interest in this study and fruitful discussions. Anne-Désirée Schmitt's very constructive and detailed reviews helped to significantly improve the manuscript. Merci beaucoup! A second anonymous reviewer is kindly acknowledged for providing a concise and encouraging report.

References

- Amini, M. (2007), The role of high- and low-temperature ocean crust alteration for the marine calcium budget, Ph.D. thesis, Christian-Albrechts-Univ., Kiel, Germany.
- Beck, J. W., R. L. Edwards, E. Ito, F. W. Taylor, J. Recy, F. Rougerie, P. Joannot, and C. Henin (1992), Sea-surface temperature from coral skeletal strontium/calcium ratios, *Science*, 257, 644–647.
- Berner, R. A. (1975), The role of magnesium in the crystal growth of calcite and aragonite from sea water, *Geochim. Cosmochim. Acta*, 39, 489–504.
- Carré, M., I. Bentaleb, O. Bruguier, E. Ordinola, N. T. Barrett, and M. Fontugne (2006), Calcification rate influence on trace elements concentrations in aragonitic bivalve shells:



- Evidences and mechanisms, *Geochim. Cosmochim. Acta*, 70(19), 4906–4920.
- Crenshaw, M. A. (1972), Inorganic composition of molluscan extrapallial fluid, *Biol. Bull.*, 143, 506–512.
- DePaolo, D. J. (2004), Calcium isotopic variations produced by biological, kinetic, radiogenic and nucleosynthetic processes, *Rev. Mineral. Geochem.*, 55, 255–288.
- Eisenhauer, A., T. F. Nägler, P. Stille, J. Kramers, N. Gussone, B. Bock, J. Fietzke, D. Hippler, and A.-D. Schmitt (2004), Proposal for international agreement on Ca notation resulting from discussions at workshops on stable isotope measurements held in Davos (Goldschmidt 2002) and Nice (EGS-AGU-EUG 2003), *Geostand. Geoanal. Res.*, 28(1), 149–151.
- Epstein, S., R. Buchsbaum, H. Lowenstam, and U. Urey (1953), Revised carbonate-water isotopic temperature scale, *Geol. Soc. Am. Bull.*, 64, 1315–1325.
- Gossling, E. M. (1992), Systematics and geographic distribution of *Mytilus*, in *The Mussel Mytilus: Ecology, Physiology, Genetics and Culture*, *Dev. Aquacult. Fish. Sci.*, vol. 25, edited by E. M. Gossling, chap. 1, pp. 1–20, Elsevier, New York.
- Gussone, N., F. Böhm, A. Eisenhauer, M. Dietzel, A. Heuser, B. M. A. Teichert, J. Reitner, G. Wörheide, and W.-C. Dullo (2005), Calcium isotope fractionation in calcite and aragonite, *Geochim. Cosmochim. Acta*, 69, 4485–4494.
- Henderson, G. M. (2002), New oceanic proxies for paleoclimate, *Earth Planet. Sci. Lett.*, 203, 1–13.
- Heuser, A., A. Eisenhauer, N. Gussone, B. Bock, B. T. Hansen, and T. F. Nägler (2002), Measurement of calcium isotopes ($\delta^{44}\text{Ca}$) using a multicollector TIMS technique, *Int. J. Mass Spectrom.*, 220, 387–399.
- Kobayashi, S. (1964), Calcification in fish and shell-fish. II. A paper electrophoretic study on the acid mucopolysaccharides and PAS positive materials of the extrapallial fluid in some molluscan species, *Bull. Jpn. Soc. Sci. Fish.*, 30, 893–907.
- Kossak, U. (2006), How climate change translates into ecological change: Impacts of warming and desalination on prey properties and predator-prey interactions in the Baltic Sea, Ph.D. thesis, Christian-Albrechts-Univ., Kiel, Germany. (Available at http://e-diss.uni-kiel.de/diss_1910/)
- Lorens, R. B., and M. L. Bender (1980), The impact of solution chemistry on *Mytilus edulis* calcite and aragonite, *Geochim. Cosmochim. Acta*, 44, 1265–1278.
- Misogianes, M. J., and N. D. Chasteen (1979), A chemical and spectral characterization of the extrapallial fluid of *Mytilus edulis*, *Anal. Biochem.*, 100, 324–334.
- Nürnberg, D., J. Bijma, and C. Hemleben (1996), Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures, *Geochim. Cosmochim. Acta*, 60(5), 803–814.
- Seed, R., and T. H. Suchanek (1992), Population and community ecology of *Mytilus*, in *The Mussel Mytilus: Ecology, Physiology, Genetics and Culture*, *Dev. Aquacult. Fish. Sci.*, vol. 25, edited by E. M. Gossling, chap. 4, pp. 87–170, Elsevier, New York.
- Skulan, J. L., D. J. DePaolo, and T. L. Owens (1997), Biological control of calcium isotopic abundances in the global calcium cycle, *Geochim. Cosmochim. Acta*, 61, 2505–2510.
- Vander Putten, E., F. Dehairs, E. Keppens, and W. Baeyens (2000), High distribution of trace elements in the calcite shell layer of modern *Mytilus edulis*: Environmental and biological controls, *Geochim. Cosmochim. Acta*, 64(6), 997–1011.
- Wada, K., and T. Fujinuki (1976), Biomineralization in bivalve molluscs with emphasis on the chemical composition of the extrapallial fluid, in *Mechanisms of Mineralization in the Invertebrates and Plants*, edited by N. Watabe and K. M. Wilbur, pp. 175–190, Univ. of S. C. Press, Columbia.
- Wilbur, K. M. (1972), Shell formation in molluscs, in *Chemical Zoology*, vol. 7, edited by M. Florkin and B. T. Scheer, chap. 3, pp. 103–145, Elsevier, New York.
- Zhu, P., and J. Macdougall (1998), Calcium isotopes in the marine environment and the oceanic calcium cycle, *Geochim. Cosmochim. Acta*, 62, 1691–1698.