https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

Ideas and perspectives: Mineralizing Fluid Control on Minor Elements in Biogenic $CaCO_3$: Insights from Otoliths

Athina Kekelou*[1], Gerald Langer*[1], Patrizia Ziveri[1, 2, 3]

[1] Institute of Environmental Science and Technology (ICTA-UAB), Universitat Autònoma de Barcelona, 08193, Bellaterra, Spain

[2] Catalan Institution for Research and Advanced Studies, ICREA, 08010, Barcelona, Spain

[3] Departament de Biologia Animal, de Biologia Vegetal i d'Ecologia, Universitat Autònoma de Barcelona, Bellaterra, Spain

*These two authors contributed equally to this work.

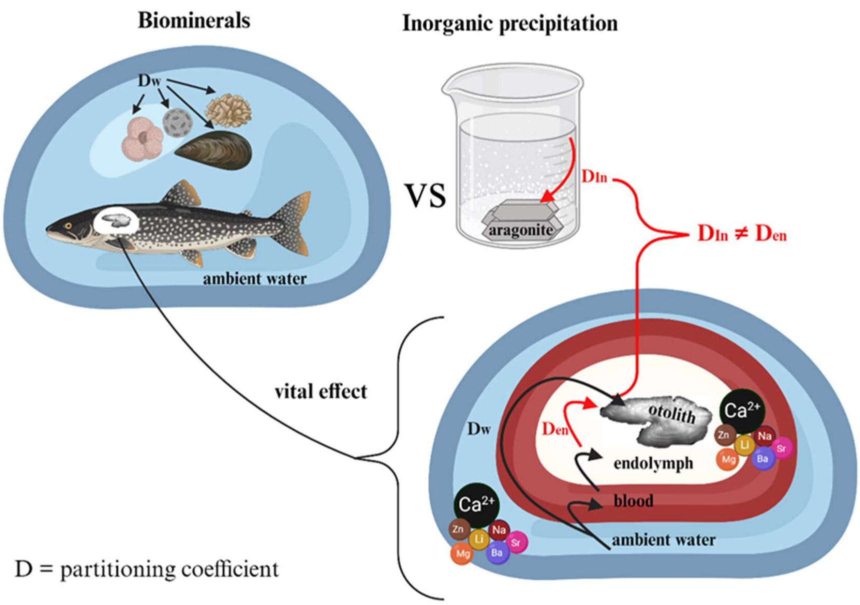
Corresponding to: Athina.Kekelou@uab.cat & Gerald.Langer@uab.cat

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

Keywords

Endolymph, otolith, partitioning of trace elements, biomineralization, vital effect

Graphical Abstract



Key Figure (Graphical Abstract) *"Mineralizing Fluid Control on Minor Elements in Biogenic CaCO₃: Insights from Otoliths" Created in BioRender. Kekelou, A. (2024) BioRender.com/s39g673*

Abstract

The minor element composition of calcium carbonate ($CaCO_3$) biominerals from marine calcifying organisms leaving a sedimentary record has been used for decades to reconstruct various biogeochemical parameters. Advancing geochemical proxies and understanding their underlying mechanisms is essential for climate reconstructions, environmental research, and investigations of biomineralization processes. Despite considerable success of proxy applications, limited mechanistic understanding still restricts their full potential. The problem is often summarized by the term "vital effect", i.e. minor element partitioning due to biological activity. The element partitioning from the calcifying fluid into the biomineral, however, is usually described in terms of inorganic precipitation of a mineral from an aqueous solution of inorganic ions. Although this assumption is central to many partitioning models it has not been tested because the

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

calcifying fluid of classic proxy archives such as foraminifera, molluscs, and coccolithophores has not been successfully sampled for element analysis. The calcifying fluid of fish otolith formation (endolymph), by contrast, was sampled and chemically analysed accompanied by corresponding otolith data. However, previous datasets have not been compared to inorganic partitioning coefficients to test this assumption. In this study, we address this gap using published data from four fish species and six elements. Our results indicate that the final stage of otolith minor element incorporation is influenced by organic matter in the endolymph fluid and therefore cannot be considered purely inorganic. Our conclusion questions a central assumption of many minor element partitioning models. This does not imply that existing models are questionable, but that they share a common oversimplification. By removing this oversimplification all kinds of different models can be improved. Our study contributes broadly to the understanding of biogenic $CaCO_3$ geochemistry, and it is relevant to the majority of existing models.

1. Introduction

The minor element (Me) and isotopic composition of marine calcium carbonate ($CaCO_3$) (mostly aragonite and calcite) biominerals from the sedimentary record has been used as a proxy for the reconstruction of specific environmental parameters such as seawater temperature since the 1950s (Katz et al., 2010; Urey et al., 1951). These geochemical proxies are instrumental in e.g. detecting effects of anthropogenic climate change on marine calcifying organisms (calcifiers) (Pallacks et al., 2023). A geochemical paleo-proxy application requires a correlation of the proxy with the target environmental parameter, and this is traditionally achieved by various calibration methods (Allen et al., 2016; Elderfield & Ganssen, 2000). The calibration of a geochemical proxy alone, however, does convey little knowledge about the processes underlying proxy signals and accuracy. This knowledge is, however, essential for developing a mechanistic understanding of the proxy and eventually will enable us to predict proxy signals using conceptual biomineralization models (Nehrke & Langer, 2023). Biomineralization models, as opposed to calculations premised on precipitation of the mineral from seawater, are required because marine calcifiers used as proxy archives do not precipitate their hard parts from seawater but from a special calcification fluid thereby introducing the problem of the vital effect (Nehrke & Langer, 2023; Urey et al., 1951). This calcification fluid is localised in the so-called site of calcification (SOC). Different proxy-archive forming calcifiers have SOCs formed by different structures such as pseudopodia (foraminifera, single-celled calcifying organisms), mantle epithelium (molluscs, invertebrate animals that form a calcified shell), or intracellular

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

vesicles (coccolithophores, single-celled calcifying algae) (Angell, 1967; Crenshaw, 1972; Langer et al 2021, Wilbur & Watabe, 1963).

In all cases, however, the proxy signal will be influenced by the transport of ions from seawater into the SOC (Nehrke & Langer, 2023). This transport can introduce partitioning steps that render the overall partitioning different from what would be expected based on inorganic precipitation from seawater. A striking example is the Sr/Ca signature in diverse calcifiers (Fig. 1). The data selected for Fig. 1 from the aragonite literature illustrate that the Sr partitioning coefficient (D_{Sr} = $(Sr/Ca)_{biomineral}$ / $(Sr/Ca)_{seawater}$) in some cases falls within the range of inorganic precipitation, in others it does not. We selected Sr incorporation in aragonitic biominerals here, but a well-known riddle is the Mg-problem, as it is often informally referred to, in calcitic biominerals (Bentov & Erez, 2006; Nehrke et al., 2013)

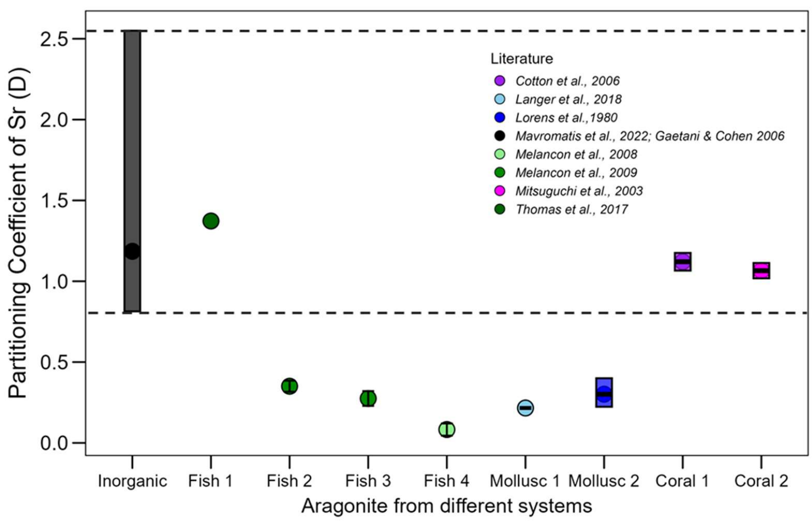


Figure 1 *Sr partitioning coefficient range (D_{Sr} = $(Sr/Ca)_{biomineral}$ / $(Sr/Ca)_{seawater}$) in different organisms with aragonite biominerals (different colours) and the inorganic aragonite the black bar (range highlighted with dashed black line). The literature of the data is given in the caption of the figure.*

An intuitive, and often used, assumption is that knowledge of the ionic composition of the calcifying fluid would solve this problem. In other words, it is expected that a partitioning coefficient calculated using the calcifying fluid minor element to Ca ratio (Me/Ca) will fall within the range of values determined in inorganic precipitation experiments (Elderfield et al., 1996; Langer et al., 2006, 2016, 2018; Stoll et al., 2012). Unfortunately, the SOCs of most classic proxy-archive forming calcifiers are too small to be sampled for element analysis (Checa, 2018; Kadan et al., 2021; Nomaki et al., 2018). Therefore, various model

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

approaches have been developed to calculate minor element partitioning into biominerals (D'Olivo & McCulloch, 2017; Elderfield et al., 1996; Hohn & Merico, 2015; Langer et al., 2006, 2016; Nehrke & Langer, 2023; Ziveri et al., 2003, 2012). These models have provided new insights into the relationship between conceptual biomineralization models and minor element partitioning, but they have, yet, failed to predict partitioning patterns based solely on independent constraints (Nehrke & Langer, 2023). Therefore, these models rely on assumptions, many of which do not account for the complexity of minor element partitioning during biomineral formation. It is, for example, by no means self-evident that a partitioning coefficient calculated using the calcifying fluid composition will fall within the range of inorganic values.

Table 1. Summary of commonly studied geochemical elements in fish otoliths, their targeted environmental or biological variables, proxy types, specific elemental ratio, relevant ecosystems, and key references.

Targeted Variable	Proxy Type	Specific elemental ratio	Ecosystem	References
Temperature	Elemental Ratios, Stable Isotope	Sr/Ca, Mg/Ca, Li/Ca, Mn/Ca, Ba/Ca, Cu/Ca, $\delta^{18}O$	Marine & Estuarine	(Cavole et al., 2023; Devereux, 1967; Miller & Hurst, 2020; Mondal et al., 2022; Morat et al., 2023; Rosales et al., 2004; Tanner et al., 2013; Willmes et al., 2019)
Salinity	Elemental Ratios, Stable Isotope	Sr/Ca, Ba/Ca, Mn/Ca, $\delta^{18}O$, $^{87}Sr/^{86}Sr$	Estuarine & Freshwater	(Höpker et al., 2022; Kerr et al., 2007; Nelson & Powers, 2020; Rosales et al., 2004)
Oxygen, Hypoxia	Elemental Ratio	Mn/Ca, Mg/Mn	Marine	(Limburg et al., 2011, 2015; Limburg & Casini, 2018)
Diet, Metabolism, Physiology	Elemental Ratios, Stable Isotope	$\delta^{13}C$, $\delta^{15}N$, Li/Ca, Mg/Ca	Marine	(Chung et al., 2019; Izzo et al., 2018; Lall & Kaushik, 2021; J. Lueders-Dumont, 2024; J. A. Lueders-Dumont et al., 2018; Martino et al., 2020, 2021; Rao et al., 2024; Shiao et al., 2018; Sirot et al., 2017; A. Sturrock et al., 2014)
Ontogeny, Life History	Elemental Ratios, Stable Isotope	Sr/Ca, Ba/Ca, Mg/Ca, $^{87}Sr/^{86}Sr$	Marine & Freshwater	(Campana, 1999; Campana & Thorrold, 2001; Halden & Friedrich, 2008; Kennedy et al., 2002; Longmore et al., 2011; Saygın et al., 2022; Wells et al., 2014; Zazzo et al., 2006)
Migration, Habitat	Elemental Ratios, Stable Isotope	Sr/Ca, Ba/Ca, Mn/Ca, $\delta^{18}O$, $\delta^{13}C$	Marine & Freshwater	(Avigliano et al., 2015; Fraile et al., 2016; Phillis et al., 2011; Sackett et al., 2024; Sturrock et al., 2012; Walther & Limburg, 2012)
Stock Discrimination	Elemental Ratios, Stable Isotope	Sr/Ca, Ba/Ca, Mg/Ca, $^{87}Sr/^{86}Sr$	Marine	(Campana & Thorrold, 2001; Longmore et al., 2011; Padilla et al., 2015; Vaisvil et al., 2023)

In this paper, we focus on fish otoliths, mostly aragonitic biominerals in the inner ears of bony fish, that are an understudied and underappreciated model system to address element partitioning patterns (Hüssy et al.,

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

2020; Melancon et al., 2005). Otoliths can be found as fish remains in the sedimentary record (Elder et al., 1996; Mellars et al., 1980) and they have been used in many ways in fisheries research, ecology, and the reconstruction of fish stock environments (Reis-Santos et al., 2023). The minor element compositions of otoliths can serve as proxies for e.g. migration patterns, salinity, and temperature (Albertsen et al., 2021; Bath Martin & Thorrold, 2005; Shiao et al., 2006). The otolith isotopic composition is also used as a proxy, e.g. habitat/migration is inferred from Sr and C isotopes, and dietary history from N and C isotopes, while O isotopes provide information about temperature and salinity (see Table 1 for an overview of otolith-based geochemical proxies). Otoliths serve as valuable proxy archives for several reasons: a) Unlike coccolithophores (which have coccoliths ranging from 2 to 20 µm) and require complex species-specific separation, otoliths allow monospecific analyses; b) Unlike foraminifera, otoliths are found in marine, freshwater, and estuarine environments, making them broadly applicable across aquatic systems;
c) Element-to-calcium ratios in individual otoliths can be spatially mapped, offering insights into the fish life history traits and seasonal patterns.

As with any other proxy archive, otolith-based proxies are subject to secondary influences. For example, Sr/Ca and Ba/Ca are influenced by their correspondent concentrations in ambient water, but also salinity and temperature (Hüssy et al., 2021).

It has also been noted that, besides environmental parameters, physiology influences minor element and isotope composition (Bareille et al., 2024; Izzo et al., 2018; Sturrock et al., 2015). The value of otoliths as geochemical proxy archives has been highlighted but is also, unsurprisingly, critically discussed (Hüssy et al., 2021; Thomas & Swearer, 2019; Walther, 2019). The latter authors emphasize that future steps towards improving otolith proxy applications critically include an understanding of the processes bringing about the proxy signal. Hüssy et al., (2021) effectively summarize the fundamental processes governing elemental and isotope fractionation into otoliths. They distinguish ion transport into the endolymph from “biomineralization” by which they mean the formation of the otolith within the endolymph. Note that often the term “biomineralization” covers both ion transport and formation of the biomineral within the SOC (Nehrke and Langer 2023). As for foraminifera, there has been an increasing interest in the relationship between partitioning (usually called fractionation when referring to isotopes) patterns and biomineralization concepts in otoliths (Campana, 1999; Hüssy et al., 2021). To understand even the most straightforward and useful proxies, such as Sr/Ca in foraminifera, both biological and inorganic processes need to be considered

(Langer et al 2016). Otoliths offer the unique opportunity to study the fractionation processes within the SOC in greater detail than is possible in classic proxy archives such as foraminifera.

An outstanding feature of otolith formation is the fact that the calcifying fluid, i.e. the endolymph, has such a large volume that it can be sampled for element analysis (Kalish, 1989). This offers the unique opportunity to measure minor element composition of both the biomineral and its parent solution (Allemand et al., 2007; Edeyer et al., 2000; Kalish 1989, 1991; Melancon et al., 2005, 2008, 2009a; Payan et al., 1997, 1998, 1999, 2002, 2004; Thomas et al., 2017). Although some of the latter studies provide the relevant data and discuss the relationship between partitioning and biomineralization processes, no study has addressed the following question: is the minor element partitioning coefficient from endolymph into otolith (in the following called De) numerically equivalent to the one from an aqueous solution of inorganic ions into aragonite? Here we therefore use the relevant datasets in the literature to address this question. We look at six different minor elements in four different species, one marine and three freshwater ones. We compare minor element partitioning coefficient from endolymph to otolith with partitioning coefficient from inorganic aragonite precipitation. This study provides a deeper mechanistic understanding of the vital effect by identifying one, so far neglected, locus of the vital effect in the calcifying organism. The aim is to test the commonly made assumption that biogenic partitioning coefficients should be indistinguishable from inorganic ones if the Me/Ca of the actual parent solution (the calcifying fluid) of biomineral formation is used as denominator (e.g. Langer et al., 2006). Our results suggest that partitioning of minor elements from endolymph into otolith cannot be modelled solely in terms of aragonite precipitation from an aqueous solution of inorganic ions. Our conclusion not only has implications for proxy understanding but also for biomineralization concepts because the latter centrally feature ideas about the composition of the calcifying fluid and its effect on biomineral formation.

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

2. Material and methods

Literature data on Me/Ca ratios in endolymph and otolith were used to calculate partitioning coefficient. The latter were compared to partitioning coefficient determined in inorganic precipitation experiments. The literature data used are summarized in Table 2.

Table 2. Literature data used in this study.

System/Organism	Elements	Reference
Inorganic aragonite	Ba	(Gaetani & Cohen, 2006; Mavromatis et al., 2018, Dietzel et al., 2004)
Inorganic aragonite	Mg	(Gaetani & Cohen, 2006; Mavromatis et al., 2022)
Inorganic aragonite	Sr	(Brazier et al., 2023; Gaetani & Cohen, 2006; Zhong & Mucci, 1989; Dietzel et al., 2004)
Inorganic aragonite	Li	(Marriott et al., 2004; Brazier et al., 2024b)
Inorganic aragonite	Zn	(Brazier, et al., 2024a)
Inorganic aragonite	Na	(Kawabata et al., 2021; Brazier et al., 2024b)
Acanthopargrus bucheri (S1)	Mg, Sr, Ba, Li	(Thomas et al., 2017)
Lota lota (S2)	Mg,Sr,Ba,Zn,Na	(Melancon et al., 2009)
Salvelinus namaycush (S3)	Mg,Sr,Ba,Zn,Na	(Melancon et al., 2009)
Sander vitreus (S4)	Mg,Sr,Ba,Zn,Na	(Melancon et al., 2008)
Patella caerulea (mollusc1)	Sr	(Langer et al., 2018)
Mytilus edulis (mollusc2)	Sr	(Lorens & Bender, 1980)
Lophelia pertusa (coral1)	Sr	(Cohen et al., 2006)
Porites australiensis (coral2)	Sr	(Mitsuguchi et al., 2003)
Sea Water	Sr	(Broecker, W. S., & Peng, T.-H. 1982)

The literature on inorganic system provides many measurements of the partitioning coefficient (D_{In}) from different experimental designs. We selected the full range of values to get a realistic overall picture of the inorganic system. For the otolith-endolymph system the literature was limited. Only three papers gave us enough data to estimate the partitioning coefficient of the elements into the otolith. The first study by Thomas et al., 2017 used a marine species, *Acanthopagrus butcheri* (S1), and the number of individuals measured was N = 3. Otoliths were diluted and measured in the same plasmamass spectrometry (ICP-MS) as the endolymph fluid. They provide the concentration of minor elements (Me) normalized to the concentration calcium of (Ca) in the otolith and the endolymph ratio, $R = [Me](mmol)/[Ca](mol)$ with the $\pm sd$ and the $range(R) = \min(R) - \max(R)$, as well the partitioning coefficient ($D \times 100$). We estimate the range of the D using a simple formula of range ratio (Eq. 1):

$$range(D_e) = \max(D_e) - \min(D_e) = \left(\frac{\max(R_{otolith})}{\min\,(R_{endolymph})}\right) - \left(\frac{\min(R_{otolith})}{\max\,(R_{endolymph})}\right) \quad (1)$$

The second and third paper provide data of the concentration of minor elements in the otolith and in the endolymph (Melancon et al., 2008, 2009a). The species that were used in these studies were the freshwater

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

species burbot *Lota lota (S2)*, lake trout *Salvelinus namaycush (S3)* and a walleye *Sander vitreus* (S4), the number of the individuals (N) that were used were N_b=18 and N_t=11 and N_w=8, respectively. In these studies, the concentrations of the elements in the otoliths were quantified by laser ablation (LA-ICP-MS) and they performed a series of ablations at the growing otolith edges that were in contact with the endolymph and represent the last 30 to 60 days of growth. They provide the average concentration of the minor elements $av[Me] \pm sd\ (ppm)$ in the otolith and in the endolymph, which we converted to mmol/mol. The ratio $R = [Me](mmol)/[Ca](mol)$ in the otolith and in the endolymph and the $av(D) \pm sd(D)$ was estimated using Eq. (2) and (3)

$$av(D_e) = \frac{av(R_{otolith})}{av(R_{endolymp}\ )}\ (2)$$

$$sd\ (D_e) = av(D_e) \times \left(\sqrt{\left(\frac{sd(R_{otolith})}{av(R_{otolith})}\right)^2} + \sqrt{\left(\frac{sd(R_{endolymph})}{av(R_{endolymph})}\right)^2} \right) (3)$$

Then the ratio and the partitioning coefficient, in the different parts of the ion transport pathway that the elements need to cross to precipitate in the otolith, were estimated. Only one paper provided sufficient data for this purpose (Melancon et al., 2009). The ion transport pathway starts from the ambient water to blood, then from blood to endolymph and the final step is from endolymph to otolith (Graphical Abstract). The partitioning coefficient that describes the last step of endolymph to otolith was estimated using the equation 4. Some extra variables were also estimated. The first was the D commonly used in biomineralization studies. This D_w is the partitioning coefficient using as parent solution the ambient water (Eq. 5). The other two Me/Ca were estimated based on the idea that the last step of the precipitation is purely inorganic (Eq. 7) and (Eq. 8). The first of those (Eq. 7), is the ratio that the otolith would have, if the last precipitation step was completely inorganic and the parent solution was the endolymph ($R_{otolith1}$) . The second (Eq. 8) is the theoretical ratio if the parent solution was water ($R_{otolith2}$).

$$D_e = \frac{R_{otolith}}{R_{endolymph}}\ (4)$$

$$D_w = \frac{R_{otolith}}{R_{water}}\ (5)$$

$$D_{In} = \frac{R_{crystal}}{R_{fluid}}\ (6)$$

$$R_{otolith1} = range(D_{In}) \times R_{endolymph}\ (7)$$

$$R_{otolith2} = range(D_{In}) \times R_{water}\ (8)$$

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

We address the following question. Does the numerical value of the minor element partitioning coefficient from endolymph into otolith equal that of the partitioning coefficient from an aqueous solution into pure aragonite? As mentioned in the introduction, Fig. 1 illustrates the range of the Sr partitioning coefficient (D) in different calcifying marine organisms, we used as parent solution seawater and the ratios of the elements in each organism from the literature (Broecker & Peng, 1982; Cohen et al., 2006; Langer et al., 2018; Lorens & Bender, 1980; Mitsuguchi et al., 1996).

3. Results

Figure 2 illustrates the partitioning coefficient of different minor elements from different fish species were compared numerically with the inorganic partitioning coefficient of the same element. To elaborate more the distinct environments, affect Ba and Sr, which demonstrate different behaviour for the marine and freshwater species something that is not observed in the other elements. For the freshwater fish were estimated both partitioning coefficient from water (D_w) and from endolymph (D_e) because data were available. The D_e of the elements Na and Sr, except for one fish (S2), fall within the inorganic range when the D_w does not. Additionally, Ba and Mg in both D_e and D_w yielded comparable results but with difference corresponding to the inorganic range. In the case of Ba, the coefficient is not within the inorganic range, while in the other instance Mg, it is. Finally, Zn is a unique case because it seems that D_w is in the range of the inorganic system, but D_e is not. From all this observation we can come to the general result that the 'vital effect' for some elements is visible and for some invisible. In the supplementary material there is also the partitioning coefficient D_e of Li in the S1 fish.

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

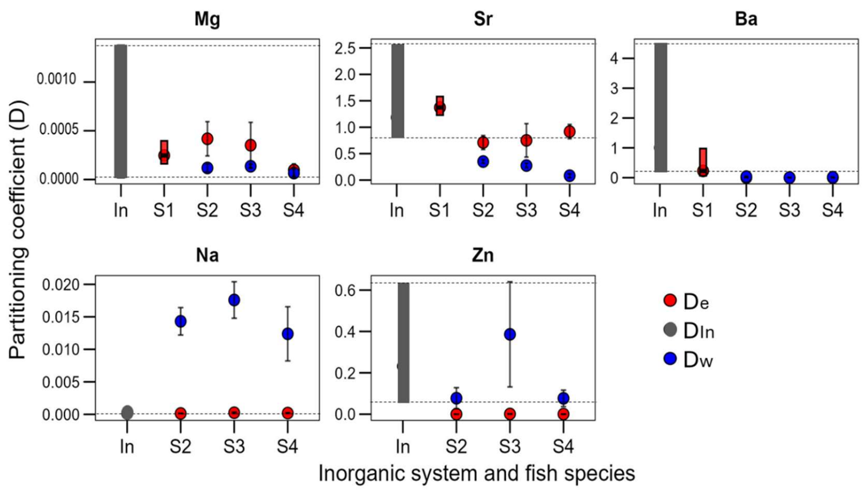


Figure 2 *The partitioning coefficient (D) per element (Mg, Sr, Ba, Na,Zn), the range of the inorganic system (In) and the mean±SD of the D in three different freshwater fish burbot Lota lota (S2), lake trout Salvelinus namaycush (S3) and a walleye Sander vitreus (S4) and the range of the marine fish the Acanthopagrus butcheri (S1). The different colors of D values, red is the D_e (endolymph as parent solution) and blue the Dw (water as parent solution) for fish and black is the DIn of the inorganic aragonite.*

Figure 3 illustrates the ion transport pathways of five different elements in the burbot Lota lota otolith. We demonstrate the same idea in Fig.S2 for the *Salvelinus namaycush* (*S3*). In almost all cases the ambient water is not sufficient to describe the co-precipitation of Me into otoliths. The ratios of elements normalized to calcium (Ca) were measured in different solutions to trace their transport pathway into the otolith. We notice that the precipitation steps from each reservoir follow the same path with the largest changes in partitioning occur during transfer from water to blood and from endolymph to otolith. Although we have different outcomes in terms of the final product the otolith. What we actually see is that knowing that the vital effect is happening in some cases we observe it, difference in otolith1 with otolith (Fig. 3, (c), (e)) and in some cases it is

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

invisible (Fig.3, (a), (b), (d)). As previously demonstrated in Figure 2, this phenomenon is influenced by both elemental and species-specific factor.

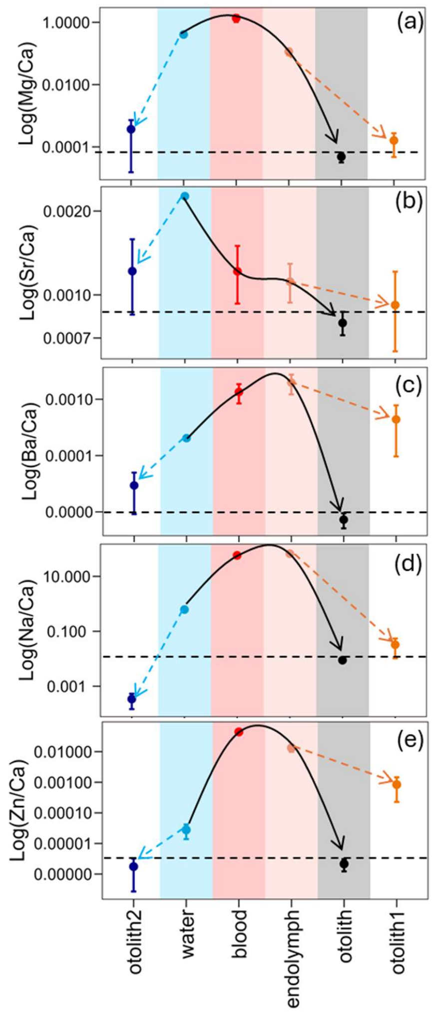


Figure 3 *Me/Ca of burbot Lota lota (S2) in different reservoirs indicated by colored areas. The white areas (otolith 1 and otolith 2) do not represent measured values but are calculated according to otolith1 =* D_{In} ** (Me/Ca)* $_{endo}$*, and otolith2 =* D_{In} ** (Me/Ca)*$_{water}$*. For* D_{In} *we used either the minimum or the maximum value depending on which one would minimize the offset between (Me/Ca) otolith-measured and (Me/Ca) otolith-calculated. The error bar represents the range of the values that the system can reach. (a) is the pathway of Mg, (b) the pathway of Sr, (c) the pathway of Ba, (d) the pathway of Na and (e) the pathway of Zn.*

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

4. Discussion

Here we challenge the assumption that biomineral formation from the calcifying fluid is fully describable in terms of the formation of synthetic monocrystals from an aqueous solution of inorganic ions. Although intuitive, this idea might underestimate the complexity of biomineral formation for, inter alia, the following reasons. Firstly, biominerals are not monocrystals but organo-mineral composite structures, implying the possibility that minor elements reside in the organic material (Cuif et al., 2010; Hüssy et al., 2021; Miller et al., 2006; Walker & Langer, 2021) Secondly, the calcifying fluid usually contains organic molecules, which could interact with inorganic ions thereby decreasing their activity ratios in solution and hence in the biomineral since mostly free ions are incorporated in the crystal (e.g. Borelli et al., 2001; Hüssy et al., 2021; Meyer et al., 2020; Moura et al., 2000; Thomas & Swearer, 2019). In the following we show that both processes do indeed influence minor element distribution into otoliths which is, therefore, not reducible to inorganic aragonite co-precipitation.

4.1 Minor element partitioning from endolymph to otolith cannot be modelled in terms of inorganic aragonite precipitation

We looked at the partitioning coefficient of six elements (Sr, Ba, Mg, Na, Zn, and Li) in four different species, S1-S4 (Fig 2, Fig S1). For our question, it is helpful to consider several elements, as opposed to just one, because results from a single element might be misleading (Langer et al., 2018). A species comparison will further strengthen the conclusions because the question concerns the endolymph-otolith system in general. The partitioning coefficients D_e of Na, Mg (mostly), Sr and Ba (in S1) fall within the range of inorganic values (Fig 2, Fig. S1). For all other elements, Zn and Li, otoliths show a partitioning behaviour different from inorganic aragonite. Taken together these results clearly show that the endolymph-otolith system produces minor element partitioning coefficients different from the ones determined in synthetic aragonite precipitation. Therefore, we conclude that minor element partitioning during otolith formation in the endolymph involves processes that do not occur during inorganic aragonite precipitation. An obvious further question is why the partitioning behaviour is both element and species specific. In general, the answer will likely involve specific organic material both in the endolymph and the otolith. In the following we will concretize this somewhat vague hypothesis.

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

4.2. Element and species specificity of partitioning behaviour

Otolith partitioning coefficient D_e of Ba and Zn (and Sr in S2 and partly S3) in freshwater species are lower than those in the inorganic system (Fig 2). In the case of Sr and Ba incorporation into the organic part of the otolith seems negligible, ruling out a significant influence of otolith organics on partitioning (Izzo et al., 2016). This strongly suggests that endolymph organic material (Borelli et al., 2001; Thomas et al., 2019) forms complexes with divalent cations, fractionating for Sr and Ba. The remaining free ions in solution are incorporated into the growing otolith aragonite, with minor element partitioning depending on crystal growth rate, in turn depending on various factors such as supersaturation, stoichiometry, and surface topography (Nehrke et al., 2007; Wolthers et al., 2013).

An example of organic material fractionating for Sr and Ba are polysaccharides such as alginates (Yuryev et al., 1979). The situation might be different for Mg which is fractionated against when forming complexes with organics thereby weakening fractionation against Mg into calcite (Mavromatis et al., 2017; Takeuchi et al., 2008). Complexation of minor elements with inorganic ligands can also affect partitioning into calcium carbonate. In the case of Mg, sulfate complexes lead to an apparently harder fractionation against Mg into calcite (Goetschl et al., 2019; Mucci et al., 1989). Since for Mg, organic and inorganic complexes influence partitioning behaviour differently the overall change in the partitioning coefficient will partly depend on the relative concentrations of these different ligands. Inorganic ligands such as sulfate, phosphate, and carbonate might play a considerable role in modifying partitioning behaviour in calcifying fluids. The modification of the partitioning behaviour will be minor element specific too. While alkali metal (e.g. Na and Li) complexes are of minor importance, Zn for example has a high affinity to form inorganic complexes with e.g. sulfate and carbonate (Krężel & Maret, 2016; Lewis & Randall, 1921; Olsher et al., 1991; Stanley & Byrne, 1990). However, Li partitioning into calcite is pH dependent (Füger et al., 2019). Since calcifying fluids are likely to feature high pH, Li partitioning into calcitic biominerals, and maybe aragonitic ones too, might display a "high pH signal". Additionally, organic complexes with Zn can comprise the majority of total Zn, for example in surface seawater down to 500m (Bruland, 1989). These naturally occurring organic ligands in seawater will be important in calcifiers using seawater as substrate supply for calcification, e.g. foraminifera (Elderfield et al., 1996). The influence of organic material in the calcifying fluid on minor element partitioning shows that the localization of the minor element in the mineral part of the biomineral does not justify the conclusion that the partitioning process is inorganic. This reasoning has nevertheless been applied to Mg partitioning into foraminiferal calcite (Branson et al., 2013).

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

The latter authors show that Mg resides in foraminiferal calcite and from this observation conclude that the partitioning behaviour of Mg is inorganic. Since Mg is an important temperature proxy (Elderfield & Ganssen, 2000), this example illustrates the usefulness of the endolymph-otolith system for the development of a process-based understanding of proxy signal formation more generally.

Why does Ba partitioning in the marine species S1 differ so strikingly from the one in the freshwater species (Fig 2)? Rather than being a species effect, this might be a methodological effect. Otoliths from the freshwater species were analyzed by LA-ICP-MS, where only the edge of the otolith was targeted to achieve a better match with the endolymph analysis (see Material and Methods). Otoliths from the marine species were dissolved whole for solution analysis by ICP-MS. The Ba/Ca of otoliths can vary substantially within single otoliths, often with high values near the otolith core (Hermann et al., 2016). This could explain both the higher De in the marine species and the larger range reaching both below and above the inorganic range (Fig 2).

The situation for Zn is different from the one for Sr and Ba because 40-60% of the Zn reside in otolith organics (McFadden et al., 2016; Miller et al., 2006). Although an effect of endolymph organics cannot be ruled out for Zn, it is equally possible that partitioning into otolith organics is different from partitioning into otolith aragonite. Differential partitioning between the organic and the mineral part of mollusc shells has been reported, supporting this possibility (Schöne et al., 2010).

To sum up, minor elements might reside either in the mineral (e.g. aragonite in otoliths) or the organic part of the biomineral. Partitioning of minor elements into the organic part is most likely different from partitioning into the mineral part. Hence partitioning is not homogeneous across a biomineral. The calcifying fluid often contains organic and, potentially, inorganic ligands that form complexes with minor elements thereby influencing partitioning into the biomineral.

4.3. Biogenic and inorganic partitioning coefficient indistinguishable: Mg, Na and Zn

The partitioning behaviour of Mg and Na seems to suggest that these elements are coprecipitated into aragonite in a manner akin to synthetic aragonite formation (Fig 2). If this was indeed so this would nevertheless not contradict our conclusion (see above), namely minor element partitioning into otoliths involves processes other than aragonite precipitation from an aqueous solution of inorganic ions. The latter conclusion rests on the behaviour of the other elements as discussed above and is not invalidated by a putatively different behaviour of Mg and Na. However, the behaviour of Mg and Na might as well merely

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

appear inorganic numerically (in terms of D_e) but the processes underlying D_e might involve organic material, i.e. the overall process of partitioning might be very different from inorganic precipitation. This phenomenon has been described for different calcifiers and is known by the term "invisible vital effect" (Nehrke & Langer, 2023 and references therein).

The likelihood of an invisible vital effect in D_e is nevertheless much smaller than in the D calculated traditionally, i.e. using the external water Me/Ca (seawater or freshwater) as denominator. We added the traditional partitioning coefficient (D_w) to our dataset (Fig 2). For Mg and Zn, D_w falls within the range of inorganic values, but from this we cannot conclude that Mg and Zn partitioning proceeds via inorganic precipitation from external water. We know that for ions to enter the endolymph they need to be transported via the blood (Hüssy et al., 2021; Mccormick & Ac Kinlay, 2000; Sturrock et al., 2015) so that there are at least two partitioning steps operative before the endolymph-otolith step. We look at these partitioning steps in the following section.

4.4. The pathway of minor elements from water to otolith

In the freshwater species S2 (Fig. 3) and S3 (Fig. S2) were the only dataset that allows us to trace the pathway of minor elements from external water into the otolith. In Fig 3 we use Me/Ca (R) in different reservoirs along the ion transport pathway as given in the literature, and we additionally calculate two further values: 1) the $R_{otolith2}$ that results from multiplying R_w by D_{In}; 2) the $R_{otolith1}$ that results from multiplying R_e by D_{In}. The D_{In} that are used are selected to minimize the offset between otolith (measured) and otolith (calculated). The aim of the figures is to illustrate the resulting (R) of different partitioning steps as they actually occur (coloured reservoirs), as opposed to the ones that would theoretically occur if D_{In} were applied.

Several things can be gleaned from this figure. The first concerns the match / mismatch of otolith and otolith1. A match indicates that partitioning from endolymph to otolith could be inorganic. This is the case for Sr, Mg, and Na. Note that the same conclusion can be drawn from Fig. 2 with the exception of D_{Sr} which does not fall within the inorganic range but is close to it. The reason for this discrepancy is that in Fig 2 a mean and standard deviation is given whereas in Fig. 3 the minimum value of D_{In} is used. The latter choice represents a conservative approach aiming at a match between otolith and otolith1. The case of Sr is therefore borderline, but its behaviour could still be considered inorganic. In stark contrast, the behaviour of Ba and Zn is clearly not inorganic.

The traditional way of calculating partitioning coefficients is from the water media where the organism lives to the biomineral because the composition of the calcifying fluid is unknown (e.g. Langer et al., 2006). This poses the central problem of the vital effect. The main question we are asking here is: can the problem of the vital effect be solved by knowledge of the composition of the calcifying fluid. The answer is yes for Sr and Na, and no for Ba, Zn, and Mg. Note that D_w of Zn and Mg show an invisible vital effect, so that using the correct parent solution can confer no numerical advantage. There is nevertheless knowledge to be gained. Knowing the values of otolith2 (Zn and Mg) merely tells us that there will be partitioning steps along the way from water into otolith, but the localization of partitioning along this pathway remains the classic "black box" (Nehrke & Langer, 2023). Here we can take a look into the black box in unprecedented detail. The step from water into blood fractionates weakly for Mg but strongly for Zn, while the following step into the endolymph fractionates weakly against both Mg and Zn. The last step from endolymph to otolith fractionates strongly against both Zn and Mg. While this step could be inorganic for Mg, it is more complex for Zn, i.e. the interaction of Zn with organics (as discussed above) contributes to this partitioning step. Biological partitioning steps are hard to predict in general, and in particular if the minor element and Ca are transported by separate transport systems.

4.5. Essential versus non-essential elements

While Ca, Na, Mg, and Zn are essential elements, i.e. needed in physiological processes, there is no known physiological role for Sr and Ba, which are therefore considered non-essential (Lall & Kaushik, 2021; Marshall, 2002; Nielsen, 2004; Salisbury& Ross, 1992). When considering minor element partitioning into biominerals the distinction between essential and non-essential elements is of great importance because essential elements have their own transport systems while non-essential elements are thought to pass through the transport systems of essential elements (Langer et al., 2006, 2009). This means that partitioning from one reservoir into another (e.g. from water into blood) can be conceptualized easier for non-essential elements, because only the partitioning of individual transport systems has to be known. If one transport system transports the minor element and another transports Ca the situation is more complicated because the two systems can be regulated independently. In the case of the non-essential elements Sr and Ba it is usually expected that they partition similarly if not with identical partitioning coefficient (Allen & Sanders, 1994; Langer et al., 2006, 2009; Nachshen & Blaustein, 1982). It is therefore surprising that the step from water to blood fractionates for Ba but against Sr, whereas the step from blood to endolymph does not fractionate at all (or only minimally) for both elements (Fig 3). The partitioning from endolymph to otolith is against both Sr and Ba, i.e. according to expectation. The fact that Ba fractionation is harder than Sr fractionation could be explained by differential Sr and Ba partitioning of cellular transporters as well as organic polymers (e.g. Nachshen & Blaustein, 1982; Yuryev et al., 1979).

5. Conclusion

In this study we used literature data on minor element composition of the endolymph- otolith system to calculate partitioning coefficient and analyse the partitioning behaviour of six elements in four species of fish. The endolymph-otolith system is outstanding because the parent solution (endolymph) of biomineral (otolith) formation can be sampled, and its elemental composition be determined. Our approach is novel since up to now the focus on traditional geochemical proxy archives (foraminifers, molluscs, and coccolithophores) has precluded such an analysis. Our data suggests that:

1) Otolith mineralization in the endolymph shows a vital effect. Partitioning from endolymph into otolith is influenced by organic material present in both endolymph and otolith and therefore cannot be reduced to aragonite precipitation from an aqueous solution of inorganic ions.
2) Differential partitioning patterns are more complex than generally assumed, as illustrated by the easy-to-conceptualize “model elements” Sr and Ba, which behave counter to expectation.
3) Future research should be specifically designed to address elemental partitioning within the endolymph, as clearly warranted by the findings of this study.

Data Availability

The data will be published in the “Mendeley data” platform with the reference as: Kekelou, Athina (2025), “Trace element incorporation in the fish otolith, inorganic crystals vs otoliths”, Mendeley Data, V2, doi: 10.17632/8ysgz5nb82.2. But also they have been submitted as Supplementary material.

Acknowledgments & Declarations

AK acknowledges funding from the Spanish Ministry of Science and Innovation through the FPI fellowship (PRE2022-102298) **GL** acknowledges funding from the Spanish Ministry of Universities through a Maria Zambrano grant and the Generalitat de Catalunya (MERS, 2021 SGR 00640). This work contributes to ICTA-UAB “María de Maeztu” Programme for Units of Excellence of the Spanish Ministry of Science and Innovation (CEX2019-000940-M;) and the BIOCAL Project (PID2020-113526RB-I00)

The authors declare that they have no conflict of interest.

Author contribution

AK: Investigation, Formal analysis, Methodology, Data Curation, Writing - Original Draft, Visualization. **GL:** Conceptualization, Investigation, Writing - Original Draft and Review & Editing, Validation, Visualization, Project administration **PZ**: Supervision, Visualization, Writing - Review & Editing.

Supplementary Material

Supplementary Figures: Figures S1 and *Figure S2* are provided in the separate supplement file. Figure S1 illustrates the partitioning coefficient (D) for Li, comparing the range of the inorganic system and the marine fish (*Acanthopagrus butcheri - S1*). And Figure S2 illustrates the Ion transport pathway of the elements Mg, Ba, Na, Sr and Zn in the *Salvelinus namaycush* (*S3*).

Data Excel file: inorganic vs otolith-endolymph

Reference

Albertsen C. M., Hüssy K., Serre S. H., Hemmer-Hansen J., & Thomsen T. B. (2021). Estimating migration patterns of fish from otolith chemical composition time series. *Canadian Journal of Fisheries and Aquatic Sciences*, 78(10), 1512–1523. https://doi.org/10.1139/cjfas-2020-0356

Allemand D., Mayer-Gostan N., De Pontual H., Boeuf G., & Payan, P. (2007). Fish Otolith Calcification in Relation to Endolymph Chemistry. *In Handbook of Biomineralization* (pp.291–308). https://doi.org/10.1002/9783527619443.ch17

Allen G. J., & Sanders D. (1994). Two Voltage-Gated, Calcium Release Channels Coreside in the Vacuolar Membrane of Broad Bean Guard Cells. *The Plant Cell*, 685–694. https://doi.org/10.1105/tpc.6.5.685

Allen K. A., Hönisch B., Eggins S. M., Haynes L. L., Rosenthal Y., & Yu J. (2016). Trace element proxies for surface ocean conditions: A synthesis of culture calibrations with planktic foraminifera. *Geochimica et Cosmochimica Acta*, 193, 197–221. https://doi.org/10.1016/j.gca.2016.08.015

Angell R. W. (1967). The Process of Chamber Formation in the Foraminifer Rosalina floridana (Cushman). *The Journal of Protozoology*, 14(4), 566–574. https://doi.org/10.1111/j.1550-7408.1967.tb02043.x

Avigliano E., Callicó-Fortunato R., Buitrago J., & Volpedo A. V. (2015). A microquímica do otólito é um indicador do habitat de Mugil curema no sudeste do Mar Caribenho? *Brazilian Journal of Biology*, 75(4), S45–S51. https://doi.org/10.1590/1519-6984.01014

Bareille G., Vignon M., Chappaz A., Fontaine A., Tabouret H., Morat F., Martin J., Aymes J. C., Daverat F., Pécheyran C., & Donard O. (2024). Freshwater fish otoliths record signals from both water and physiological processes: new insights from Sr/Ca and Ba/Ca ratios. *Canadian Journal of Fisheries and Aquatic Sciences*, 81(2), 223–240. https://doi.org/10.1139/cjfas-2022-0030

Bath Martin G., & Thorrold S. (2005). Temperature and salinity effects on magnesium, manganese, and barium incorporation in otoliths of larval and early juvenile spot Leiostomus xanthurus. *Marine Ecology Progress Series*, 293, 223–232. https://doi.org/10.3354/meps293223

Bentov S., & Erez J. (2006). Impact of biomineralization processes on the Mg content of foraminiferal shells: A biological perspective. *Geochemistry, Geophysics, Geosystems, 7*(1). https://doi.org/10.1029/2005GC001015

Bernd R. Schöne, Zengjie Zhang, Dorit Jacob, David P. Gillikin, Thomas Tütken, D.Garbe-Schönberg, Ted MccoN.Naugey, & Analia Soldati. (2010). Effect of organic matrices on the determination of the trace element chemistry (Mg, Sr, Mg/Ca, Sr/Ca) of aragonitic bivalve shells (Arctica islandica)—Comparison of ICP-OES and LA-ICP-MS data. *Geochemical Journal, 44(1), 23–37*. https://doi.org/10.2343/geochemj.1.0045

BorelliG., Mayer-Gostan N., De Pontual H., Boeuf G., & Payan P. (2001). Biochemical Relationships Between Endolymph and Otolith Matrix in the Trout (Oncorhynchus mykiss) and Turbot (Psetta maxima). *Calcified Tissue International*, 69(6), 356–364. https://doi.org/10.1007/s00223-001-2016-8

Branson O., Redfern S. A. T., Tyliszczak T., Sadekov A., Langer G., Kimoto K., & Elderfield H. (2013). The coordination of Mg in foraminiferal calcite. *Earth and Planetary Science Letters*, 383, 134–141. https://doi.org/10.1016/j.epsl.2013.09.037

Brazier J.-M., Blanchard M., Méheut M., Schmitt A.-D., Schott J., & Mavromatis V. (2023). Experimental and theoretical investigations of stable Sr isotope fractionation during its incorporation in

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

aragonite. *Geochimica et Cosmochimica Acta*, *358*, 134–147. https://doi.org/10.1016/j.gca.2023.08.013

Brazier J. M., Goetschl K. E., Dietzel M., & Mavromatis V. (2024a). Effect of mineral growth rate on Zinc incorporation into calcite and aragonite. *Chemical Geology*, 643. https://doi.org/10.1016/j.chemgeo.2023.121821

Brazier J. M., Harrison A. L., Rollion-Bard C., & Mavromatis V. (2024b). Controls of temperature and mineral growth rate on lithium and sodium incorporation in abiotic aragonite. *Chemical Geology*, 654. https://doi.org/10.1016/j.chemgeo.2024.122057

Broecker W. S., & Peng T.-H. (1982). TRACERS IN THE SEA.

Bruland K. W. (1989). Complexation of zinc by natural organic ligands in the central North Pacific. *Limnology and Oceanography*, 34(2), 269–285. https://doi.org/10.4319/lo.1989.34.2.0269

Campana S. (1999). Chemistry and composition of fish otoliths: pathways, mechanisms and applications. *Marine Ecology Progress Series*, 188, 263–297. https://doi.org/10.3354/meps188263

Campana S. E., & Thorrold S. R. (2001). Otoliths, increments, and elements: keys to a comprehensive understanding of fish populations? *Canadian Journal of Fisheries and Aquatic Sciences*, 58(1), 30–38. https://doi.org/10.1139/f00-177

Cavole L. M., Limburg K. E., Gallo N. D., Vea Salvanes A. G., Ramírez-Valdez A., Levin L. A., Oropeza O. A., Hertwig A., Liu M. C., & McKeegan K. D. (2023). Otoliths of marine fishes record evidence of low oxygen, temperature and pH conditions of deep Oxygen Minimum Zones. *Deep-Sea Research Part I: Oceanographic Research Papers,* 191. https://doi.org/10.1016/j.dsr.2022.103941

Checa A. G. (2018). Physical and Biological Determinants of the Fabrication of Molluscan Shell Microstructures. *Frontiers in Marine Science*, 5. https://doi.org/10.3389/fmars.2018.00353

Chung M.-T., Trueman C. N., Godiksen J. A., & Grønkjær P. (2019). Otolith δ13C values as a metabolic proxy: approaches and mechanical underpinnings. *Marine and Freshwater Research*, 70(12), 1747. https://doi.org/10.1071/MF18317

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

Cohen A. L., Gaetani G. A., Lundälv T., Corliss B. H., & George R. Y. (2006). Compositional variability in a cold-water scleractinian, Lophelia pertusa: New insights into "vital effects." *Geochemistry, Geophysics, Geosystems, 7*(12). https://doi.org/10.1029/2006GC001354

Crenshaw M. A. (1972). The inorganic composition of molluscan extrapallial fluid. *The Biological Bulletin*, 143(3), 506–512. https://doi.org/10.2307/1540180

Cuif J.-P., Dauphin Y., & Sorauf J. E. (2010). Biominerals and Fossils Through Time. *Cambridge University Press*. https://doi.org/10.1017/CBO9780511781070

Devereux I. (1967). Temperature Measurements from Oxygen Isotope Ratios of Fish Otoliths. *Science*, 155(3770), 1684–1685. https://doi.org/10.1126/science.155.3770.1684

Dietzel M., Gussone N., & Eisenhauer A. (2004). Co-precipitation of Sr2+ and Ba2+ with aragonite by membrane diffusion of CO2 between 10 and 50 °C. *Chemical Geology*, 203(1–2), 139–151. https://doi.org/10.1016/j.chemgeo.2003.09.008

D'Olivo J. P., & McCulloch M. T. (2017). Response of coral calcification and calcifying fluid composition to thermally induced bleaching stress. *Scientific Reports*, 7(1), 2207. https://doi.org/10.1038/s41598-017-02306-x

Edeyer A., De Pontual H., Payan P., Troadec H., Sévère A., & Mayer-Gostan N. (2000). Daily variations of the saccular endolymph and plasma compositions in the turbot Psetta maxima: relationship with the diurnal rhythm in otolith formation. In Source: Marine *Ecology Progress Series* (Vol. 192:287-294).

Elder K. L., Jones G. A. & Bolz G. (1996). Distribution of otoliths in surficial sediments of the U.S. Atlantic continental shelf and slope and potential for reconstructing Holocene fish stocks. *Paleoceanography,* 11(3), 359–367. https://doi.org/10.1029/96PA00042

Elderfield H., Bertram C. J. & Erez J. (1996). A biomineralization model for the incorporation of trace elements into foraminiferal calcium carbonate. *Earth and Planetary Science Letters*, 142(3–4), 409–423. https://doi.org/10.1016/0012-821X(96)00105-7

Elderfield H., & Ganssen G. (2000). Past temperature and δ18O of surface ocean waters inferred from foraminiferal Mg/Ca ratios. *Nature*, 405(6785), 442–445. https://doi.org/10.1038/35013033

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

Fraile I., Arrizabalaga H., Santiago J., Goñi N., Arregi I., Madinabeitia S., Wells R. J. D., & Rooker J. R. (2016). Otolith chemistry as an indicator of movements of albacore (Thunnus alalunga) in the North Atlantic Ocean. *Marine and Freshwater Research,* 67(7), 1002. https://doi.org/10.1071/MF15097

Füger A., Konrad F., Leis A., Dietzel M., & Mavromatis V. (2019). Effect of growth rate and pH on lithium incorporation in calcite. *Geochimica et Cosmochimica Acta*, 248, 14–24. https://doi.org/10.1016/j.gca.2018.12.040

Gaetani G. A., & Cohen A. L. (2006). Element partitioning during precipitation of aragonite from seawater: A framework for understanding paleo proxies. *Geochimica et Cosmochimica Acta,* 70(18), 4617–4634. https://doi.org/10.1016/j.gca.2006.07.008

Goetschl K. E., Purgstaller B., Dietzel M., & Mavromatis V. (2019). Effect of sulfate on magnesium incorporation in low-magnesium calcite. *Geochimica et Cosmochimica Acta,* 265, 505–519. https://doi.org/10.1016/j.gca.2019.07.024

Halden N. M., & Friedrich L. A. (2008). Trace-element distributions in fish otoliths: natural markers of life histories, environmental conditions and exposure to tailings effluence. *Mineralogical Magazine,* 72(2), 593–605. https://doi.org/10.1180/minmag.2008.072.2.593

Hermann T. W., Stewart D. J., Limburg K. E., & Castello L. (2016). Unravelling the life history of Amazonian fishes through otolith microchemistry. *Royal Society Open Science*, 3(6), 160206. https://doi.org/10.1098/rsos.160206

Hohn S., & Merico A. (2015). Quantifying the relative importance of transcellular and paracellular ion transports to coral polyp calcification. *Frontiers in Earth Science*, 2. https://doi.org/10.3389/feart.2014.00037

Höpker S. N., Wu, H. C., Lucassen F., Sadio O., Brochier T., Nuworkpor I. Y., Kasemann S. A., Merschel P., & Westphal H. (2022). Sr Isotope Ratios ($^{87}Sr/^{86}Sr$) in Water and Fish Otoliths as Estuarine Salinity Tracers: Case Studies from Three NW African Rivers. *Estuaries and Coasts*, 45(6), 1780–1802. https://doi.org/10.1007/s12237-021-01041-x

Hüssy K., Limburg K. E., de Pontual H., Thomas O. R. B., Cook P. K., Heimbrand Y., Blass M., & Sturrock A. M. (2021). Trace Element Patterns in Otoliths: The Role of Biomineralization. *Reviews in*

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

Fisheries Science and Aquaculture (Vol. 29, Issue 4, pp. 445–477). Taylor and Francis Ltd. https://doi.org/10.1080/23308249.2020.1760204

Izzo C., Doubleday Z. A., & Gillanders B. M. (2016). Where do elements bind within the otoliths of fish? *Marine and Freshwater Research*, 67(7), 1072. https://doi.org/10.1071/MF15064

Izzo C., Reis-Santos P., & Gillanders B. M. (2018). Otolith chemistry does not just reflect environmental conditions: A meta-analytic evaluation. *Fish and Fisheries*, 19(3), 441–454. https://doi.org/10.1111/faf.12264

Kadan Y., Tollervey F., Varsano N., Mahamid J., & Gal A. (2021). Intracellular nanoscale architecture as a master regulator of calcium carbonate crystallization in marine microalgae. *Proceedings of the National Academy of Sciences*, 118(46). https://doi.org/10.1073/pnas.2025670118

Kalish J. M. (1989). Otolith microchemistry: validation of the effects of physiology, age and environment on otolith composition. *Journal of Experimental Marine Biology and Ecology*, 132(3), 151–178. https://doi.org/10.1016/0022-0981(89)90126-3

Kalish J. M. (1991). Determinants of otolith chemistry: seasonal variation in the composition of blood plasma, endolymph and otoliths of bearded rock cod Pseudophycis barbatus. *Marine Ecology Progress Series*, 74, 137–159.

Katz M. E., Cramer B. S., Franzese A., Honisch B., Miller K. G., Rosenthal Y., & Wright J. D. (2010). Traditional and emerging geochemical proxies in foraminifera. *The Journal of Foraminiferal Research*, 40(2), 165–192. https://doi.org/10.2113/gsjfr.40.2.165

Kawabata T., Takeda Y., Hori M., Kandori K., & Yaji T. (2021). Partitioning of sodium into calcium carbonates synthesized at 10–40 °C: Influence of organic ligands and temperature. *Chemical Geology*, 559. https://doi.org/10.1016/j.chemgeo.2020.119904

Kennedy B. P., Klaue A., Blum J. D., Folt C. L., & Nislow K. H. (2002). Reconstructing the lives of fish using Sr isotopes in otoliths. *Canadian Journal of Fisheries and Aquatic Sciences*, 59(6), 925–929. https://doi.org/10.1139/f02-070

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

Kerr L., Secor D., & Kraus R. (2007). Stable isotope (δ13C and δ18O) and Sr/Ca composition of otoliths as proxies for environmental salinity experienced by an estuarine fish. *Marine Ecology Progress Series*, 349, 245–253. https://doi.org/10.3354/meps07064

Krężel A., & Maret W. (2016). The biological inorganic chemistry of zinc ions. Archives of *Biochemistry and Biophysics*, 611, 3–19. https://doi.org/10.1016/j.abb.2016.04.010

Lall S. P., & Kaushik S. J. (2021). Nutrition and Metabolism of Minerals in Fish. *Animals,* 11(9), 2711. https://doi.org/10.3390/ani11092711

Langer G., Gussone N., Nehrke G., Riebesell U., Eisenhauer A., Kuhnert H., Rost B., Trimborn S., & Thoms S. (2006). Coccolith strontium to calcium ratios in Emiliania huxleyi: The dependence on seawater strontium and calcium concentrations. *Limnology and Oceanography,* 51(1), 310–320. https://doi.org/10.4319/lo.2006.51.1.0310

Langer G., Nehrke G., Thoms S., & Stoll H. (2009). Barium partitioning in coccoliths of Emiliania huxleyi. *Geochimica et Cosmochimica Acta*, 73(10), 2899–2906. https://doi.org/10.1016/j.gca.2009.02.025

Langer G., Sadekov A., Nehrke G., Baggini C., Rodolfo-Metalpa R., Hall-Spencer J. M., Cuoco E., Bijma J., & Elderfield H. (2018). Relationship between mineralogy and minor element partitioning in limpets from an Ischia CO2 vent site provides new insights into their biomineralization pathway. *Geochimica et Cosmochimica Acta*, 236, 218–229. https://doi.org/10.1016/j.gca.2018.02.044

Langer G., Sadekov A., Thoms S., Keul N., Nehrke G., Mewes A., Greaves M., Misra S., Reichart G.-J., de Nooijer L. J., Bijma J., & Elderfield H. (2016). Sr partitioning in the benthic foraminifera Ammonia aomoriensis and Amphistegina lessonii. *Chemical Geology*, 440, 306–312. https://doi.org/10.1016/j.chemgeo.2016.07.018

Langer G, Taylor A.R, Walker C.E, Meyer E.M, Ben Joseph O, Gal A, Harper G.M, Probert I, Brownlee C, Wheeler G.L. (2021) Role of silicon in the development of complex crystal shapes in coccolithophores. *New Phytol*. 2021 Sep;231(5):1845-1857. doi: 10.1111/nph.17230

Lewis G. N., & Randall M. (1921). The activity coefficient of strong electrolytes. *Journal of the American Chemical Society*, 43(5), 1112–1154. https://doi.org/10.1021/ja01438a014

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

Limburg K. E., & Casini M. (2018). Effect of marine hypoxia on Baltic Sea cod Gadus morhua: Evidence from otolith chemical proxies. Frontiers in Marine Science, 5(DEC). https://doi.org/10.3389/fmars.2018.00482

Limburg K. E., Olson C., Walther Y., Dale D., Slomp C. P., & Høie H. (2011). Tracking Baltic hypoxia and cod migration over millennia with natural tags. Proceedings of the National Academy of Sciences of the United States of America, 108(22). https://doi.org/10.1073/pnas.1100684108

Limburg K. E., Walther B. D., Lu Z., Jackman G., Mohan J., Walther Y., Nissling A., Weber P. K., & Schmitt A. K. (2015). In search of the dead zone: Use of otoliths for tracking fish exposure to hypoxia. Journal of Marine Systems, 141, 167–178. https://doi.org/10.1016/j.jmarsys.2014.02.014

Longmore C., Trueman C. N., Neat F., O'Gorman E. J., Milton J. A., & Mariani S. (2011). Otolith geochemistry indicates life-long spatial population structuring in a deep-sea fish, Coryphaenoides rupestris. Marine Ecology Progress Series, 435, 209–224. https://doi.org/10.3354/meps09197

Lorens R. B., & Bender M. L. (1980). The impact of solution chemistry on Mytilus edulis calcite and aragonite. *Geochimtco Er Cormuchimico Acra*, 44, 1265–1278.

Lueders-Dumont J. (2024). Postcards from prehistoric marine food webs: nitrogen isotopes in fish otoliths as a paleoecological archive. https://doi.org/10.1130/abs/2024AM-403326

Lueders-Dumont J. A., Wang X. T., Jensen O. P., Sigman D. M., & Ward B. B. (2018). Nitrogen isotopic analysis of carbonate-bound organic matter in modern and fossil fish otoliths. Geochimica et Cosmochimica Acta, 224, 200–222. https://doi.org/10.1016/j.gca.2018.01.001

Marriott C. S., Henderson G. M., Crompton R., Staubwasser M., & Shaw S. (2004). Effect of mineralogy, salinity, and temperature on Li/Ca and Li isotope composition of calcium carbonate. *Chemical Geology,* 212(1–2), 5–15. https://doi.org/10.1016/j.chemgeo.2004.08.002

Marshall W. S. (2002). Na (+), Cl (-), Ca (2+) and Zn (+2) transport by fish gills: retrospective review and prospective synthesis. *Journal of Experimental Zoology*, 293(3), 264–283. https://doi.org/10.1002/jez.10127

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

Martino J. C., Doubleday Z. A., Chung M.-T., & Gillanders B. M. (2020). Experimental support towards a metabolic proxy in fish using otolith carbon isotopes. Journal of Experimental Biology, 223(6). https://doi.org/10.1242/jeb.217091

Martino J. C., Doubleday Z. A., Fowler A. J., & Gillanders B. M. (2021). Corrigendum to: Identifying physiological and environmental influences on otolith chemistry in a coastal fishery species. Marine and Freshwater Research, 72(6), 922. https://doi.org/10.1071/MF20196_CO

Mavromatis V., Brazier J. M., & Goetschl K. E. (2022). Controls of temperature and mineral growth rate on Mg incorporation in aragonite. *Geochimica et Cosmochimica Acta*, 317, 53–64. https://doi.org/10.1016/j.gca.2021.10.015

Mavromatis V., Goetschl K. E., Grengg C., Konrad F., Purgstaller B., & Dietzel M. (2018). Barium partitioning in calcite and aragonite as a function of growth rate. *Geochimica et Cosmochimica Acta,* 237, 65–78. https://doi.org/10.1016/j.gca.2018.06.018

Mavromatis V., Immenhauser A., Buhl D., Purgstaller B., Baldermann A., & Dietzel M. (2017). Effect of organic ligands on Mg partitioning and Mg isotope fractionation during low-temperature precipitation of calcite in the absence of growth rate effects. *Geochimica et Cosmochimica Acta*, 207, 139–153. https://doi.org/10.1016/j.gca.2017.03.020

Mccormick S., & Ac Kinlay D. M. (2000). Ion Regulation In Fish. 4th Ed. Prentice-Hall, 85–89.

McFadden A., Wade B., Izzo C., Gillanders B. M., Lenehan C. E., & Pring A. (2016). Quantitative electron microprobe mapping of otoliths suggests elemental incorporation is affected by organic matrices: Implications for the interpretation of otolith chemistry. *Marine and Freshwater Research*, 67(7), 889–898. https://doi.org/10.1071/MF15074

Melancon S., Fryer B. J., Gagnon J. E., & Ludsin S. A. (2008). Mineralogical approaches to the study of biomineralization in fish otoliths. *Mineralogical Magazine*, 72(2), 627–637. https://doi.org/10.1180/minmag.2008.072.2.627

Melancon S., Fryer B. J., Ludsin S. A., Gagnon J. E., & Yang Z. (2005). Effects of crystal structure on the uptake of metals by lake trout (Salvelinus namaycush) otoliths. *Canadian Journal of Fisheries and Aquatic Sciences,* 62(11), 2609–2619. https://doi.org/10.1139/f05-161

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

Melancon S., Fryer B. J., & Markham J. L. (2009). Chemical analysis of endolymph and the growing otolith: Fractionation of metals in freshwater fish species. *Environmental Toxicology and Chemistry*, 28(6), 1279–1287. https://doi.org/10.1897/08-358.1

Mellars P. A., Wilkinson M. R., & Fieller N. R. J. (1980). Fish Otoliths as Indicators of Seasonality in Prehistoric Shell Middens: The Evidence from Oronsay (Inner Hebrides). *Proceedings of the Prehistoric Society*, 46(NA), 19–44. https://doi.org/10.1017/S0079497X00009300

Meyer E. M., Langer G., Brownlee C., Wheeler G. L., & Taylor A. R. (2020). Sr in coccoliths of Scyphosphaera apsteinii: Partitioning behavior and role in coccolith morphogenesis. *Geochimica et Cosmochimica Acta*, 285, 41–54. https://doi.org/10.1016/j.gca.2020.06.023

Miller J. A., & Hurst T. P. (2020). Growth Rate, Ration, and Temperature Effects on Otolith Elemental Incorporation. Frontiers in Marine Science, 7. https://doi.org/10.3389/fmars.2020.00320

Miller M. B., Clough A. M., Batson J. N., & Vachet R. W. (2006). Transition metal binding to cod otolith proteins. *Journal of Experimental Marine Biology and Ecology*, 329(1), 135–143. https://doi.org/10.1016/j.jembe.2005.08.016

Mitsuguchi, T., Matsumoto, E. & Uchida, T. Mg/Ca and Sr/Ca ratios of Porites coral skeleton: Evaluation of the effect of skeletal growth rate. Coral Reefs 22, 381–388 (2003). https://doi.org/10.1007/s00338-003-0326-1

Mondal S., Chakrabarti R., & Ghosh P. (2022). A multi-proxy (δ44/40Ca, Sr/Ca, and Δ47) study of fish otoliths for determination of seawater temperature. Chemical Geology, 605, 120950. https://doi.org/10.1016/j.chemgeo.2022.120950

Morat F., Blamart D., Bounket B., Argillier C., Carrel G., & Maire A. (2023). Reconstructing the thermal history of fish juveniles using stable oxygen isotope analysis of otoliths. Frontiers in Environmental Science, 11. https://doi.org/10.3389/fenvs.2023.1213239

Moura G., Vilarinho L., Santos A. C., & Machado J. (2000). Organic compounds in the extrapalial fluid and haemolymph of Anodonta cygnea (L.) with emphasis on the seasonal biomineralization process. *Comparative Biochemistry and Physiology Part B: Biochemistry and Molecular Biology*, 125(3), 293–306. https://doi.org/10.1016/S0305-0491(99)00192-3

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

Mucci A., Canuel R., & Zhong S. (1989). The solubility of calcite and aragonite in sulfate-free seawater and the seeded growth kinetics and composition of the precipitates at 25°C. *Chemical Geology*, 74(3–4), 309–320. https://doi.org/10.1016/0009-2541(89)90040-5

Nachshen D. A., & Blaustein M. P. (1982). Influx of calcium, strontium, and barium in presynaptic nerve endings. *The Journal of General Physiology*, 79(6), 1065–1087. https://doi.org/10.1085/jgp.79.6.1065

Nehrke G., Keul, N., Langer G., de Nooijer L. J., Bijma J., & Meibom A. (2013). A new model for biomineralization and trace-element signatures of Foraminifera tests. *Biogeosciences,* 10(10), 6759–6767. https://doi.org/10.5194/bg-10-6759-2013

Nehrke G., & Langer G. (2023). Proxy Archives Based on Marine Calcifying Organisms and the Role of Process-Based Biomineralization Concepts. *Minerals*, 13(4). https://doi.org/10.3390/min13040561

Nehrke G., Reichart G. J., Van Cappellen P., Meile C., & Bijma J. (2007). Dependence of calcite growth rate and Sr partitioning on solution stoichiometry: Non-Kossel crystal growth. *Geochimica et Cosmochimica Acta*, 71(9), 2240–2249. https://doi.org/10.1016/j.gca.2007.02.002

Nelson T. R., & Powers S. P. (2020). Elemental Concentrations of Water and Otoliths as Salinity Proxies in a Northern Gulf of Mexico Estuary. Estuaries and Coasts, 43(4), 843–864. https://doi.org/10.1007/s12237-019-00686-z

Nomaki H., LeKieffre C., Escrig S., Meibom A., Yagyu S., Richardson E. A., Matsuzaki T., Murayama M., Geslin E., & Bernhard J. M. (2018). Innovative TEM-coupled approaches to study foraminiferal cells. *Marine Micropaleontology*, 138, 90–104. https://doi.org/10.1016/j.marmicro.2017.10.002

Olsher Uriel., Izatt R. M., Bradshaw J. S., & Dalley N. Kent. (1991). Coordination chemistry of lithium ion: a crystal and molecular structure review. *Chemical Reviews*, 91(2), 137–164. https://doi.org/10.1021/cr00002a003

Padilla A. J., Brown R. J., & Wooller M. J. (2015). Strontium isotope analyses (87Sr/86Sr) of otoliths from anadromous Bering cisco (Coregonus laurettae) to determine stock composition. ICES Journal of Marine Science, 72(7), 2110–2117. https://doi.org/10.1093/icesjms/fsv096

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

Pallacks S., Ziveri P., Schiebel R., Vonhof H., Rae J. W. B., Littley E., Garcia-Orellana J., Langer G., Grelaud M., & Martrat B. (2023). Anthropogenic acidification of surface waters drives decreased biogenic calcification in the Mediterranean Sea. *Communications Earth & Environment*, 4(1), 301. https://doi.org/10.1038/s43247-023-00947-7

Payan P., Borelli G., Boeuf G., & Mayer-Gostan N. (1998). Relationship between otolith and somatic growth: consequence of starvation on acid-base balance in plasma and endolymph in the rainbow trout Oncorhynchus mykiss. *In Fish Physiology and Biochemistry* (Vol. 19).

Payan P., Borelli G., Priouzeau F., De Pontual H., Bœuf G., & Mayer-Gostan N. (2002). Otolith growth in trout Oncorhynchus mykiss : supply of Ca2+ and Sr2+ to the saccular endolymph. *Journal of Experimental Biology*, 205(17), 2687–2695. https://doi.org/10.1242/jeb.205.17.2687

Payan P., De Pontual H., Bœuf G., & Mayer-Gostan N. (2004). Endolymph chemistry and otolith growth in fish. *Comptes Rendus - Palevol*, 3(6-7 SPEC.ISS.), 535–547. https://doi.org/10.1016/j.crpv.2004.07.013

Payan P., Edeyer A., Pontual N. DE, Borelli G., Boeuf G., Mayer-Gostan N., Lè ne De Pontual H., & Mayer-Gostan N. (1999). Chemical composition of saccular endolymph and otolith in fish inner ear: lack of spatial uniformity. *American physiological society, 277(1), 123-131,* doi:10.1152/ajpregu.1999.277.1.R123

Payan P., Kossmann H., Watrin A., Mayer-Gostan N., & Boeuf G. (1997). Ionic Composition of Endolymph in Teleosts: Origin and Importance of Endolymph Alkalinity. *Journal of Experimental Biology*, 200(13), 1905–1912. https://doi.org/10.1242/jeb.200.13.1905

Phillis C. C., Ostrach D. J., Ingram B. L., & Weber P. K. (2011). Evaluating otolith Sr/Ca as a tool for reconstructing estuarine habitat use. Canadian Journal of Fisheries and Aquatic Sciences, 68(2), 360–373. https://doi.org/10.1139/F10-152

Pors Nielsen, S. (2004). The biological role of strontium. Bone, 35(3), 583–588. https://doi.org/10.1016/j.bone.2004.04.026

Rao Z. C., Lueders-Dumont J. A., Stringer G. L., Ryu Y., Zhao K., Myneni S. C., Oleynik S., Haug G. H., Martinez-Garcia A., & Sigman D. M. (2024). A nitrogen isotopic shift in fish otolith–bound organic matter during the Late Cretaceous. Proceedings of the National Academy of Sciences, 121(32). https://doi.org/10.1073/pnas.2322863121

Reis-Santos P., Gillanders B. M., Sturrock A. M., Izzo C., Oxman D. S., Lueders-Dumont J. A., Hüssy K., Tanner S. E., Rogers T., Doubleday Z. A., Andrews A. H., Trueman C., Brophy D., Thiem J. D., Baumgartner L. J., Willmes M., Chung M. T., Charapata P., Johnson R. C., … Walther B. D. (2023). Reading the biomineralized book of life: expanding otolith biogeochemical research and applications for fisheries and ecosystem-based management. *Reviews in Fish Biology and Fisheries 33(2), 411–449. Springer Science and Business Media Deutschland GmbH*. https://doi.org/10.1007/s11160-022-09720-z

Rosales I., Robles S., & Quesada S. (2004). Elemental and Oxygen Isotope Composition of Early Jurassic Belemnites: Salinity vs. Temperature Signals. Journal of Sedimentary Research, 74(3), 342–354. https://doi.org/10.1306/112603740342

Sackett D. K., Chrisp J. K., & Farmer T. M. (2024). Isotopes and otolith chemistry provide insight into the biogeochemical history of mercury in southern flounder across a salinity gradient. Environmental Science: Processes & Impacts, 26(2), 233–246. https://doi.org/10.1039/D3EM00482A

Salisbury F. B., & Ross C. W. (1992). Plant Physiology. *Wadsworth Publishing Company*.

Saygın S., Polat N., Willmes M., Lewis L. S., Hobbs J. A., Atıcı A. A., & Elp M. (2022). Strontium isotopes in otoliths reveal a diversity of natal origins for Tarek (Alburnus tarichi) in Lake Van, Turkey. Fisheries Research, 255, 106441. https://doi.org/10.1016/j.fishres.2022.106441

Shiao J. C., Ložys L., Iizuka Y., & Tzeng W. N. (2006). Migratory patterns and contribution of stocking to the population of European eel in Lithuanian waters as indicated by otolith Sr:Ca ratios. *Journal of Fish Biology*, 69(3), 749–769. https://doi.org/10.1111/j.1095-8649.2006.01147.x

Sirot C., Grønkjær P., Pedersen J., Panfili J., Zetina-Rejon M., Tripp-Valdez A., Ramos-Miranda J., Flores-Hernandez D., Sosa-Lopez A., & Darnaude A. (2017). Using otolith organic matter to detect diet shifts in Bardiella chrysoura, during a period of environmental changes. Marine Ecology Progress Series, 575, 137–152. https://doi.org/10.3354/meps12166

Stanley J. K., & Byrne R. H. (1990). Inorganic complexation of Zinc (II) in seawater. *Geochimica et Cosmochimica Acta*, 54(3), 753–760. https://doi.org/10.1016/0016-7037(90)90370-Z

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

Stoll H., Langer G., Shimizu N., & Kanamaru K. (2012). B/Ca in coccoliths and relationship to calcification vesicle pH and dissolved inorganic carbon concentrations. Geochimica et *Cosmochimica Acta*, 80, 143–157. https://doi.org/10.1016/j.gca.2011.12.003

Sturrock A. M., Hunter E., Milton J. A., Johnson R. C., Waring C. P., & Trueman C. N. (2015). Quantifying physiological influences on otolith microchemistry. *Methods in Ecology and Evolution*, 6(7), 806–816. https://doi.org/10.1111/2041-210X.12381

Sturrock A. M., Trueman C. N., Darnaude A. M., & Hunter E. (2012). Can otolith elemental chemistry retrospectively track migrations in fully marine fishes? Journal of Fish Biology, 81(2), 766–795. https://doi.org/10.1111/j.1095-8649.2012.03372.x

Sturrock A., Trueman C., Milton J., Waring C., Cooper M., & Hunter E. (2014). Physiological influences can outweigh environmental signals in otolith microchemistry research. Marine Ecology Progress Series, 500, 245–264. https://doi.org/10.3354/meps10699

Takeuchi T., Sarashina I., Iijima M., & Endo K. (2008). In vitro regulation of CaCO3 crystal polymorphism by the highly acidic molluscan shell protein Aspein. *FEBS Letters*, 582(5), 591–596. https://doi.org/10.1016/j.febslet.2008.01.026

Tanner S. E., Reis-Santos P., Vasconcelos R. P., Fonseca V. F., França S., Cabral H. N., & Thorrold S. R. (2013). Does otolith geochemistry record ambient environmental conditions in a temperate tidal estuary? Journal of Experimental Marine Biology and Ecology, 441, 7–15. https://doi.org/10.1016/j.jembe.2013.01.009

Thomas O. R. B., Ganio K., Roberts B. R., & Swearer S. E. (2017). Trace element–protein interactions in endolymph from the inner ear of fish: implications for environmental reconstructions using fish otolith chemistry. *Metallomics,* 9(3), 239–249. https://doi.org/10.1039/c6mt00189k

Thomas O. R. B., & Swearer S. E. (2019). Otolith Biochemistry—A Review. In Reviews in *Fisheries Science and Aquaculture* (Vol. 27, Issue 4, pp. 458–489). Taylor and Francis Inc. https://doi.org/10.1080/23308249.2019.1627285

Thomas O. R. B., Swearer, S. E., Kapp, E. A., Peng, P., Tonkin-Hill, G. Q., Papenfuss, A., Roberts, A., Bernard, P., & Roberts, B. R. (2019). The inner ear proteome of fish. *FEBS Journal*, 286(1), 66–81. https://doi.org/10.1111/febs.14715

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

Urey H. C., Lowenstam H. A. , Epstein S., & McKinney C. R. (1951). Measurement of Paleotemperatures and Temperatures of the Upper Cretaceous of England, Denmark, and the Southeastern United States. *Geological Society of America Bulletin*, 62(4), 399–416.

Vaisvil A., Willmes M., Enriquez E. J., Klein Z. B., & Caldwell C. A. (2023). A needle in a haystack: strontium isotopes (87Sr/86Sr) in otoliths identify origin of largemouth bass from a large Southwest reservoir. Canadian Journal of Fisheries and Aquatic Sciences, 80(12), 1857–1868. https://doi.org/10.1139/cjfas-2023-0148

Walker J. M., & Langer G. (2021). Coccolith crystals: Pure calcite or organic-mineral composite structures? *Acta Biomaterialia*, 125, 83–89. https://doi.org/10.1016/j.actbio.2021.02.025

Walther B. D. (2019). The art of otolith chemistry: interpreting patterns by integrating perspectives. *Marine and Freshwater Research*, 70(12), 1643. https://doi.org/10.1071/MF18270

Walther B. D. & Limburg K. E. (2012). The use of otolith chemistry to characterize diadromous migrations. Journal of Fish Biology, 81(2), 796–825. https://doi.org/10.1111/j.1095-8649.2012.03371.x

Wells B. K., Campana S. E., & Gillanders B. M. (2014). Otolith chemistry to describe movements and life-history parameters of fishes: Hypotheses, assumptions, limitations and inferences. https://www.researchgate.net/publication/231180600

Wilbur K. M., & Watabe N. (1963). Experimental studies on calcification in molluscs and the alga coccolithus huxleyi. *Annals of the New York Academy of Sciences*, 109(1), 82–112. https://doi.org/10.1111/j.1749-6632.1963.tb13463.x

Willmes M., Lewis L. S., Davis B. E., Loiselle L., James H. F., Denny C., Baxter R., Conrad J. L., Fangue N. A., Hung T. C., Armstrong R. A., Williams I. S., Holden P., & Hobbs J. A. (2019). Calibrating temperature reconstructions from fish otolith oxygen isotope analysis for California's critically endangered Delta Smelt. Rapid Communications in Mass Spectrometry, 33(14), 1207–1220. https://doi.org/10.1002/rcm.8464

Wolthers M., Di Tommaso D., Du Z., & de Leeuw N. H. (2013). Variations in calcite growth kinetics with surface topography: molecular dynamics simulations and process-based growth kinetics modelling. *CrystEngComm,* 15(27), 5506. https://doi.org/10.1039/c3ce40249e

https://doi.org/10.5194/egusphere-2025-5251
Preprint. Discussion started: 7 November 2025

Yuryev V. P., Grinberg N. V., Braudo E. E., & Tolstoguzov V. B. (1979). A study of the boundary conditions for the gel formation of alginates of polyvalent metals. *Starch - Stärke*, 31(4), 121–124. https://doi.org/10.1002/star.19790310406

Zazzo A., Smith G. R., Patterson W. P., & Dufour E. (2006). Life history reconstruction of modern and fossil sockeye salmon (Oncorhynchus nerka) by oxygen isotopic analysis of otoliths, vertebrae, and teeth: Implication for paleoenvironmental reconstructions. Earth and Planetary Science Letters, 249(3–4), 200–215. https://doi.org/10.1016/j.epsl.2006.07.003

Zhong S., & Mucci A. (1989). Calcite and aragonite precipitation from seawater solutions of various salinities: Precipitation rates and overgrowth compositions. *Chemical Geology,* 78 (3-4), 283-299. https://doi.org/10.1016/0009-2541(89)90064-8

Ziveri P., Stoll H., Probert I., Klaas C., Geisen M., Ganssen G., & Young J. (2003). Stable isotope 'vital effects' in coccolith calcite. *Earth and Planetary Science Letters*, 210(1–2), 137–149. https://doi.org/10.1016/S0012-821X(03)00101-8

Ziveri P., Thoms S., Probert I., Geisen M., & Langer G. (2012). A universal carbonate ion effect on stable oxygen isotope ratios in unicellular planktonic calcifying organisms. *Biogeosciences*, 9(3), 1025–1032. https://doi.org/10.5194/bg-9-1025-2012