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

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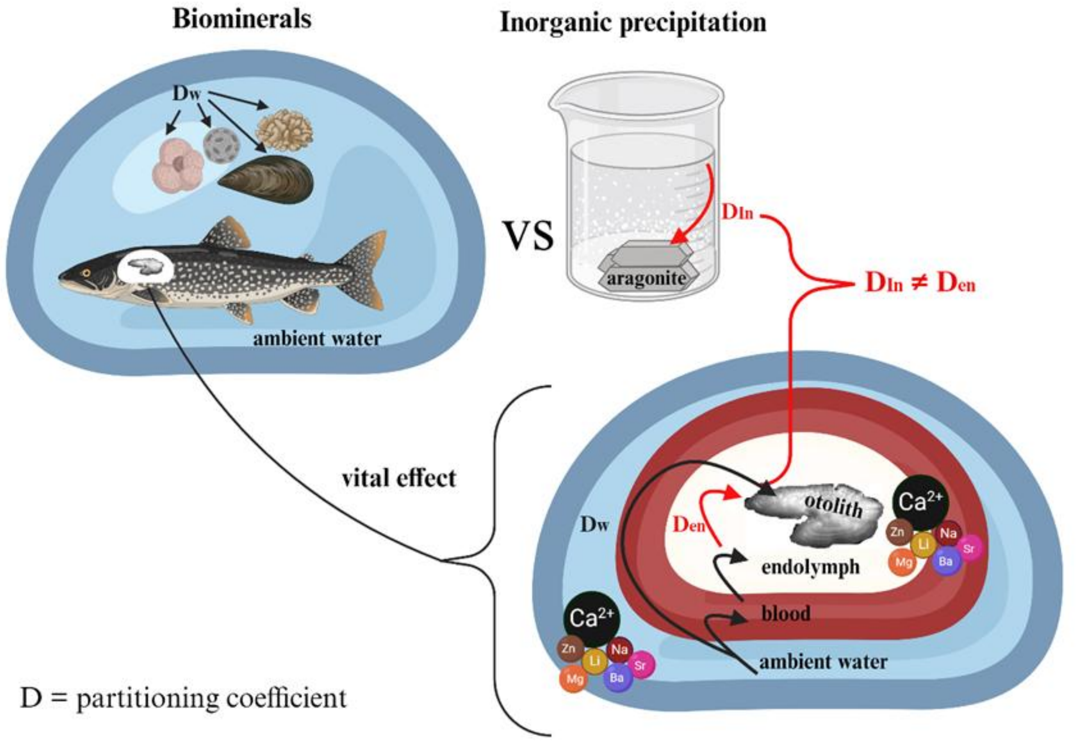
Keywords

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

Graphical Abstract



Key Figure (Graphical Abstract) “Mineralizing Fluid Control on Foreign Elements in Biogenic $CaCO_3$: Insights from Otoliths” Created in BioRender. Kekelou, A. (2024) BioRender.com/s39g673

Abstract

The foreign 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. foreign 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 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 foreign 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 foreign 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 foreign 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) (Druffel E.R.M. 1997.; Katz et al., 2010; 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 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. Specifically, the fact that Mg/Ca does not simply reflect inorganic temperature-modulated partitioning but is strongly affected by biological (vital) effects. Organisms can actively regulate Mg transport, potentially resulting in calcifying fluids with varying Mg/Ca ratios. Additionally, Mg might partly reside in the organics of a biomineral (Schöne et al 2010), as opposed to the mineral phase (Branson et al 2013) exhibiting different partitioning behaviour in organic and mineral phase respectively. These factors might cause biomineral Mg/Ca to deviate from what would be expected from inorganic precipitation from seawater (Bentov & Erez, 2006; Nehrke et al., 2013)."

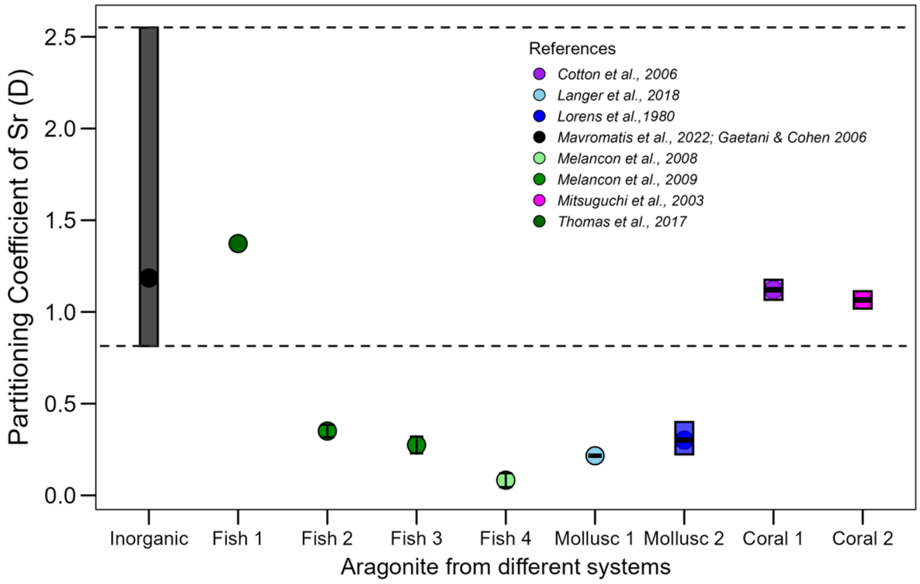


Figure 1. Sr partitioning coefficient range (DSr = (Sr/Ca) biomineral / (Sr/Ca) seawater) observed in different organisms with aragonite biominerals (shown in various colors) compared with the range for inorganic aragonite (black bar, with the full range indicated by the dashed black line). The references of the data are listed in the figure legend.

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 foreign element (Me) 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 approaches have been developed to calculate foreign 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 foreign 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 foreign 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., 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 foreign 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 planktonic foraminifera that live and calcify exclusively in marine environments and benthic foraminifera that are found also in brackish environments, otoliths biomineralize in teleost fishes across marine, brackish, and freshwater habitats, providing a potential archive of environmental conditions across diverse 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 foreign 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 foreign 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 foreign 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 foreign elements in four different species, one marine and three freshwater ones. We compare foreign 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 foreign 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.

2. Material and methods

2.1 Data collection and data handling

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 (Fish 1)	Mg, Sr, Ba, Li	Thomas et al., 2017
Lota lota (Fish 2)	Mg, Sr, Ba, Zn, Na	Melancon et al., 2009
Salvelinus namaycush (Fish 3)	Mg, Sr, Ba, Zn, Na	Melancon et al., 2009
Sander vitreus (Fish 4)	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. In the study of Thomas et al., 2017 they used a marine species, *Acanthopagrus butcheri* (Sp1), and the number of individuals measured was N = 3. Otoliths were diluted and measured with an inductively coupled plasma mass spectrometer (ICP-MS) as the endolymph fluid. They provide the concentration of foreign 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):

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

In the other two available studies with data meeting the criteria required for these estimates, were in a form of “concentration of foreign elements” in the otolith and in the endolymph (Melancon et al., 2008, 2009a). The species that were used in these studies were the freshwater species burbot *Lota lota* (Sp2), lake trout *Salvelinus namaycush* (Sp3) and a walleye *Sander vitreus* (Sp4), the number of the individuals (N) that were used were N_{burbot}=18 and N_{trout}=11 and N_{walley}=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 foreign 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)

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

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

2.2 Partitioning coefficient estimations

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 (Eq. 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 $(R_{otolith2})$.

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

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

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

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

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

We address the following question. Does the numerical value of the foreign 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

The partitioning coefficient of various foreign elements from four fish species was comparatively analyzed with the inorganic partitioning coefficient of the same element (Fig. 2). To elaborate further, the distinct environments have a different impact on Ba, which exhibit divergent patterns among marine and freshwater species. We observe that for Ba in the Sp1 (marine) their D is within the range of inorganic values while the Sp2, Sp3, Sp4 are below the inorganic range. This phenomenon stands in contrast to the behavior observed in Mg that all fish otoliths D are in the range of the inorganic D_{In} of Mg. The D_e of the elements Na and Sr, with the borderline case of Sr in one fish (Sp2), fall within the inorganic range when the D_w does not. Zn represents a distinctive case; while D_w appears to be within the range of the inorganic system, D_e is not. A comprehensive analysis of the available evidence suggests that the "vital effect" manifests in some elements while remaining invisible in others. The supplementary material contains the partitioning coefficient D_e of Li in only for the Sp1 which is above the D_{In} of Li.

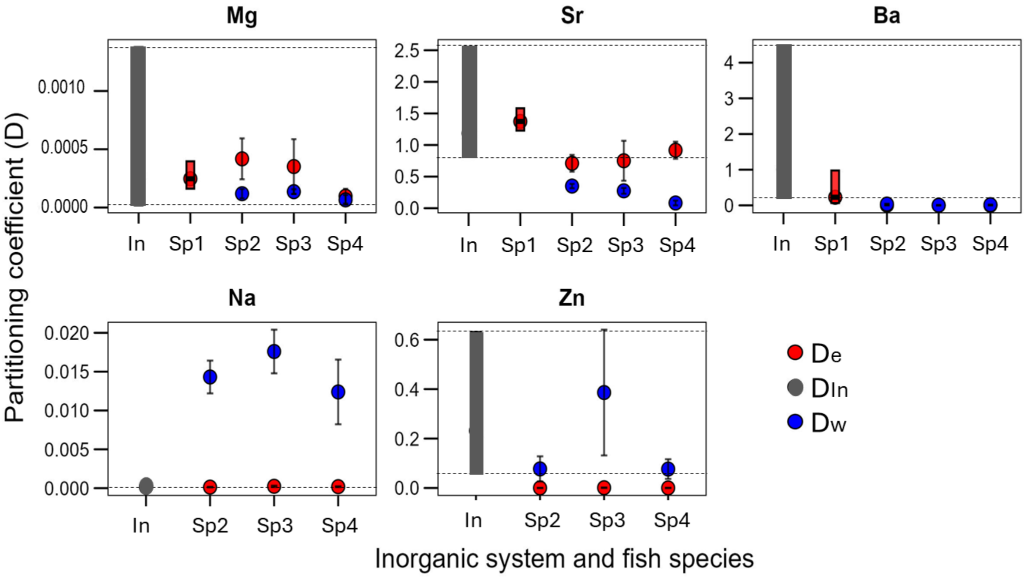


Figure 2 The partitioning coefficient (D) per element (Mg, Sr, Ba, Na, Zn), the range of the inorganic system (In) and the mean±SD of the D in three different freshwater fish burbot *Lota lota (Sp2)*, lake trout *Salvelinus namaycush (Sp3)* and a walleye *Sander vitreus (Sp4)* and the range of the marine fish the *Acanthopagrus butcheri (Sp1)*. Colour code: 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.

The ion transport pathways of five distinct elements of the Sp2 otolith are demonstrated (Fig. 3) and for the Sp3 (Fig. S2). The ratios of elements normalized to calcium (Ca) were measured in different solutions to trace their transport pathway into the otolith. Foreign elements of the ambient water pass to the blood and then to the endolymph where the biomineral is precipitated. The largest partitioning steps occur during the transition from water to blood and from endolymph to otolith. Despite the different patterns in the outcomes, it has been demonstrated that, in certain instances, the occurrence of the vital effect is visible as evidenced by the observation of a discrepancy in otolith1 relative to otolith (Fig. 3, c, e). Conversely, in other instances, the vital effect remains invisible, (Fig. 3, a, b, d).

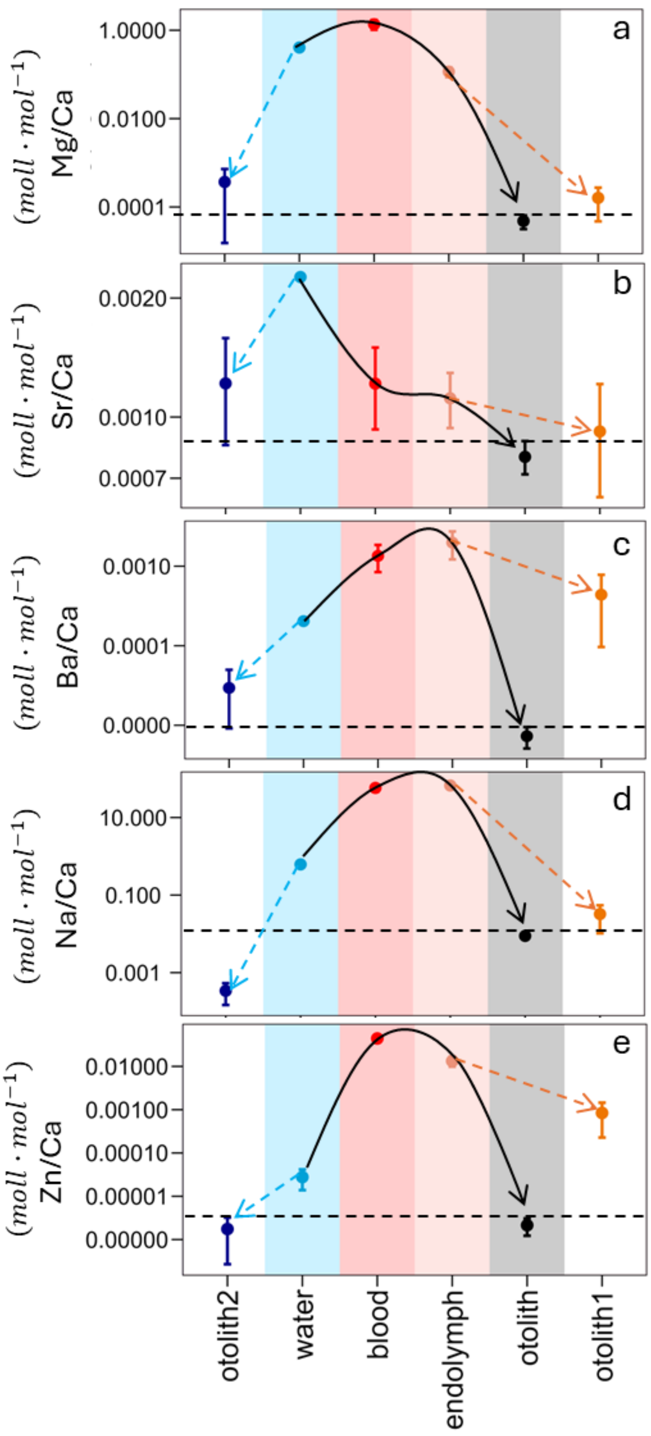


Figure 3 Me/Ca of burbot *Lota lota (Sp2)* in different reservoirs indicated by colored areas. The white areas (otolith 1 and otolith 2) do not represent measured values but are calculated according to otolith1 = D_{In} * $(Me/Ca)_{endo}$, and otolith2 = D_{In} * $(Me/Ca)_{water}$. For D_{In} we used 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. All the data are displayed on a log_{10}-scaled y-axis.

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 foreign 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 foreign element distribution into otoliths which is, therefore, not reducible to inorganic aragonite co-precipitation.

4.1 Foreign 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, Sp1-Sp4 (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 Sp1) fall within the range of inorganic values (Fig. 2, Fig S1). For the remaining 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 foreign element partitioning coefficients different from the ones determined in synthetic aragonite precipitation. Therefore, we conclude that foreign 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.

4.2 Element and species specificity of partitioning behaviour

Otolith partitioning coefficients D_e of Ba and Zn (and Sr in Sp2 and partly Sp3) 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 foreign 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 foreign 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 foreign element specific too. While alkali metal (e.g. Na and Li) complexes are of foreign 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”.

Why does Ba partitioning in the marine species Sp1 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). 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 foreign element partitioning shows that the localization of the foreign 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). The latter authors show that Mg resides in foraminiferal calcite and from this observation conclude that its 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.

Please note that foraminiferal shells are calcitic while otoliths are aragonitic. This difference in the calcium carbonate polymorph used by different organisms has implications for numerical values of partitioning coefficients (Langer et al 2018), but has no bearing on the argument made above. We claim that the fact that Mg resides in the mineral phase of a biomineral, as opposed to the organic phase, is not sufficient to support the inference that the partitioning process is a case of inorganic co-precipitation. This claim holds regardless of the calcium carbonate mineral into which Mg is incorporated, and regardless of the Mg/Ca of the respective mineral. Foraminifera, for example, comprise low-Mg (e.g. *Ammonia*), intermediate-Mg (e.g. *Amphistegina*), and high-Mg (e.g. *Heterostegina*) species (Mewes et al 2014, Mewes et al 2015, Raitzsch et al 2010). In the example mentioned above (Branson et al 2013), both a low-Mg species (*Orbulina*) and an intermediate-Mg species (*Amphistegina*) are discussed. The author’s argument, as well as our findings, apply equally to both species; and would do so for any other species.

To sum up, foreign elements might reside either in the mineral (e.g. aragonite in otoliths) or the organic part of the biomineral. Partitioning of foreign 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 foreign elements thereby influencing partitioning into the biomineral.

4.3 Biogenic and inorganic partitioning coefficient numerically identical: 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 foreign 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 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 foreign elements from water to otolith

In the freshwater species Sp2 (Fig. 3) and Sp3 (Fig. S 2) were the only dataset that allows us to trace the pathway of foreign 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 ambient water 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 foreign 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 foreign 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 foreign 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 foreign 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 (2026), “Mineralizing Fluid Control on Foreign Elements in Biogenic $CaCO_3$: Insights from Otoliths”, Mendeley Data, V3, doi: 10.17632/8ysgz5nb82.3 . But also they have been submitted as Supplementary material.

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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: Fig. S1 and *Fig. S2* are provided in the separate supplement file. Fig. S1 illustrates the partitioning coefficient (D) for Li, comparing the range of the inorganic system and the marine fish (*Acanthopagrus butcheri* - *Sp1*). And Fig. S2 illustrates the Ion transport pathway of the elements Mg, Ba, Na, Sr and Zn in the *Salvelinus namaycush* (*Sp3*).

Data Excel file: inorganic vs otolith-endolymph

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