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Iodine content of fish otoliths in species found in diverse habitats

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Abstract Expansion of aquatic deoxygenation has altered the quality and availability of habitats and worsened body condition for many fish species through past decades. Identifying complementary chemical redox proxies in fish otoliths, in addition to Mn/Ca, would strengthen the ability to identify hypoxia exposure in a diversity of aquatic habitats. I/Ca ratios have been used in marine sediments and bio-mineralized materials for reconstruction of past redox conditions. In order to explore influences from various endogenous and exogenous processes, a large data set of I/Ca ratios from cores of otoliths, including fishes from fresh, estuarine, and coastal waters across 30 species within 10 taxonomic orders, were reported with other chemical proxies (Mn/Ca and Sr/Ca) using LA-ICP-MS. Our results suggest no single abiotic factor, including redox condition and salinity derived from Mn/Ca and Sr/Ca, predicts I/Ca values, while they may be correlated for specific fish species. Iodine may be related to organic matter in the cores of otoliths for some species. Maternal transfer, habitat change, dietary source, phylogeny, and ecology may also influence I/Ca ratios. Based on these exploratory results, we suggest a range of future research directions to further evaluate the factors controlling biomineralization of otolith iodine and its utility as a redox proxy.

Keywords Fish otolith · Redox proxies · Iodine · Microchemistry · Trace element

Introduction

Ocean deoxygenation and hypoxia have been expanding in open and coastal waters since the mid-twentieth century, driven by increased global temperatures and nutrient discharges to coastal waters (Diaz and Rosenberg 2008; Schmidtko et al. 2017; Breitburg et al. 2018). Dissolved oxygen is crucial for sustaining biodiversity in aquatic systems

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(Vaquer-Sunyer and Duarte 2008). Large-scale horizontal expansion and shoaling of oxygen minimum zones (OMZ) have resulted in habitat compression of fish to shallower waters in estuarine and coastal waters (Eby and Crowder 2002; Stramma et al. 2012) and declines of fish body condition in the Baltic Sea (Casini et al. 2016; Limburg and Casini 2019). In freshwater ecosystems, the global spread of hypoxia, associated with human activities and nutrient release (Jenny et al. 2016), also has complex influences on ecology, behavior, habitat, and physiology of fishes (Pollock et al. 2007).

Fish otoliths are biomineralized inner-ear carbonate structures in teleost fishes that assist the perception of sound and gravity (Popper et al. 1982; Campana and Neilson 1985) and can provide chronological information through continual accretion of protein-rich and mineral-dominant increments (Campana and Neilson 1985). Increasingly, otolith growth increment patterns are studied together with microchemical analyses to quantify lifetime use of different physicochemical environments as well as physiological events (e.g., Campana 1999; Elsdon et al. 2008; Sturrock et al. 2015; Izzo et al. 2018), albeit with complexities imposed by individual fish life histories (Walther 2019).

Otolith Mn concentrations have been used as proxies for the exposure to hypoxia by an individual fish (e.g., Limburg et al. 2015; Altenritter and Walther 2019; Limburg and Casini 2019; Samson 2021). Theoretically, the reduced species Mn^{2+} and Mn^{3+} can be dissolved and mobilized from sediments into water under suboxic and low pH conditions, after which they can be incorporated into otoliths as increased Mn/Ca or Mn/Mg signals (Dorval et al. 2007; Limburg et al. 2011, 2015; Mohan et al. 2012). Developing additional and independent redox-sensitive proxies from fish otoliths may help to improve uncertainties about the Mn hypoxia proxy (such as influences of pH, growth rate and ambient Mn availability) and expand the application of redox proxies in more diverse habitats. The I/Ca ratio, a recently developed redox proxy for marine carbonate sediments and bio-mineralized carbonate materials (see the next section), is a good candidate. Here, we review the geochemistry of iodine and potential influences from a wide range of exogenous and endogenous processes on I/Ca values in fish otoliths.

I/Ca as a redox proxy

Iodine is crucial for organismal physiology (e.g., as the antioxidant in kelps and an essential component of thyroid hormones) and is an important indicator of seawater redox conditions because of the wide range of oxidation states (Küpper et al. 2011). In seawater, iodine has a long residence time of around 300,000 years compared to the thousand-year timescale of global ocean mixing, resulting in a globally uniform marine total iodine concentration of 0.45 μM (Elderfield and Truesdale 1980). The total concentration of marine iodine is predominantly controlled by burial of organic matter, which is balanced by primary production and organic matter decomposition (Lu et al. 2010).

There are two thermodynamically stable iodine species in the open ocean: the reduced form iodide (I^-) which dominates at depth in anoxic basins (Wong and Brewer 1977) and the oxidized form iodate (IO_3^-) which is the main iodine species in well-oxygenated waters (Truesdale and Bailey 2000). As suggested by a synthetic experiment, iodate is the only species that can be incorporated into carbonate lattices in proportion to its ambient concentration (Lu et al. 2010), by substitution for CO_3^{2-} (Podder et al. 2017; Feng and Redfern 2018). Therefore, low I/Ca ratios in well-preserved marine carbonate rocks commonly suggest an oxygen depleted condition when they were deposited, because iodide in reducing waters cannot be incorporated into the carbonate lattice and vice versa.

The I/Ca proxy has been explored in marine carbonate rocks, and fluctuations in this proxy correlate with major shifts in ocean-atmosphere oxygen levels throughout the history of the Earth (e.g., Hardisty et al. 2014; Lu et al. 2017, 2018; He et al. 2020). This proxy has also been widely used to reconstruct ocean deoxygenation events in conjunction with major climate changes and bio-crises across deep-time scales (e.g., Zhou et al. 2015; Edwards et al. 2018; Lowery et al. 2018; Liu et al. 2019). In addition, I/Ca ratios in foraminifera from marine core-top samples have been shown to reflect dissolved oxygen content in modern seawater (Glock et al. 2014; Lu et al. 2016, 2020a) and data from recent marine sediments were used to quantify oceanic redox dynamics during glacial cycles (Lu et al. 2016, 2020a, b; Hoogakker et al. 2018). Thus, I/Ca ratios in abiogenic and biogenic carbonates (e.g., fish otoliths) hold great promise for modern and historical reconstructions of oxygen conditions including hypoxia. Considering different redox behaviors of I and Mn (Fig. 1a), we hypothesize a negative correlation between I/Ca and Mn/Ca in our otolith samples, and we expect I/Ca to show different patterns for those sampled from distinct redox conditions.

Iodine patterns in otoliths

Iodine is present in the "salt fraction" of the endolymph fluid within which otoliths form (Thomas et al. 2017) and is typically present in the otolith core where proteins are enriched (Limburg et al. 2015), indicating both endogenous and exogenous influences. In this section, we review various processes that influence the uptake, transport, and incorporation of iodine into otoliths, including salinity, habitat use, dietary source, maternal transfer, thyroid, ecology, and phylogeny (Figs. 1 and 2).

Salinity influences iodine concentration in seawaters, and we hypothesize that I/Ca in otoliths covaries with salinity and salinity proxies (e.g., Sr/Ca) for the following reasons (Fig. 1b). First, iodine concentrations in freshwater can be an order of magnitude lower than that in marine water (Fehn 2012) and uptake of trace elements from water passing across the gill is a primary source for many freshwater species (Hüssy et al. 2020). Second, compared to freshwater fish, higher concentrations of iodine are usually found in muscles and other tissues of marine fishes (e.g., Eckhoff and Maage 1997; Haldimann et al. 2005; Sobolev et al. 2020).

Along the growth of the otolith, the newly accreted layers can incorporate minor and trace elements that may be associated with the habitat environment of the fish (Campana 1999). Therefore, habitat change may also influence I/Ca values in otoliths (Fig. 1c). Compared to I/Ca values from otolith cores, I/Ca quantified across annuli is more indicative of migration and

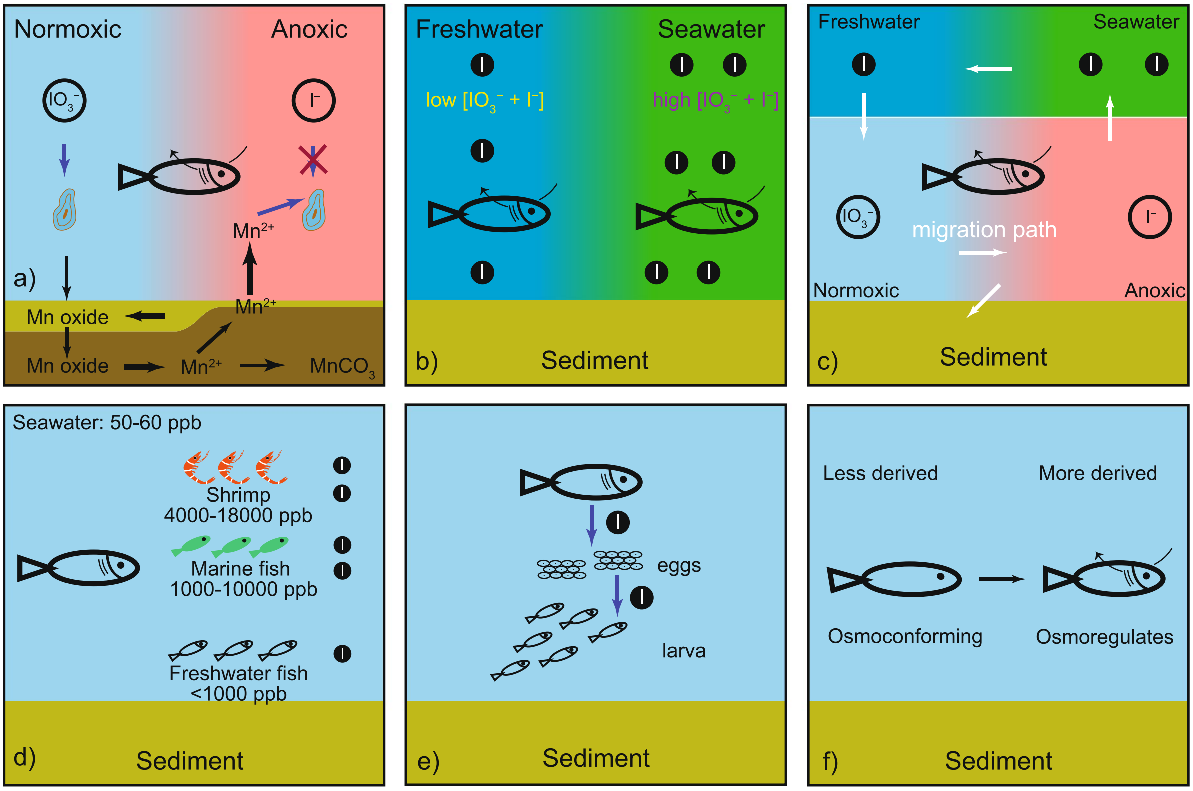

Fig. 1 Conceptual models showing the potential factors that influence I/Ca ratios found in fish otoliths, including (**a**) redox conditions, (**b**) salinity changes, (**c**) habitat changes, (**d**) examples of diet source, (**e**) maternal transferring, (**f**) phylogeny and ecology

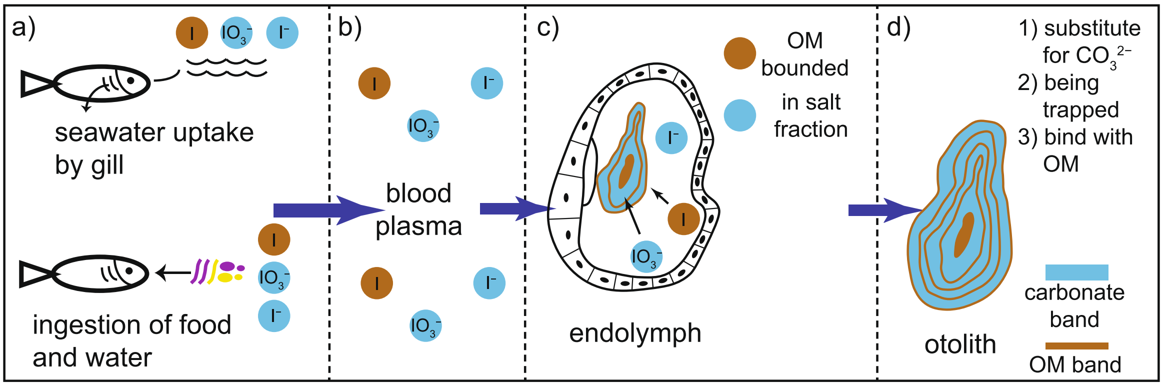

Fig. 2 Potential iodine incorporation path to otoliths. Dark yellow solid circles represent organic related iodine, while blue ones show inorganic related iodine. "OM" in the figure represent organic matter. The bands and ovals in (**a**) represent water and food, and the purple and yellow represent high and low iodine content, respectively. Figure is based loosely on Fig. 1 in Hüssy et al. (2020)

habitat changes of fishes in post-larval life history stages.

Iodine content varies greatly in different dietary sources. After digested food passes through gut membranes, iodine can be transported into blood plasma (Campana 1999; Hüssy et al. 2020; Fig. 2). Therefore, switching dietary sources between prey that have dramatically different iodine concentrations could potentially influence the I/Ca values within otoliths of the consumer as well (Fig. 1d).

Maternal transfer may influence the trace element signals in herring otoliths. For example, elevated concentrations of Mn and other elements (e.g., Mg and Ba) in the primordia of herrings might be related to maternal transfer (Ruttenberg et al. 2005; Fig. 1e), rather than the chemistry of the environment experienced during their egg and larval stages (Brophy et al. 2004), especially considering that some Mn can also be bound to protein components of otoliths (Izzo et al. 2016). Therefore, we hypothesize that the iodine chemistry of the cores of herring otoliths could be different.

For all vertebrates, iodine is a key component of thyroid hormones (THs) (Küpper et al. 2011). Thus, physiological processes related to the synthesis and release of THs could alter the availability of iodine in plasma for growth of otoliths. For example, TH levels increase during fish metamorphosis, so I/Ca on transects of otoliths of flatfish and some diadromous (e.g., salmonid and eel) species could decrease during metamorphic transitions. In addition, although the role of THs on reproduction is still unclear, TH levels are known to change with reproductive cycles (e.g., during gametogenesis and spawning) as well as vary with circadian and seasonal cycles (Deal and Volkoff 2020). Also, osmoregulation of some teleosts (especially euryhaline fishes) may involve the thyroid gland and TH levels can even be influenced by food sources (Deal and Volkoff 2020). All of these processes may contribute to I/Ca variation across life history transects of otoliths.

I/Ca in fish otoliths may also be influenced by phylogeny (Fig. 1f), since from primitive fishes to the most advanced teleosts, a greater control of the extracellular and intracellular environment has evolved (Ballantyne et al. 1987; Wright 2007). For example, hagfishes, the most primitive taxa, maintain plasma ions at the same concentration as in sea water by osmoconforming to their seawater environment, but more derived teleosts evolved to ionoregulate and osmoregulate to adapt to their environment (Ballantyne et al. 1987; Wright 2007). Therefore, I/Ca patterns of different taxonomies should be investigated, but it should be noted that taxonomic differences in I/Ca can also be related to their various movements, habitat use patterns, and trophic interactions.

The factors (e.g., redox, salinity and taxonomy) we discussed above may be confounded naturally. First, hypoxia usually develops in nearshore regions and restricted basins because of upwelling processes, high riverine nutrient input, and limited connection to the open ocean. In those regions, lower salinity is also expected due to the contribution from freshwater input. Second, distinct physiologies of fishes across taxa may influence the incorporation of trace elements and thus the dynamics of the chemical proxies. But influences from taxonomy and divergent environments are also confounded, because some species inhabit only a narrow range of environmental conditions.

Research design and goals

This work aims at a broad initial investigation into the potential of I/Ca in fish otoliths to serve as a proxy of environmental conditions. To investigate and disentangle influences from all the factors discussed above, we need to maximize the range of physiochemical habitats, geographic locations and taxonomic diversity. For this exploratory work, analyzing samples from the natural environment is an efficient first step to assess patterns and potential drivers of observed proxy variation to guide future field and experimental studies. First, we focus on ambient salinities and redox conditions that are known to influence the concentration and speciation of iodine, by surveying the empirical relationship between I/Ca ratios and other established proxies (e.g., Sr/Ca and Mn/Ca). Second, we discuss other factors with potential influences on I/Ca, such as habitat change, maternal transfer, and species of iodine used. Third, we sample ten taxonomic orders to investigate influences from phylogeny and ecology. Last, we outline frameworks for future research that will be essential for understanding chemical behavior of iodine in otoliths and expand the suite of tools available to assess hypoxia exposure.

Samples and methods

Fish species and sampling sites

In this study, we capitalized on previous analyses of 30 fish species across 10 orders, ranging from freshwater to marine environments and from hypoxic to normoxic conditions, collected over the course of several years (Fig. 3). Generally, we expect I/Ca values show different patterns corresponding to ambient water conditions. The data set was separated into two parts for analysis. First, data from 144 samples (most samples ranged in ages from 0 to 7) collected in North America, the Baltic Sea and the Amazon River (Fig. 3), were compiled to determine influences from the extrinsic environment and intrinsic physiology across different fish species on the I/Ca ratio. This data set included all taxonomic orders in Table 1. For simplification, this data set is called the "Multi-Species" data set. Second, a separate set of 200 flounder samples (ranged in ages from 2 to 18), which were acquired more recently in different surveys from Baltic Sea, were compiled to examine variations of I/Ca within a taxonomic order of a single basin. These samples were taken from two closely related flounder species, *Platichthys flesus* and *Platichthys solemdali* in Baltic Sea basin (referred as "Single-Genus" data set, Table 1). These samples of *Platichthys* spp. were collected from different sampling subdivisions (SD) assigned by the International Council for the Exploration of the Seas (ICES) and display a systematic change of salinity, from most saline at Kiel Bay to least saline by the Latvian coast (Fig. 3b).

Otolith preparation

For all samples, the largest pair of otoliths was removed, cleaned, embedded in epoxy, and sectioned to expose the cores. For every taxon, sagittae were randomly chosen from either left or right side, except Cyprinidae and Siluridae, for which lapilli were used (to limit analysis to aragonitic otolith from ostariophysans). Iodine data were obtained using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the College of Environmental Science and Forestry in Syracuse, NY. A New Wave (ESI) 193-nm solid state laser and a PerkinElmer Elan DRC-e quadrupole ICP-MS were used here. Before being laser ablated, all the samples were cleaned with 95% ethanol and then air-dried, which has been examined by Limburg et al. (2010). All otoliths of the Single-Genus data set and at least half of the Multi-Species data set were pre-ablated. Then, samples were ablated with a laser to acquire a continuous transect across otolith increments from edge to edge and passing through the core. The ablated material was transported via a carrier gas into an ionizing plasma, and ion masses were quantified spectrometrically.

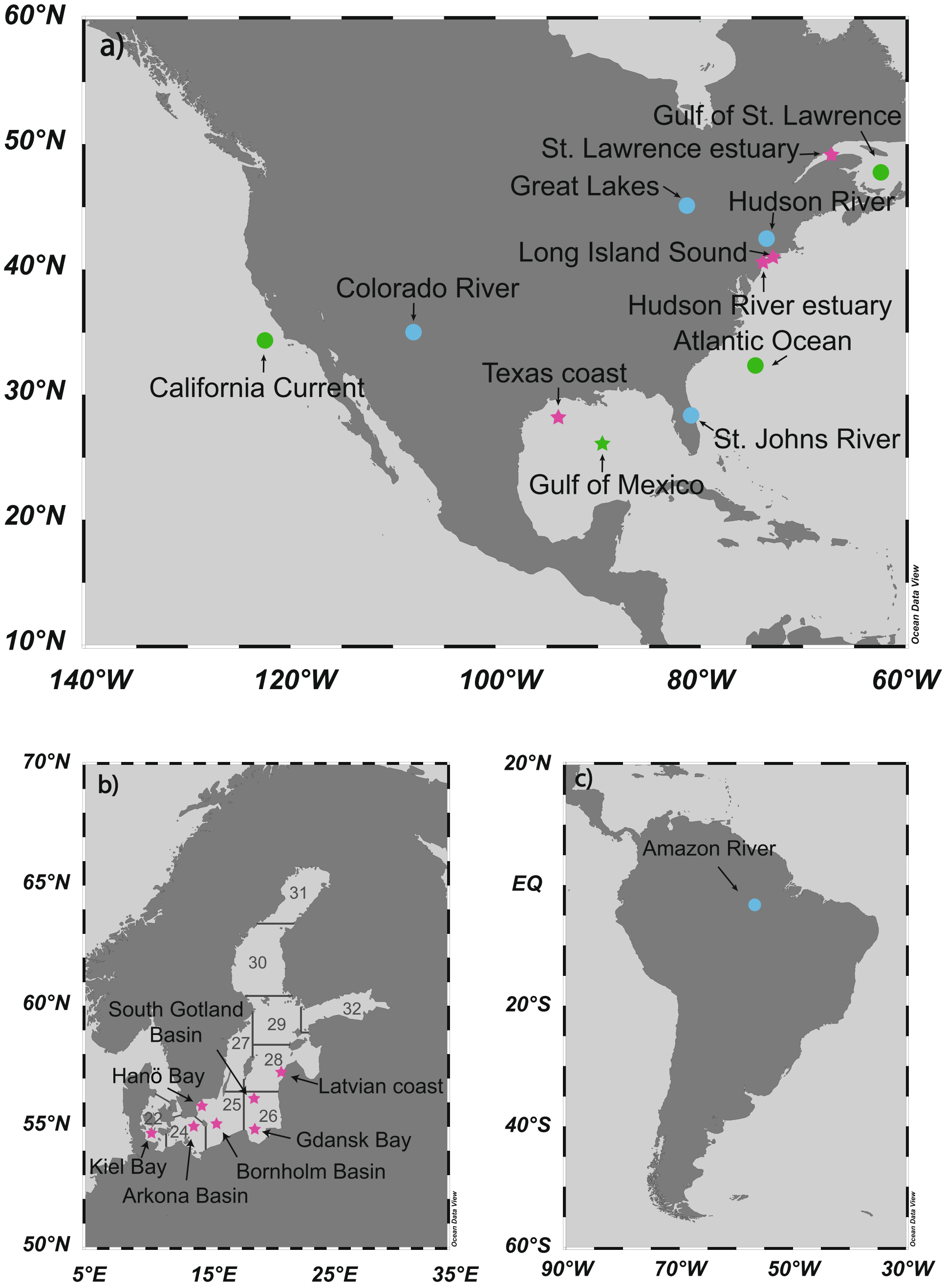

Fig. 3 Maps of sampling sites. (**a**) Sampling sites in North American. (**b**) Map of Baltic Sea, pink stars show locations where otolith samples were collected. Higher ICES subdivision (SD) numbers in the map generally go northward into lower salinity. (**c**) The sampling site in South America continents. Key: blue = freshwater, pink = estuary, green = seawater, circle = normoxic, star = hypoxic. Keys in the map only represent the general redox and salinity conditions of the sampling locations, which may not be exactly recorded in the cores of otoliths analyzed here

Table 1 Numbers of fishes used in this study of different taxonomic orders and sampling locations

Location Order	Amazon	Atlantic Ocean	Baltic Sea	Colorado River	Great Lakes	Gulf of Mexico	Hudson River	Long Island Sound	Pacific Ocean	St. Johns River	St. Lawrence River coast	Texas coast
Clupeiformes							22			1		
Cypriniformes				6								
Gadiformes			28									
Perciformes			10		2	5						
Percopsiformes					14							
Salmoniformes							1					
Scorpaeniformes									4			
Anguilliformes			2				6					
Siluriformes	2											
Pleuronectiformes		15	213*					2			5	6

The table shows number of otoliths collected from different locations and orders. *Among the 213 samples of Pleuronectiformes (mostly flounders) of Baltic Sea, 13 were collect on 2005 and 2011 and discussed in Multi-Species data set; 200 were collect in 2014-2015 and discussed in Single-Genus data set.

Iodine analysis

For the Multi-Species data set, the laser ablation spot diameters were 35 µm (*N* = 26), 50 µm (*N* = 34), 75 µm (*N* = 38), and 100 µm (*N* = 46), and the diameters were consistent for each species (except for few samples that were analyzed at a different time; see more details in Online Resource 2). Laser ablation transit speeds were 3–5 µm/s. For the Single-Genus data set, the laser spot size was 100 µm and the transit speed was 5 µm/s. The USGS MACS-3 standard (Wilson et al. 2008) was used for calibration and instrument drift corrections. Blanks were run prior to firing the laser on the sample and were averaged for each otolith and subtracted from respective transects, to correct for background drift. Details of the analytic procedure can be found in Limburg et al. (2015). Iodine analyses were all conducted for this study and are reported here for the first time.

Repeated measurement of the standards shows the RSD ranged from 10 to 50%, but detailed analysis suggested our I/Ca results are not uniformly biased by the iodine background (Online Resources 1). Iodine and other halogens are difficult to analyze via LA-ICP-MS because of their high backgrounds and low ionization efficiencies. This may be mitigated by increasing the dwell time of counting detections, as pointed out by Fusswinkel et al. (2018), who used a fourfold greater dwell on ^{127}I than on other isotopes. By increasing the dwell time on I to 0.4 s, recently one of us (KL) obtained RSDs between 6 and 7%, on par with other analytes. It is also important to check the homogeneity of standards; for example, the carbonate standard most often used in our previous analyses (MACS-3, Wilson et al. 2008) was discovered to have heterogeneous distributions of I in its matrix, whereas the US Geological Survey's phosphate reference material (MAPS) and carbonate reference material GP-4 are more uniform (Lazartigues et al. 2014).

Under the current iodine analysis method and machine condition, most samples present distinct iodine signals from the background of transects near the cores. Therefore, if not mentioned specifically, trace element data reported here (I/Ca, Mn/Ca, and Sr/Ca) were extracted from cores of otoliths where the protein content is highest (Jolivet et al. 2008), by averaging seven laser replicates centered on cores of transects. Except for six samples, element ratios from transects and margins are not reported separately here, because of low signals and invariant profile. The criteria we used to identify the core include the distances from the edge to the core on a photograph and peaks or valley of elements in key analytes at or near that distance. Our data may only be representative of the exposure history to environmental conditions (e.g., hypoxia and salinity) of larval stages for a range of taxa rather than the entire life of fish. Thus, the discussion mainly focuses on the correlation between I/Ca and other trace element proxies within otoliths, rather than temporally and spatially mis-matched water condition of sampling locations. In addition, it should be noted that fish larvae are less likely to have exposure to hypoxia, considering their pelagic ecology and low survival rate, although all samples came from fish that survived the larval stage.

Results

I/Ca distribution across space and species

I/Ca ratios from otolith cores grouped by phylogenetic order (Fig. 4) showed different mean values and distribution ranges. I/Ca ranges were scattered for Anguilliformes, Clupeiformes, Cypriniformes, and Pleuronectiformes, with 25th to 75th percentiles in the range of ~ 0.001 to 0.008×10^{-3} and mean values were all greater than 0.004×10^{-3}. On the other hand, for Percopsiformes, Gadiformes, and Perciformes, I/Ca values showed a relatively narrower range and lower mean values (Fig. 4), with differences between 25th and 75th percentiles all smaller than 0.002×10^{-3} and mean values all below 0.004×10^{-3}. Here, orders or species that had sample sizes less than five individuals are not included in the discussion. It

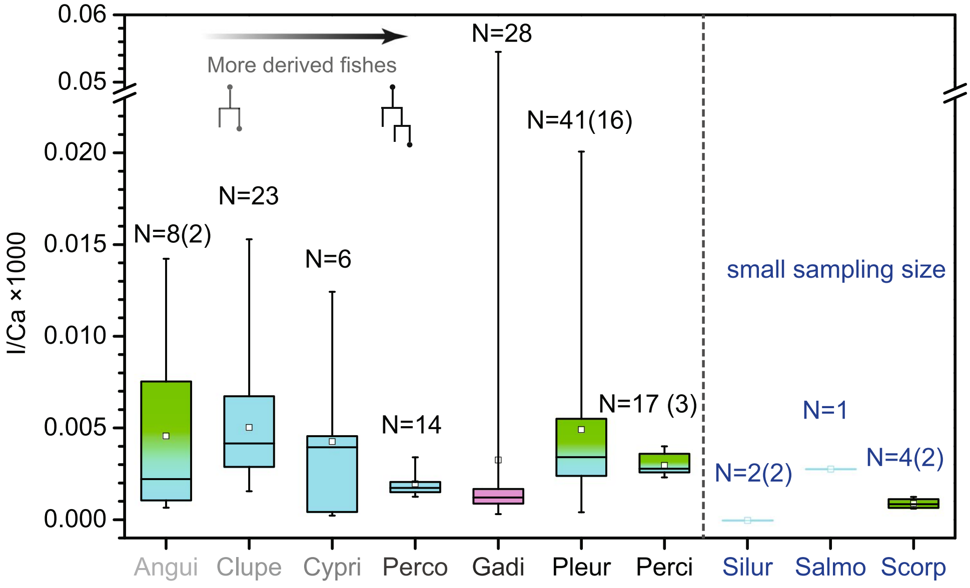

Fig. 4 Box plots showing I/Ca ratios from otolith cores of different fish orders. Some fish orders may include several different species. Taxonomic groups are ordered left-to-right from less derived to more derived, up to the dashed line. Samples to the right of the dashed line are also ordered phylogenetically but have small sample sizes (*N* < 5). Anguilliformes, Clupeiformes, and Cypriniformes have closer relationship with their ancestor on the phylogenetic tree comparing to other fishes (Betancur et al. 2017; Hughes et al. 2018). Blue represents freshwater, pink represents estuary (including Baltic Sea), and green represents marine. Boxes with color transitioning from blue to green represent samples from at least two salinity environments. The colors of boxes only represent the salinity environments which our samples come from, not that the taxonomic orders are solely from these environments. Numbers in parentheses show the number of species tested (> 1). Abbreviations for order names: Augui = Anguilliformes, Clupe = Clupeiformes, Cypri = Cypriniformes, Perco = Percopsiformes, Gadi = Gadiformes, Pleur = Pleuronectiformes, Perci = Perciformes, Silur = Siluriformes, Salmo = Salmoniformes, Scorp = Scorpaeniformes. Each box shows the 25th to 75th percentile and whiskers represent the maximum and minimum of the dataset. Lines within boxes show medians and small squares show means. Keys for box plots are same for the following figures, if not noted separately. There is an axis break for I/Ca ×1000

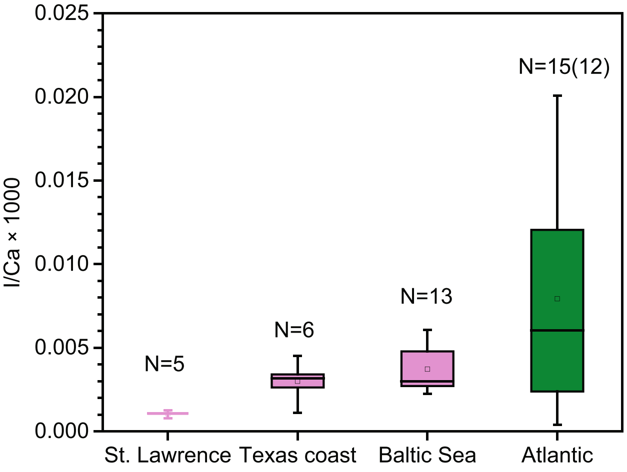

Fig. 5 I/Ca ratio from otolith cores of flounders collected in St. Lawrence River coast, Texas coast, Baltic Sea, and Atlantic Ocean. Single-Genus data set (Fig. 6) samples are not included here. The number in parentheses represents the number of species sampled in the open Atlantic. Colors for box plots are same as Fig. 4

also should be noted that five fish orders in our Multi-Species data set included only a single species from one location (Online Resource 2).

In addition, I/Ca ratios from otolith cores varied among different species of Pleuronectiformes from various locations (Fig. 5). I/Ca were ~ 0.001×10^{-3} for Greenland Halibut sampled near the estuary and gulf of the St. Lawrence River and were slightly higher for Southern Flounder from the Texas coast (~ 0.001 to 0.005×10^{-3}) and Baltic Sea Flounder (~ 0.002 to 0.006×10^{-3}). Flounders from various locations in the Atlantic Ocean, which include 12 species of 5 families, showed the largest I/Ca range (from near detection limit to 0.02×10^{-3}) and highest mean value (Fig. 5).

Baltic Sea Flounders, comprising the "Single-Genus" data set, were grouped by their sampling locations ($N = 200$; Fig. 6). Most samples have I/Ca from otolith cores below 0.02×10^{-3}. Aside from otoliths from Bornholm Basin, which had I/Ca ratios below 0.005×10^{-3} in most samples, all other samples had I/Ca ratios within a similar range with 25th to 75th percentile in between ~ 0.001×10^{-3} and 0.010×10^{-3}. Hanö Bay ($N = 51$), South Gotland Basin ($N = 23$), and Latvia offshore/coast ($N = 96$) had the largest sample sizes, and other locations all had < 10 otolith samples.

I/Ca versus other element to Ca ratios

For most samples in the Multi-Species data set, Sr/Ca ratios from otolith cores were between ~ 1 and 6×10^{-3} (Fig. 7a). All eel samples of Anguilliformes had high and scattered Sr/Ca ratios (> 6×10^{-3}) and all American Shad samples within the Clupeiformes showed low Sr/Ca (< 3×10^{-3}) (Fig. 7a). Regressions of Sr/Ca against I/Ca showed no significant relationship for the whole Multi-Species data set ($N =$

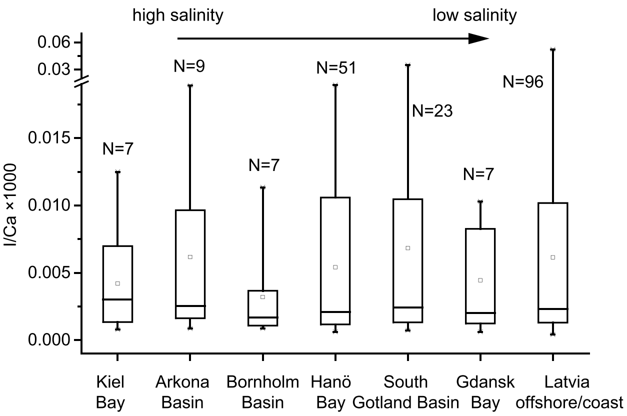

Fig. 6 Box plots of I/Ca from otolith cores of Single-Genus data set of *Platichthys* spp. from different locations of Baltic Sea (Fig. 3b). Locations are arranged from higher to lower salinity from left to right on the X-axis based on their relative distance to the inlet area. There is an axis break for I/Ca ×1000

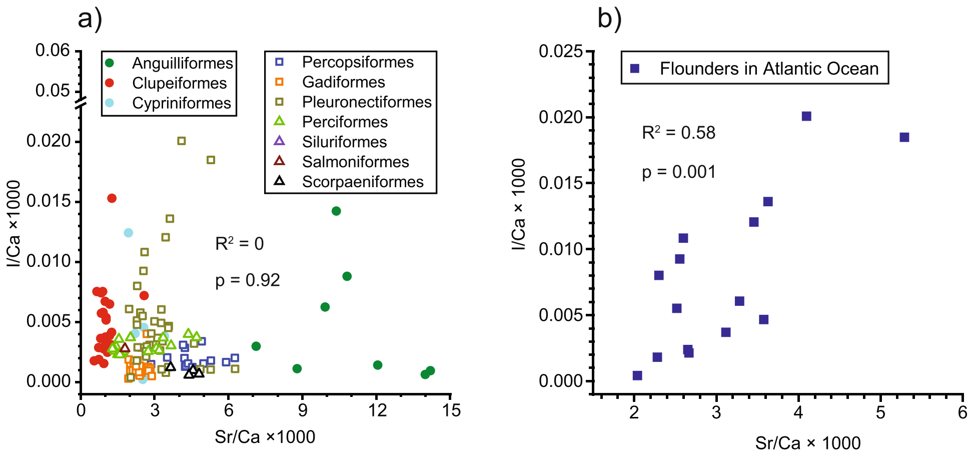

Fig. 7 (**a**) I/Ca vs. Sr/Ca (of otolith cores) cross plot for samples ($N = 144$) of Multi-Species data set including 10 taxonomic orders; (**b**) I/Ca vs. Sr/Ca plot for flounders in Atlantic Ocean Pleuronectiformes, with a $R^2 = 0.58$. *P* value shows the result of hypothesis test (null hypothesis = slope of the linear regression is zero; same for Fig. 8). There is an axis break for I/Ca ×1000 in (**a**)

144) or within individual taxonomic order (Fig. 7a), except for Atlantic Ocean flounders, in which a positive correlation between the two elemental ratios was observed ($R^2 = 0.58$, $p = 0.001$, Fig. 7b).

For both Multi-Species and Single-Genus data sets, high Mn/Ca ratios from otolith cores were only found in samples with low I/Ca values, and high I/Ca ratios were only found in those with low Mn/Ca values (for example, flounders and American Shad in Fig. 8a and Latvian coast, South Gotland Basin and Hanö Bay in Fig. 8b, depicted by the yellow triangles). But most data were scattered with low Mn/Ca and I/Ca ratios. No significant linear correlations were observed between I/Ca and Mn/Ca for either data sets (R^2 values were all lower than 0.1) nor when considering different species and locations of samples (Fig. 8a, b).

Even when subdividing the Multi-Species data set by the level of taxonomic order, no significant correlations were found between I/Ca and Mn/Ca from otolith cores (Fig. S3), except for Southern Flounder (Texas coast) and Atlantic Croaker (Gulf of Mexico) at the level of species (Fig. 8c). Finally, results from the Clupeiformes were investigated separately, because they contain relatively more scattered and larger ranges of I/Ca and Mn/Ca ratios (Fig. 8d). Therefore, a clear negative correlation between I/Ca and Mn/Ca was not found within our data set.

I/Ca transects across otoliths

For Baltic Sea Flounders, I/Ca and Mn/Ca transects typically showed inverse trends within the cores, with I/Ca peaks corresponding with Mn/Ca troughs, although the magnitude and synchrony of peaks and troughs varied among samples (Fig. 9). I/Ca peaks are also observed in other taxa besides Baltic Sea Flounders based on our visual inspection, and we acknowledge that for few samples, we either under-polish or over-polish such that either the core is not exposed or has been polished away. Here, six otolith transects are selected as examples (Fig. 9). For Greenland Halibut, although Mn/Ca showed an overall broad peak near the core, the inverse relationship was still found with a small dip in Mn/Ca at the core (Fig. 9f). Across palindromic transects that passed from edge to edge through the core, most Mn/Ca patterns showed several high peaks that were not perfectly symmetrical on either side of the core, because the growth increments tended to be more compressed on one side of the core compared to the other side. However, most I/Ca ratios outside of the core were lower than those near the core and showed frequent variations. Interestingly, there were clear palindromic spikes of I/Ca on either side of the core in a Baltic Sea Flounder sample (Fig. 9e), and the I/Ca ratios in this otolith were approximately fivefold greater than the vast majority of our other samples. This was the

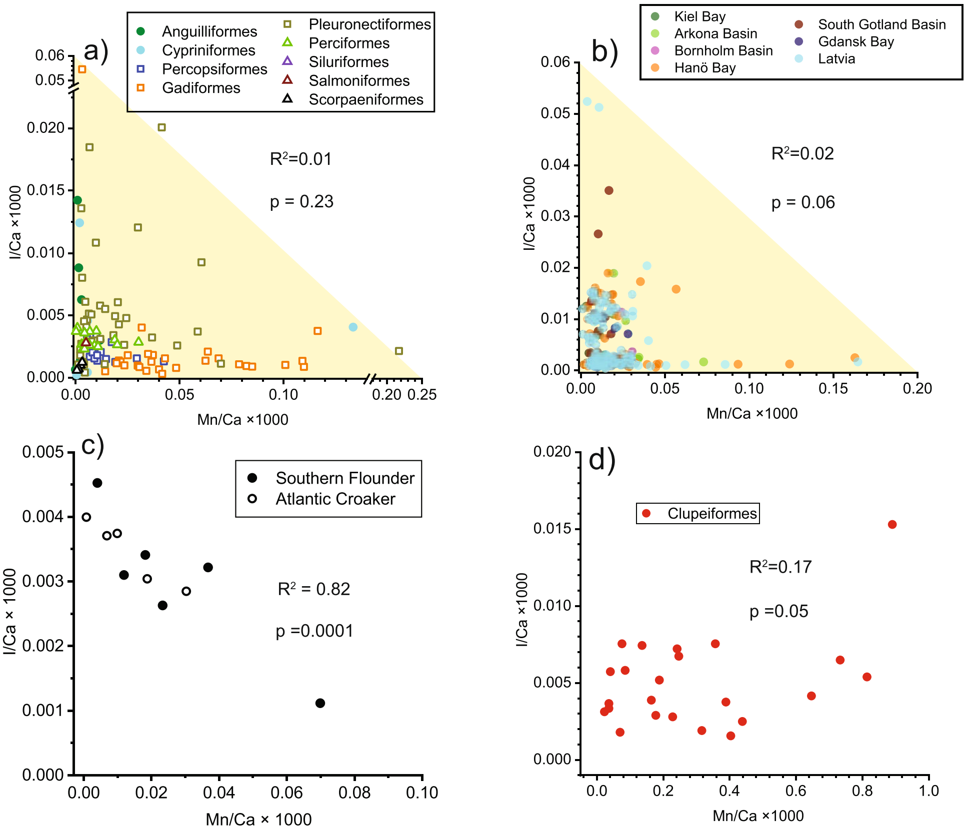

Fig. 8 Cross plots for I/Ca vs. Mn/Ca from otolith cores for the whole (**a**) Multi-Species ($N = 144$) and (**b**) Single-Genus ($N = 200$) data sets. (**c**) Southern Flounder of Pleuronectiformes and Atlantic Croaker of Perciformes showing a negative correlation with a $R^2 = 0.82$. (**d**) Cross plot for American Shad (Clupeiformes) showing scattered I/Ca and Mn/Ca values. Most of data can be enclosed by right triangles in (**a**) and (**b**). There is an axis break for both axes in (**a**)

only otolith among hundreds that were analyzed that showed such a pattern.

Discussion

Straightforward correlations between I/Ca and other trace elements (e.g., Sr and Mn) were not observed here, probably because core iodine is incorporated in as yet poorly understood ways into the organic matrix. However, redox conditions and salinity can exert controls on I/Ca for specific species. In addition, transects of I/Ca across otoliths can potentially be indicative of individual lifetime hypoxia exposure history, but the dynamics of iodine speciation and the mechanism of incorporation into otoliths must be better understood. Last, values of I/Ca within cores of otoliths varied among different fish species and sampling environments, suggesting influence both from phylogeny and ecology.

Salinity change

Otolith Sr/Ca can be used to track salinity change in diadromous and estuarine fishes (Brown et al. 2009), with low Sr/Ca often corresponding to low salinity and vice versa. However, except for the Atlantic Ocean flounders which showed a positive correlation between Sr/Ca and I/Ca within otolith cores, no significant covariation was found between Sr/Ca and I/Ca for most of the Multi-Species data set (Fig. 7). This may indicate a minor influence of salinity change on otolith I/Ca, although the effects of variable sample sizes and physiological differences among taxonomic orders cannot be ruled out. Alternatively, tributary bedrock geology and

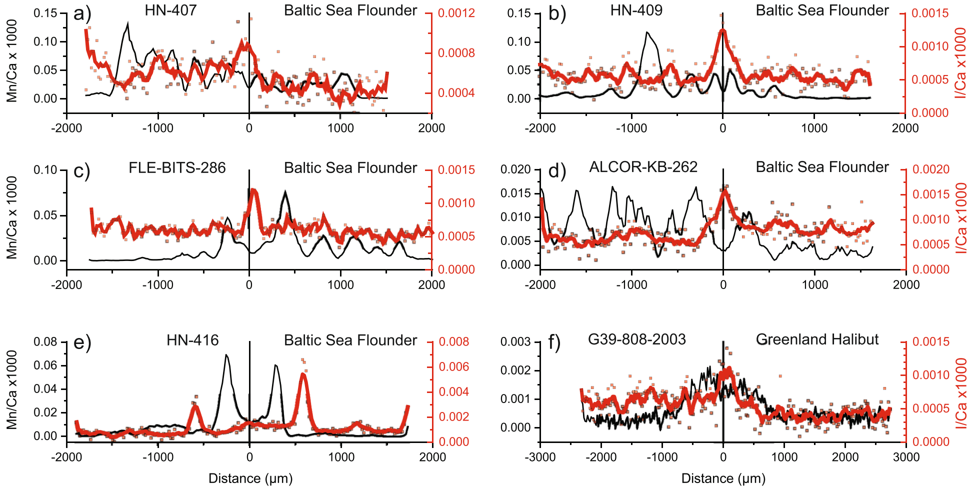

Fig. 9 Examples of I/Ca and Mn/Ca profiles through the cross sections of otoliths from Baltic Sea Flounders (**a–e**) and a Greenland Halibut from St. Lawrence River coast (**f**). Small red squares represent raw I/Ca data and red lines show 5-point averaged I/Ca values. Black lines are Mn/Ca profiles across sections. The horizontal axis shows the distance to the core of the otolith

freshwater Sr composition (Walther and Limburg 2012), ambient temperature change (e.g., Bath et al. 2000; Kraus and Secor 2004), life history stage (Walther et al. 2010), and even reproductive cycles and growth rate (Sturrock et al. 2014, 2015) can decouple an otherwise tighter relationship between Sr/Ca and I/Ca ratios.

The Single-Genus data set of Baltic Sea Flounder provided the greatest opportunity to evaluate putative relationships between salinity and I/Ca ratios. The influence of the connectivity of Baltic Sea is limited, since several tagging studies suggest that flounder populations are in general locally restricted in their distributions with few individuals crossing into adjacent sub-basins during migrations (Aro 1989, 2002; Bagge and Steffensen 1989). Because the salinity of the Baltic Sea is balanced by inflows of saline water from the North Sea (Atlantic Ocean) and riverine freshwater inflows, the salinity gradient decreases from regions closer to the inlet area to those more distant from the inlet area (Fig. 3b). However, fish from the lower salinity regions, such as the Gdansk Bay, the Gotland Basin, and the Latvian coast, show similar I/Ca ratios from otolith cores as locations closer to the inlet (Fig. 6). These observations suggest that the influence of salinity on I/Ca is not ubiquitous and most likely species-dependent or location-dependent.

Redox condition

Contrary to the hypothesis, we did not observe significant negative correlations between I/Ca and Mn/Ca ratios from otolith cores either for the Multi-Species or Single-Genus data sets (Fig. 8a, b), nor within each individual order (Fig. S3). On the other hand, a qualitative negative relationship cannot be totally ruled out, because most of our data, enclosed by yellow triangles, suggests high I/Ca and high Mn/Ca ratios are not observed from the same otoliths samples (Fig. 8a, b). Therefore, the relationship between these two elemental ratios is not as straightforward as initially assumed (Fig. 8a, b). The negative correlation between I/Ca and Mn/Ca from otolith cores found in Southern Flounder and Atlantic Croaker also suggests that redox control may produce distinct patterns for different species (Fig. 8c). This interpretation of Mn/Ca should be considered with caution, since insufficient Mn-bearing sediment could also result in low Mn content, even under hypoxia, as is suggested by the absence of elevated otolith Mn/Ca in lab-reared Atlantic Croakers under hypoxic conditions (Mohan et al. 2014).

In addition, as the Bornholm and Gotland basins in the Baltic Sea have experienced persistent hypoxia in past decades (Carstensen et al. 2014), we expected lower I/Ca in otoliths from these two regions.

However, I/Ca ratios of samples from the southern Gotland Basin were comparable to those from more oxic regions (Fig. 6), although our samples were not taken in the vicinity of the anoxic Gotland Deep. Otoliths of the Bornholm Basin that were collected right above the Bornholm Deep showed a lower I/Ca range, but it is unclear whether that pattern was driven by redox conditions in that basin or simply due to a relatively smaller sample size (Fig. 6).

Currently, the data do not strongly support I/Ca as a redox proxy in otoliths. In the future, direct empirical relationships between I/Ca, hypoxia volume, and dissolved O_2 level should be explored for fishes inhabiting waters of a large redox gradient. If possible, investigating a wider range of I/Ca and Mn/Ca is recommended to supplement the current data sets. More samples of Southern Flounder and Atlantic Croaker are required to further validate the negative correlation between I/Ca and Mn/Ca in this study (Fig. 8c). Lastly, laboratory experiments that rear fish in water spiked with different iodine species (iodide and iodate) and isotopes are helpful to distinguish the endogenous and exogenous influences on the incorporation and speciation of iodine.

I/Ca transect and iodine incorporation pathways

In analyses of flounder otoliths, iodine was often concentrated near the core of otoliths, as is indicated by significant I/Ca peaks, whereas Mn/Ca ratios were lower (Fig. 9). This inverse relationship between Mn and I near otolith cores was also observed in Baltic Cod (Limburg and Casini 2018) and could be explained by their respective redox behaviors. However, the interpretation is not supported by directly cross-plotting I/Ca vs. Mn/Ca values together from otolith cores (Fig. 8). These discrepancies in the redox proxy relationships should be considered and require further examination based on the following two assumptions.

One of the basic assumptions for I/Ca as a redox proxy is that the iodine species (IO_3^-) is incorporated into otoliths in proportion to its concentrations in ambient waters at the time of accretion (Lu et al. 2010). However, the otolith is separated by endolymphatic epithelium, gill epithelium, and gut membrane from ambient water (Campana 1999; Hüssy et al. 2020; Fig. 2). The iodine species ingested by fish from water or food, as well as further speciation changes from blood plasma into the endolymph within the otolithic capsule, is currently unclear. Therefore, we recommend that future studies compare I/Ca in the increments of otoliths with other independent hydrologic records (e.g., dissolved oxygen concentration and hypoxia volume). These studies could be performed on fish reared in aquaculture pens that have known histories or tagged fish with natural archival tags (Darnaude and Hunter 2018). Also, micro-sampling and separation of iodine species (e.g. inorganic versus organic) within blood and endolymph should be conducted (Fig. 2).

Another assumption is that IO_3^- is the only form incorporated into carbonates (Lu et al. 2010). However, the initial kernel of a forming otolith *in embryo*, called the primordium, contains relatively higher levels of organic matter and elevated I/Ca ratios (Jolivet et al. 2008; Zhang et al. 2008; Fig. 2). Organically bound iodine levels in marine sediments may be indirectly related to seawater redox conditions but are typically orders of magnitude higher than inorganic iodine in carbonate sediments (Elderfield and Truesdale 1980; Zhou et al. 2017). Therefore, if otoliths contain a mixture of iodine associated with both organic matter and the carbonate crystal (Fig. 2), it may be more difficult to interpret this element as a proxy for water redox conditions. The interaction of iodine with organic matter in otolith could be untangled by decalcification of analyzed otoliths and subsequent quantification of iodine in the remaining protein alone.

Habitat change

The majority of I/Ca ratios from otolith cores reported here are associated primarily with larval stages of fish. However, the I/Ca ratios obtained from growth bands could record more physiochemical information of the environment with which fish interacts throughout its growth and development history (Fig. 1c). One sample in our data set showed strong variations of I/Ca across the increments (Fig. 9e), but it is not currently possible to test if those signals were related to movement across physiochemically distinct habitats without corroborating knowledge of this individual's movement history. Future studies could focus on I/Ca profiles in otoliths of laboratory-reared and naturally tagged fish that are known to live in chemically different habitats through their lives in order to explore the importance of habitat change and migration on this emerging proxy.

Maternal transferring process in herring samples

Maternal transfer of Mn as well as variation in uptake dynamics among individuals may have contributed to the relatively larger and more variable Mn/Ca values found in our American Shad (Clupeiformes), which were distinct from other fishes within the Multi-Species data set (Figs. 4 and 8d). However, in the absence of verified information on maternal environments or details on the incubation conditions, our data do not allow us to confirm or reject the possibility of maternal transfer on the I/Ca proxy at this point. Future studies could focus on iodine in otoliths of fish whose eggs are incubated under different ambient iodine conditions, as well as comparing incubation environment chemistry and core I/Ca ratios of their offspring.

Phylogeny and ecology

Species within Teleostei, which diversified since the late Paleozoic (Betancur et al. 2017; Hughes et al. 2018), have developed more sophisticated ion regulation strategies to adjust to different salinities (Fig. 1f). The scattered I/Ca ranges of less-derived fishes (e.g., Anguilliformes, Clupeiformes and Cypriniformes) and narrower ranges of I/Ca in more-derived species (e.g., Percopsiformes, Gadiformes and Perciformes) may be influenced by phylogenetic constraints (Fig. 4). A larger number of samples is expected in the future to minimize the influences of unbalanced sampling.

The observed I/Ca ranges of Pleuronectiformes from the Canadian Maritime coast (Greenland Halibut, *Reinhardtius hippoglossoides*), the Texas coast (Southern Flounder, *Paralichthys lethostigma*), and the Baltic Sea (*Platichthys flesus* and *P. solemdali*) all had relatively low and narrow ranges of I/Ca values (Fig. 5). However, our analysis of flounders from the Atlantic Ocean, which contained 12 species of 5 families, showed a broader distribution of I/Ca values (Fig. 5). The more complex ecologies of those species could explain the larger range of observed I/Ca values within otolith cores, but we cannot rule out the influences from other factors such as salinity, temperature, the range of habitats used, and growth rate. The species *P. flesus* and *P. solemdali* of the Baltic Sea Flounders are two reproductively isolated and parapatric species that have two reproductive behaviors: offshore spawning of pelagic eggs and coastal spawning of demersal eggs (Momigliano et al. 2018). The moderate scatter in the observed I/Ca range in the core of Baltic Sea Flounders (Fig. 5) suggests taxonomic differences in ecological controls on iodine uptake may also be closely matched by spawning behavior.

Summary and future prospects

I/Ca ratios from cores of otoliths collected from different fish species across freshwater, estuarine, and coastal waters were measured by LA-ICP-MS. We observed no simple dominant control on I/Ca from either redox condition or salinity change for most samples, while influences are found in specific species. Habitat change, dietary source, maternal transfer, phylogeny, and ecology could complicate the usage of I/Ca as a redox proxy, but the knowledge on the relative importance of these factors is currently limited. Future research on developing an I/Ca proxy in otolith will need to address several important aspects:

- Establish a solid empirical relationship between redox and otolith I/Ca ratios. Firstly, explore the response of otolith I/Ca ratios to the changing concentration of iodate and iodide in the ambient water to separate influences from extrinsic environment and intrinsic physiology. Secondly, validate and test the sensitivity of an otolith I/Ca proxy in conjunction with an independent redox proxy (Mn/Ca) and hydrological parameters (e.g., hypoxia volume and dissolved O_2 level). The experiments should be conducted across a large redox gradient and include a variety of species.
- Extend the theoretical understanding of the otolith I/Ca proxy. Firstly, study the contribution of organically bound iodine to the I/Ca records extracted from different parts of otoliths (e.g., post-larval increments vs. primordia) through de-calcification or organic matter removal processes. Secondly, investigate whether the organically bound iodine is also related to redox condition or physiology. Thirdly, study concentration and speciation change of iodine in blood plasma and endolymph to understand its incorporation

path across different membranes, possibly through micro-sampling and isotope labeling methods.

- Consider manipulating factors (Fig. 1), such as changing habit over the lives of fishes, controlling diet source, and incubation environment, as independent variables in laboratory-rearing experiments.

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Data availability The datasets generated during and/or analyzed during the current study are available in supplementary files.

Declarations

Ethics approval Southern Flounder were collected under approved IACUC protocol AUP-2010-00066 at the University of Texas at Austin. Atlantic Croaker carcasses were obtained from standard fisheries independent monitoring surveys by the United States National Oceanic and Atmospheric Administration SEAMAP program, and thus IACUC approval was not required. Most samples from Hudson River and East Coast of US were collected under IACUC protocol 102313, 170501, 170701, and 190601. For fish samples from Baltic Basin, all of the otoliths were received after being extracted from fish upon capture, and thus no field-based experiments have been conducted by any of the authors.

Conflict of interest The authors declare no competing interests.

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