

1 Ideas and perspectives: Mineralizing Fluid Control
2 on Foreign Elements in Biogenic CaCO₃: Insights
3 from Otoliths

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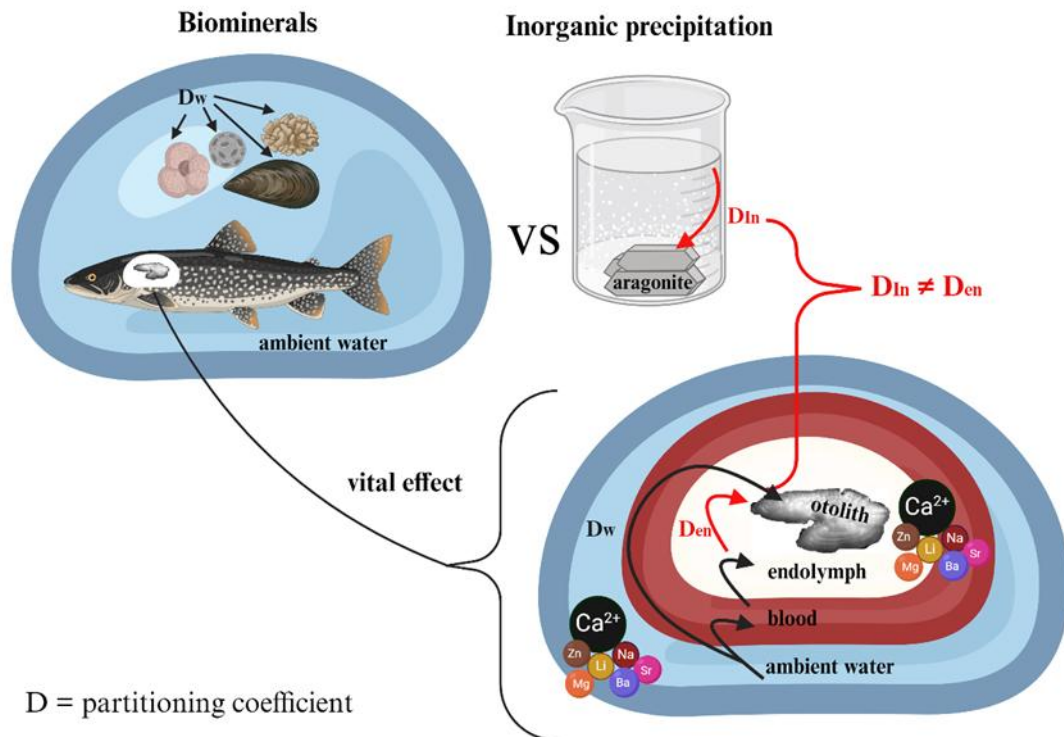
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14 Keywords

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

16 Graphical Abstract



17

18 **Key Figure (Graphical Abstract)** “Mineralizing Fluid Control on Foreign Elements in Biogenic $CaCO_3$: Insights
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20 Abstract

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

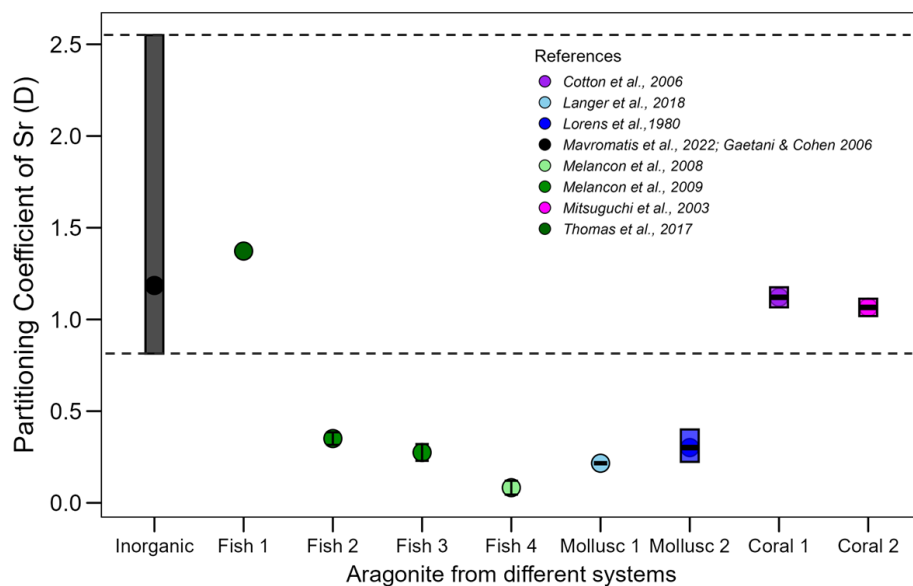
30 calcifying fluid of classic proxy archives such as foraminifera, molluscs, and coccolithophores has not been
31 successfully sampled for element analysis. The calcifying fluid of fish otolith formation (endolymph), by
32 contrast, was sampled and chemically analysed accompanied by corresponding otolith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

41 1. Introduction

42 The foreign element (Me) and isotopic composition of marine calcium carbonate (CaCO_3) (mostly
43 aragonite and calcite) biominerals from the sedimentary record has been used as a proxy for the
44 reconstruction of specific environmental parameters such as seawater temperature since the 1950s (Katz et
45 al., 2010; Urey et al., 1951). These geochemical proxies are instrumental in e.g. detecting effects of
46 anthropogenic climate change on marine calcifying organisms (calcifiers) (Druffel E.R.M. 1997.; Katz et
47 al., 2010; Pallacks et al., 2023). A geochemical paleo-proxy application requires a correlation of the proxy
48 with the target environmental parameter, and this is traditionally achieved by various calibration methods
49 (Allen et al., 2016; Elderfield & Ganssen, 2000). The calibration of a geochemical proxy alone, however,
50 does convey little knowledge about the processes underlying proxy signals and accuracy. This knowledge
51 is, however, essential for developing a mechanistic understanding of the proxy and eventually will enable
52 us to predict proxy signals using conceptual biomineralization models (Nehrke & Langer, 2023).
53 Biomineralization models, as opposed to calculations premised on precipitation of the mineral from
54 seawater, are required because marine calcifiers used as proxy archives do not precipitate their hard parts
55 from seawater but from a special calcification fluid thereby introducing the problem of the vital effect
56 (Nehrke & Langer, 2023; Urey et al., 1951). This calcification fluid is localised in the so-called site of
57 calcification (SOC). Different proxy-archive forming calcifiers have SOCs formed by different structures
58 such as pseudopodia (foraminifera, single-celled calcifying organisms), mantle epithelium (molluscs,

59 invertebrate animals that form a calcified shell), or intracellular vesicles (coccolithophores, single-celled
60 calcifying algae) (Angell, 1967; Crenshaw, 1972; Langer et al 2021, Wilbur & Watabe, 1963).

61 In all cases, however, the proxy signal will be influenced by the transport of ions from seawater into the
62 SOC (Nehrke & Langer, 2023). This transport can introduce partitioning steps that render the overall
63 partitioning different from what would be expected based on inorganic precipitation from seawater. A
64 striking example is the Sr/Ca signature in diverse calcifiers (Fig. 1). The data selected for Fig. 1 from the
65 aragonite literature illustrate that the Sr partitioning coefficient ($D_{Sr} = (Sr/Ca)_{\text{biomineral}} / (Sr/Ca)_{\text{seawater}}$) in
66 some cases falls within the range of inorganic precipitation, in others it does not. We selected Sr
67 incorporation in aragonitic biominerals here, but a well-known riddle is the Mg-problem, as it is often
68 informally referred to, in calcitic biominerals. Specifically, the fact that Mg/Ca does not simply reflect
69 inorganic temperature-modulated partitioning but is strongly affected by biological (vital) effects.
70 Organisms can actively regulate Mg transport, potentially resulting in calcifying fluids with varying Mg/Ca
71 ratios. Additionally, Mg might partly reside in the organics of a biomineral (Schöne et al 2010), as opposed
72 to the mineral phase (Branson et al 2013) exhibiting different partitioning behaviour in organic and mineral
73 phase respectively. These factors might cause biomineral Mg/Ca to deviate from what would be expected
74 from inorganic precipitation from seawater (Bentov & Erez, 2006; Nehrke et al., 2013).”



75
76 **Figure 1.** Sr partitioning coefficient range ($D_{Sr} = (Sr/Ca)_{\text{biomineral}} / (Sr/Ca)_{\text{seawater}}$) observed in different
77 organisms with aragonite biominerals (shown in various colors) compared with the range for inorganic aragonite (black
78 bar, with the full range indicated by the dashed black line). The references of the data are listed in the figure legend.

79 An intuitive, and often used, assumption is that knowledge of the ionic composition of the calcifying fluid
80 would solve this problem. In other words, it is expected that a partitioning coefficient calculated using the
81 calcifying fluid foreign element (Me) to Ca ratio (Me/Ca) will fall within the range of values determined in
82 inorganic precipitation experiments (Elderfield et al., 1996; Langer et al., 2006, 2016, 2018; Stoll et al.,
83 2012). Unfortunately, the SOC_s of most classic proxy-archive forming calcifiers are too small to be sampled
84 for element analysis (Checa, 2018; Kadan et al., 2021; Nomaki et al., 2018). Therefore, various model
85 approaches have been developed to calculate foreign element partitioning into biominerals (D’Olivo &
86 McCulloch, 2017; Elderfield et al., 1996; Hohn & Merico, 2015; Langer et al., 2006, 2016; Nehrke &
87 Langer, 2023; Ziveri et al., 2003, 2012). These models have provided new insights into the relationship
88 between conceptual biomineralization models and foreign element partitioning, but they have, yet, failed
89 to predict partitioning patterns based solely on independent constraints (Nehrke & Langer, 2023).
90 Therefore, these models rely on assumptions, many of which do not account for the complexity of foreign
91 element partitioning during biomineral formation. It is, for example, by no means self-evident that a
92 partitioning coefficient calculated using the calcifying fluid composition will fall within the range of
93 inorganic values.

94 Table 1. Summary of commonly studied geochemical elements in fish otoliths, their targeted environmental or
95 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, $\delta^{18}\text{O}$	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, $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$	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	$\delta^{13}\text{C}$, $\delta^{15}\text{N}$, 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, $^{87}\text{Sr}/^{86}\text{Sr}$	Marine & Freshwater	Campana, 1999; Campana & Thorrold, 2001; Halden & Friedrich, 2008; Kennedy et al., 2002; Longmore et al., 2011; Saygin et

				al., 2022; Wells et al., 2014; Zazzo et al., 2006
Migration, Habitat	Elemental Ratios, Stable Isotope	Sr/Ca, Ba/Ca, Mn/Ca, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$	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, $^{87}\text{Sr}/^{86}\text{Sr}$	Marine	Campana & Thorrold, 2001; Longmore et al., 2011; Padilla et al., 2015; Vaisvil et al., 2023

96

97 In this paper, we focus on fish otoliths, mostly aragonitic biominerals in the inner ears of bony fish, that are
98 an understudied and underappreciated model system to address element partitioning patterns (Hüssy et al.,
99 2020; Melancon et al., 2005). Otoliths can be found as fish remains in the sedimentary record (Elder et al.,
100 1996; Mellars et al., 1980) and they have been used in many ways in fisheries research, ecology, and the
101 reconstruction of fish stock environments (Reis-Santos et al., 2023). The foreign element compositions of
102 otoliths can serve as proxies for e.g. migration patterns, salinity, and temperature (Albertsen et al., 2021;
103 Bath Martin & Thorrold, 2005; Shiao et al., 2006). The otolith isotopic composition is also used as a proxy,
104 e.g. habitat/migration is inferred from Sr and C isotopes, and dietary history from N and C isotopes, while
105 O isotopes provide information about temperature and salinity (see Table 1 for an overview of otolith-based
106 geochemical proxies). Otoliths serve as valuable proxy archives for several reasons: a) Unlike
107 coccolithophores (which have coccoliths ranging from 2 to 20 μm) and require complex species-specific
108 separation, otoliths allow monospecific analyses; b) Unlike planktonic foraminifera that live and calcify
109 exclusively in marine environments and benthic foraminifera that are found also in brackish environments,
110 otoliths biomineralize in teleost fishes across marine, brackish, and freshwater habitats, providing a
111 potential archive of environmental conditions across diverse aquatic systems; c) Element-to-calcium ratios
112 in individual otoliths can be spatially mapped, offering insights into the fish life history traits and seasonal
113 patterns.

114 As with any other proxy archive, otolith-based proxies are subject to secondary influences. For example,
115 Sr/Ca and Ba/Ca are influenced by their correspondent concentrations in ambient water, but also salinity
116 and temperature (Hüssy et al., 2021). It has also been noted that, besides environmental parameters,
117 physiology influences foreign element and isotope composition (Bareille et al., 2024; Izzo et al., 2018;
118 Sturrock et al., 2015). The value of otoliths as geochemical proxy archives has been highlighted but is also,
119 unsurprisingly, critically discussed (Hüssy et al., 2021; Thomas & Swearer, 2019; Walther, 2019). The latter
120 authors emphasize that future steps towards improving otolith proxy applications critically include an

121 understanding of the processes bringing about the proxy signal. Hüsey et al., (2021) effectively summarize
122 the fundamental processes governing elemental and isotope fractionation into otoliths. They distinguish ion
123 transport into the endolymph from “biomineralization” by which they mean the formation of the otolith
124 within the endolymph. Note that often the term “biomineralization” covers both ion transport and formation
125 of the biomineral within the SOC (Nehrke and Langer 2023). As for foraminifera, there has been an
126 increasing interest in the relationship between partitioning (usually called fractionation when referring to
127 isotopes) patterns and biomineralization concepts in otoliths (Campana, 1999; Hüsey et al., 2021). To
128 understand even the most straightforward and useful proxies, such as Sr/Ca in foraminifera, both biological
129 and inorganic processes need to be considered (Langer et al 2016). Otoliths offer the unique opportunity to
130 study the fractionation processes within the SOC in greater detail than is possible in classic proxy archives
131 such as foraminifera.

132 An outstanding feature of otolith formation is the fact that the calcifying fluid, i.e. the endolymph, has such
133 a large volume that it can be sampled for element analysis (Kalish, 1989). This offers the unique opportunity
134 to measure foreign element composition of both the biomineral and its parent solution (Allemand et al.,
135 2007; Edeyer et al., 2000; Kalish 1989, 1991; Melancon et al., 2005, 2008, 2009a; Payan et al., 1997, 1998,
136 1999, 2002, 2004; Thomas et al., 2017). Although some of the latter studies provide the relevant data and
137 discuss the relationship between partitioning and biomineralization processes, no study has addressed the
138 following question: is the foreign element partitioning coefficient from endolymph into otolith (in the
139 following called D_e) numerically equivalent to the one from an aqueous solution of inorganic ions into
140 aragonite? Here we therefore use the relevant datasets in the literature to address this question. We look at
141 six different foreign elements in four different species, one marine and three freshwater ones. We compare
142 foreign element partitioning coefficient from endolymph to otolith with partitioning coefficient from
143 inorganic aragonite precipitation. This study provides a deeper mechanistic understanding of the vital effect
144 by identifying one, so far neglected, locus of the vital effect in the calcifying organism. The aim is to test
145 the commonly made assumption that biogenic partitioning coefficients should be indistinguishable from
146 inorganic ones if the Me/Ca of the actual parent solution (the calcifying fluid) of biomineral formation is
147 used as denominator (e.g. Langer et al., 2006). Our results suggest that partitioning of foreign elements
148 from endolymph into otolith cannot be modelled solely in terms of aragonite precipitation from an aqueous
149 solution of inorganic ions. Our conclusion not only has implications for proxy understanding but also for

150 biomineralization concepts because the latter centrally feature ideas about the composition of the calcifying
 151 fluid and its effect on biomineral formation.

152 2. Material and methods

153 2.1 Data collection and data handling

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

157 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
<i>Acanthopargus bucheri</i> (Fish 1)	Mg, Sr, Ba, Li	Thomas et al., 2017
<i>Lota lota</i> (Fish 2)	Mg, Sr, Ba, Zn, Na	Melancon et al., 2009
<i>Salvelinus namaycush</i> (Fish 3)	Mg, Sr, Ba, Zn, Na	Melancon et al., 2009
<i>Sander vitreus</i> (Fish 4)	Mg, Sr, Ba, Zn, Na	Melancon et al., 2008
<i>Patella caerulea</i> (mollusc1)	Sr	Langer et al., 2018
<i>Mytilus edulis</i> (mollusc2)	Sr	Lorens & Bender, 1980
<i>Lophelia pertusa</i> (coral1)	Sr	Cohen et al., 2006
<i>Porites australiensis</i> (coral2)	Sr	Mitsuguchi et al., 2003
Sea Water	Sr	Broecker, W. S., & Peng, T.-H. 1982

158

159 The literature on inorganic system provides many measurements of the partitioning coefficient (D_{In}) from
 160 different experimental designs. We selected the full range of values to get a realistic overall picture of the
 161 inorganic system. For the otolith-endolymph system the literature was limited. Only three papers gave us
 162 enough data to estimate the partitioning coefficient of the elements into the otolith. In the study of Thomas
 163 et al., 2017 they used a marine species, *Acanthopargus butcheri* (Sp1), and the number of individuals
 164 measured was $N = 3$. Otoliths were diluted and measured with an inductively coupled plasma mass
 165 spectrometer (ICP-MS) as the endolymph fluid. They provide the concentration of foreign elements (Me)
 166 normalized to the concentration calcium of (Ca) in the otolith and the endolymph ratio, $R =$
 167 $[Me](mmol)/[Ca](mol)$ with the $\pm sd$ and the $range(R) = \min(R) - \max(R)$, as well the partitioning
 168 coefficient ($D \times 100$). We estimate the range of the D using a simple formula of range ratio (Eq. 1):

$$169 \quad range(D_e) = \max(D_e) - \min(D_e) = \left(\frac{\max(R_{otolith})}{\min(R_{endolymph})} \right) - \left(\frac{\min(R_{otolith})}{\max(R_{endolymph})} \right) \quad (1)$$

170 In the other two available studies with data meeting the criteria required for these estimates, were in a form
 171 of “concentration of foreign elements” in the otolith and in the endolymph (Melancon et al., 2008, 2009a).
 172 The species that were used in these studies were the freshwater species burbot *Lota lota* (Sp2), lake trout
 173 *Salvelinus namaycush* (Sp3) and a walleye *Sander vitreus* (Sp4), the number of the individuals (N) that
 174 were used were $N_{burbot}=18$ and $N_{trout}=11$ and $N_{walleye}=8$, respectively. In these studies, the concentrations of
 175 the elements in the otoliths were quantified by laser ablation (LA-ICP-MS) and they performed a series of
 176 ablations at the growing otolith edges that were in contact with the endolymph and represent the last 30 to
 177 60 days of growth. They provide the average concentration of the foreign elements $av[Me] \pm sd$ (ppm)
 178 in the otolith and in the endolymph, which we converted to mmol/mol. The ratio $R =$
 179 $[Me](mmol)/[Ca](mol)$ in the otolith and in the endolymph and the $av(D) \pm sd(D)$ was estimated using
 180 Eq. (2) and (3)

$$181 \quad av(D_e) = \frac{av(R_{otolith})}{av(R_{endolymph})} \quad (2)$$

$$182 \quad sd(D_e) = av(D_e) \times \left(\sqrt{\left(\frac{sd(R_{otolith})}{av(R_{otolith})} \right)^2} + \sqrt{\left(\frac{sd(R_{endolymph})}{av(R_{endolymph})} \right)^2} \right) \quad (3)$$

183 2.2 Partitioning coefficient estimations

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

195
$$D_e = \frac{R_{otolith}}{R_{endolymph}} \quad (4)$$

196
$$D_w = \frac{R_{otolith}}{R_{water}} \quad (5)$$

197
$$D_{In} = \frac{R_{crystal}}{R_{fluid}} \quad (6)$$

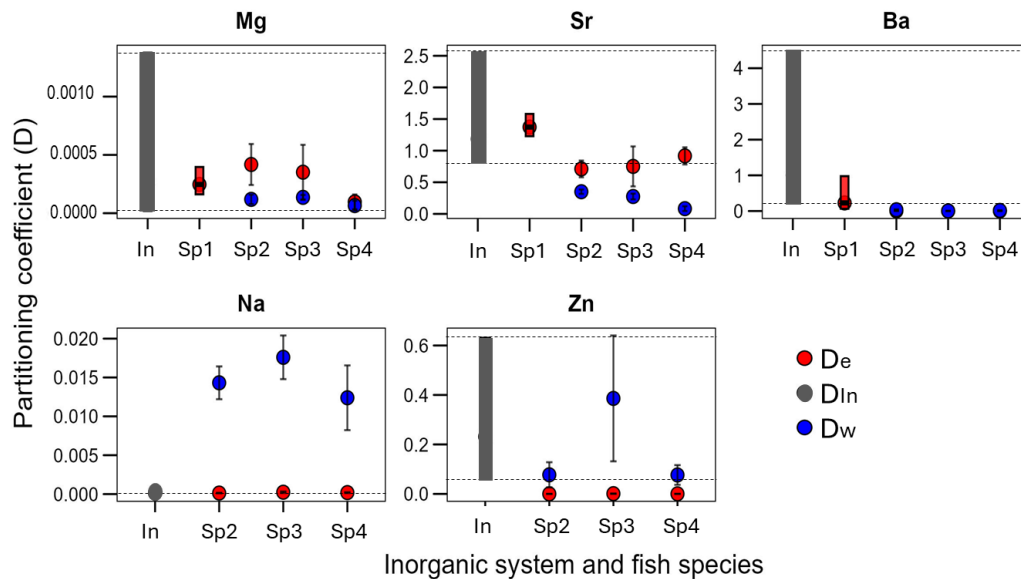
198
$$R_{otolith1} = range(D_{In}) \times R_{endolymph} \quad (7)$$

199
$$R_{otolith2} = range(D_{In}) \times R_{water} \quad (8)$$

200 We address the following question. Does the numerical value of the foreign element partitioning coefficient
201 from endolymph into otolith equal that of the partitioning coefficient from an aqueous solution into pure
202 aragonite? As mentioned in the introduction, Fig. 1 illustrates the range of the Sr partitioning coefficient
203 (D) in different calcifying marine organisms, we used as parent solution seawater and the ratios of the
204 elements in each organism from the literature (Broecker & Peng, 1982; Cohen et al., 2006; Langer et al.,
205 2018; Lorens & Bender, 1980; Mitsuguchi et al., 1996).

206 3. Results

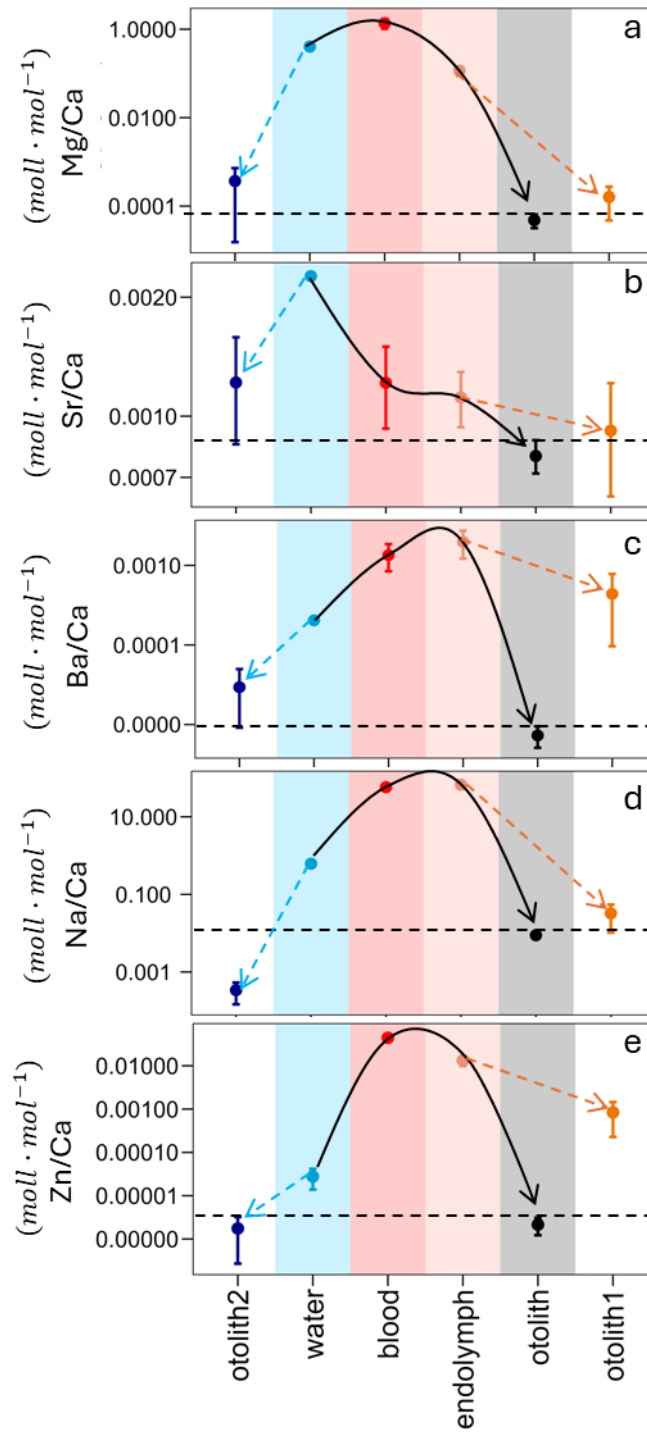
207 The partitioning coefficient of various foreign elements from four fish species was comparatively analyzed
208 with the inorganic partitioning coefficient of the same element (Fig. 2). To elaborate further, the distinct
209 environments have a different impact on Ba, which exhibit divergent patterns among marine and freshwater
210 species. We observe that for Ba in the Sp1 (marine) their D is within the range of inorganic values while
211 the Sp2, Sp3, Sp4 are below the inorganic range. This phenomenon stands in contrast to the behavior
212 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
213 Na and Sr, with the borderline case of Sr in one fish (Sp2), fall within the inorganic range when the D_w does
214 not. Zn represents a distinctive case; while D_w appears to be within the range of the inorganic system, D_e is
215 not. A comprehensive analysis of the available evidence suggests that the "vital effect" manifests in some
216 elements while remaining invisible in others. The supplementary material contains the partitioning
217 coefficient D_e of Li in only for the Sp1 which is above the D_{In} of Li.



218

219 **Figure 2** The partitioning coefficient (D) per element (Mg, Sr, Ba, Na, Zn), the range of the inorganic system (In) and
 220 the mean±SD of the D in three different freshwater fish burbot *Lota lota* (Sp2), lake trout *Salvelinus namaycush* (Sp3)
 221 and a walleye *Sander vitreus* (Sp4) and the range of the marine fish the *Acanthopagrus butcheri* (Sp1). Colour code:
 222 red is the D_e (endolymph as parent solution) and blue the D_w (water as parent solution) for fish and black is the D_{In}
 223 of the inorganic aragonite.

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



232

233 **Figure 3** Me/Ca of burbot *Lota lota* (*Sp2*) in different reservoirs indicated by colored areas. The white areas (otolith 1
 234 and otolith 2) do not represent measured values but are calculated according to $\text{otolith1} = D_{\text{In}} * (\text{Me/Ca})_{\text{endo}}$, and
 235 $\text{otolith2} = D_{\text{In}} * (\text{Me/Ca})_{\text{water}}$. For D_{In} we used either the minimum or the maximum value depending on which one
 236 would minimize the offset between (Me/Ca) otolith-measured and (Me/Ca) otolith-calculated. The error bar represents
 237 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,
 238 d) the pathway of Na and e) the pathway of Zn. All the data are displayed on a \log_{10} -scaled y-axis.

239 4. Discussion

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

251 4.1 Foreign element partitioning from endolymph to otolith cannot be modelled in terms
252 of inorganic aragonite precipitation

253 We looked at the partitioning coefficient of six elements (Sr, Ba, Mg, Na, Zn, and Li) in four different
254 species, Sp1-Sp4 (Fig. 2, Fig S1). For our question, it is helpful to consider several elements, as opposed
255 to just one, because results from a single element might be misleading (Langer et al., 2018). A species
256 comparison will further strengthen the conclusions because the question concerns the endolymph-otolith
257 system in general. The partitioning coefficients D_e of Na, Mg (mostly), Sr and Ba (in Sp1) fall within the
258 range of inorganic values (Fig. 2, Fig S1). For the remaining elements, Zn and Li, otoliths show a
259 partitioning behaviour different from inorganic aragonite. Taken together these results clearly show that the
260 endolymph-otolith system produces foreign element partitioning coefficients different from the ones
261 determined in synthetic aragonite precipitation. Therefore, we conclude that foreign element partitioning
262 during otolith formation in the endolymph involves processes that do not occur during inorganic aragonite
263 precipitation. An obvious further question is why the partitioning behaviour is both element and species
264 specific. In general, the answer will likely involve specific organic material both in the endolymph and the
265 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

295 within single otoliths, often with high values near the otolith core (Hermann et al., 2016). This could explain
296 both the higher De in the marine species and the larger range reaching both below and above the inorganic
297 range (Fig. 2).

298 The situation for Zn is different from the one for Sr and Ba because 40-60% of the Zn reside in otolith
299 organics (McFadden et al., 2016; Miller et al., 2006). Although an effect of endolymph organics cannot be
300 ruled out for Zn, it is equally possible that partitioning into otolith organics is different from partitioning
301 into otolith aragonite. Differential partitioning between the organic and the mineral part of mollusc shells
302 has been reported, supporting this possibility (Schöne et al., 2010). Additionally, organic complexes with
303 Zn can comprise the majority of total Zn, for example in surface seawater down to 500m (Bruland, 1989).
304 These naturally occurring organic ligands in seawater will be important in calcifiers using seawater as
305 substrate supply for calcification, e.g. foraminifera (Elderfield et al., 1996). The influence of organic
306 material in the calcifying fluid on foreign element partitioning shows that the localization of the foreign
307 element in the mineral part of the biomineral does not justify the conclusion that the partitioning process is
308 inorganic. This reasoning has nevertheless been applied to Mg partitioning into foraminiferal calcite
309 (Branson et al., 2013). The latter authors show that Mg resides in foraminiferal calcite and from this
310 observation conclude that its partitioning behaviour of Mg is inorganic. Since Mg is an important
311 temperature proxy (Elderfield & Ganssen, 2000), this example illustrates the usefulness of the endolymph-
312 otolith system for the development of a process-based understanding of proxy signal formation more
313 generally.

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

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

330 4.3 Biogenic and inorganic partitioning coefficient numerically identical: Mg, Na and Zn

331 The partitioning behaviour of Mg and Na seems to suggest that these elements are coprecipitated into
332 aragonite in a manner akin to synthetic aragonite formation (Fig. 2). If this was indeed so this would
333 nevertheless not contradict our conclusion (see above), namely foreign element partitioning into otoliths
334 involves processes other than aragonite precipitation from an aqueous solution of inorganic ions. The latter
335 conclusion rests on the behaviour of the other elements as discussed above and is not invalidated by a
336 putatively different behaviour of Mg and Na. However, the behaviour of Mg and Na might as well merely
337 appear inorganic numerically (in terms of D_e) but the processes underlying D_e might involve organic
338 material, i.e. the overall process of partitioning might be very different from inorganic precipitation. This
339 phenomenon has been described for different calcifiers and is known by the term “invisible vital effect”
340 (Nehrke & Langer, 2023 and references therein).

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

349 4.4 The pathway of foreign elements from water to otolith

350 In the freshwater species Sp2 (Fig. 3) and Sp3 (Fig. S 2) were the only dataset that allows us to trace the
351 pathway of foreign elements from external water into the otolith. In Fig. 3 we use Me/Ca (R) in different
352 reservoirs along the ion transport pathway as given in the literature, and we additionally calculate two
353 further values: 1) the $R_{otolith2}$ that results from multiplying R_w by D_{In} ; 2) the $R_{otolith1}$ that results from

354 multiplying R_c by D_{in} . The D_{in} that are used are selected to minimize the offset between otolith (measured)
355 and otolith (calculated). The aim of the figures is to illustrate the resulting (R) of different partitioning steps
356 as they actually occur (coloured reservoirs), as opposed to the ones that would theoretically occur if D_{in}
357 were applied.

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

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

381 4.5 Essential versus non-essential elements

382 While Ca, Na, Mg, and Zn are essential elements, i.e. needed in physiological processes, there is no known
383 physiological role for Sr and Ba, which are therefore considered non-essential (Lall & Kaushik, 2021;
384 Marshall, 2002; Nielsen, 2004; Salisbury & Ross, 1992). When considering foreign element partitioning
385 into biominerals the distinction between essential and non-essential elements is of great importance because
386 essential elements have their own transport systems while non-essential elements are thought to pass
387 through the transport systems of essential elements (Langer et al., 2006, 2009). This means that partitioning
388 from one reservoir into another (e.g. from water into blood) can be conceptualized easier for non-essential
389 elements, because only the partitioning of individual transport systems has to be known. If one transport
390 system transports the foreign element and another transports Ca the situation is more complicated because
391 the two systems can be regulated independently. In the case of the non-essential elements Sr and Ba it is
392 usually expected that they partition similarly if not with identical partitioning coefficient (Allen & Sanders,
393 1994; Langer et al., 2006, 2009; Nachshen & Blaustein, 1982). It is therefore surprising that the step from
394 water to blood fractionates for Ba but against Sr, whereas the step from blood to endolymph does not
395 fractionate at all (or only minimally) for both elements (Fig. 3). The partitioning from endolymph to otolith
396 is against both Sr and Ba, i.e. according to expectation. The fact that Ba fractionation is harder than Sr
397 fractionation could be explained by differential Sr and Ba partitioning of cellular transporters as well as
398 organic polymers (e.g. Nachshen & Blaustein, 1982; Yuryev et al., 1979).

399 5. Conclusion

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

- 406 1) Otolith mineralization in the endolymph shows a vital effect. Partitioning from endolymph into
407 otolith is influenced by organic material present in both endolymph and otolith and therefore cannot
408 be reduced to aragonite precipitation from an aqueous solution of inorganic ions.

409 2) Differential partitioning patterns are more complex than generally assumed, as illustrated by the easy-
410 to-conceptualize “model elements” Sr and Ba, which behave counter to expectation.

411 3) Future research should be specifically designed to address elemental partitioning within the
412 endolymph, as clearly warranted by the findings of this study.

413 Data Availability

414 The data will be published in the “Mendeley data” platform with the reference as Kekelou, Athina (2026),
415 “Mineralizing Fluid Control on Foreign Elements in Biogenic CaCO₃: Insights from Otoliths”, Mendeley
416 Data, V3, doi: 10.17632/8ysgz5nb82.3 . But also they have been submitted as Supplementary material.

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424 Competing interests

425 The authors declare that they have no conflict of interest.

426 Author contribution

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

430 Supplementary Material

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

435 Data Excel file: inorganic vs otolith-endolymph

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