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Yu. Egorova[1], Yu. Kuzmenko[1], T. Spesivy[1], B.P.V. Hunt[1, 2], E.A. Pakhomov[1, 2]*

[1] University of British Columbia, 2207 Main Mall #2020,
Vancouver, BC, Canada, V6T 1Z4;
[2] Hakai Institute, Heriot Bay, BC, Canada, V0P 1H0

ANALYSIS OF Sr AND Ba PROFILES MEASURED BY ULTRA-HIGH-RESOLUTION MASS SPECTROMETRY LA-ICP-MS IN OTOLITHS OF JUVENILE ANADROMOUS SOCKEYE SALMON *ONCORHYNCHUS NERKA* IN THE EARLY MARINE LIFE-HISTORY STAGE AS A PROXY FOR FRESH TO MARINE WATER TRANSITION

The strontium (Sr) and barium (Ba) profiles in otoliths of juvenile sockeye salmon *Oncorhynchus nerka* from British Columbia are measured using a Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) system and analyzed. The highest possible measurement resolution (near-daily) was used to assess variability and repeatability of the breakpoint (marine entry) estimates inferred from Sr:Ca and Ba:Ca ratios. Such resolution for the otolith chemical composition (to an accuracy of 2 μm) was reached using the rotating slit, which width was close to the daily circulus width of the otoliths. So, daily or 2-day changes in the elemental composition were recorded during the period of transition to the marine environment. Sr profiles were generally similar among the fish, starting with low values of Sr:Ca in the fresh water and increasing sharply after the marine entry. The Ba:Ca signal was more complex, showing in most cases a dramatic increase immediately before the breakpoint. Besides, multiple peaks in the Ba profiles were recorded prior to the marine transition with a significant difference of their number between fish from different populations. A breakpoint was detectable in the Ba profiles 3–11 μm prior to its appearance in the Sr profiles. The complexity of Ba profiles may cause erroneous estimates of the marine entry date; thus, the Sr signal is a more reliable marker of marine transition for juvenile sockeye.

** Egorova Yulia, post-graduate student, e-mail: yegorova@eoas.ubc.ca; Kuzmenko Yulia, post-graduate student, e-mail: ykuzmen@eoas.ubc.ca; Spesivy Tymofey, laboratory technician, e-mail: tim.spesivy@gmail.com; Hunt Brian P.V., assistant professor, e-mail: b.hunt@oceans.ubc.ca; Pakhomov Evgeny A., PhD, professor, director of institute, e-mail: epakhomov@eoas.ubc.ca.*

Егорова Юлия, аспирант, Университет Британской Колумбии, Ванкувер, Британская Колумбия, Канада V6T 1Z4, e-mail: yegorova@eoas.ubc.ca; Кузьменко Юлия, аспирант, Университет Британской Колумбии, Ванкувер, Британская Колумбия, Канада V6T 1Z4, e-mail: ykuzmen@eoas.ubc.ca; Спесивый Тимофей, техник, Университет Британской Колумбии, Ванкувер, Британская Колумбия, Канада V6T 1Z4, e-mail: tim.spesivy@gmail.com; Хант Брайан П.В., доцент, Университет Британской Колумбии, Ванкувер, Британская Колумбия, Канада V6T 1Z4; Хакай институт, Хериот-Бэй, Британская Колумбия, Канада, V0P 1H0, e-mail: b.hunt@oceans.ubc.ca; Пахомов Евгений А., кандидат биологических наук, профессор, директор института, Университет Британской Колумбии, Ванкувер, Британская Колумбия, Канада V6T 1Z4; Хакай институт, Хериот-Бэй, Британская Колумбия, Канада, V0P 1H0, e-mail: epakhomov@eoas.ubc.ca.

Key words: sockeye salmon, smolt, laser ablation, otolith, strontium, barium, marine entry, rotating slit, segmented regression analysis, Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS).

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Анализируются профили концентраций стронция и бария в отолитах ювенильной нерки *Oncorhynchus nerka* Британской Колумбии (Канада), определенные методом лазерной масс-спектрометрии с индуктивно-связанной плазмой (LA-ICP-MS). Рассмотрены вариабельность и повторяемость оценок точки перехода лососей в морскую среду по профилям соотношений Sr:Ca и Ba:Ca с максимально возможным (околосуточным) разрешением. Высокая точность анализа химического состава отолитов (по слоям толщиной до 2 мкм) достигнута с применением круговой прорези, ширина которой близка к ширине суточных колец отолитов, что дало возможность проанализировать изменения в элементном составе отолитов при миграции рыбы в морскую среду обитания с точностью в 1–2 дня. Профили стронция в целом были сходны у всех изученных рыб с низкими величинами Sr:Ca в начальный пресноводный период и резким их повышением при переходе в морскую среду. Вариации Ba:Ca были более сложными, с резким ростом перед переходом в соленую воду, кроме того, перед переходом наблюдалось несколько пиков концентрации бария, число которых было разным у рыб разного происхождения. На профиле бария рост концентрации наблюдался на 3–11 мкм раньше, чем на профиле стронция. Сложность профиля бария может привести к ошибке в определении точки перехода в морскую среду, поэтому профиль стронция является более надежным маркером перехода молоди нерки к морскому обитанию.

Ключевые слова: нерка, молодь, лазерная спектрометрия, отолит, стронций, барий, переход в морскую среду, круговая прорезь, кусочная регрессия, индуктивно-связанная плазма.

Introduction

Pacific salmonids are currently a focal point of scientific interest in the North Pacific [www.npafc.org]. The fresh-to-saline water transition and the subsequent early marine stage are considered a critical period in the life history of Pacific salmon and are associated with the highest mortality [Preikshot et al., 2012; Welch et al., 2013; Naydenko et al., 2016]. The factors controlling their growth and mortality are not well understood during this period, in part, due to the challenges in reconstructing the life history with a resolution high enough to resolve the habitat use during the short early marine stage.

Otolith microchemistry analysis is an important tool for reconstructing the environmental life history of fish [Campana, 1999; Campana & Thorrold, 2001]. Daily life history reconstruction based on fish otolith microanalysis is a rapidly developing field of research [Barnes, Gillanders, 2013]. The point of marine entry, growth rates, and environmental conditions can be reliably assessed through high-resolution measurements of various chemical elements [Campana & Gagné, 1995; Quinn et al., 1999; Martin et al., 2013; Stocks et al., 2014]. However, the duration of habitat occupancy during the early marine stage can vary dramatically, being rather short in some cases [Stocks et al., 2014; Egorova, 2016]. Thus, precise and accurate estimation of the point of marine entry on the basis of otoliths is crucial for accurately matching the fish growth with the environmental conditions to which the fish was exposed and for building predictive models of juveniles' condition upon leaving the coastal environment [Egorova, 2016].

One of the most precise tools for obtaining chronological information from otoliths is Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) [Gray, 1985; Denoyer et al., 1991; Hoff & Fuiman, 1995; Jones & Chen, 2003]. LA-ICP-MS provides high sensitivity that allows to detect elements at low concentrations [Denoyer et al., 1991;

Edmonds et al., 1991, 1995; Jones & Chen, 2003]. One of the advantages of using LA-ICP-MS is various adjustments that can be made to increase the precision and accuracy of data retrieval. Such adjustments are a shorter dwell time (fewer targeted elements) [Warter & Müller, 2017], the application of a rectangular slit [Stocks et al., 2014], or a combination two or more elemental ratios [McCulloch et al., 2005].

Most otolith studies based on LA-ICP-MS have either used raster scan or spot analysis with a spatial resolution of 30–50 μm [Brophy et al., 2003; Barnett-Johnson et al., 2005; Palace et al., 2007; Huelga-Suarez et al., 2013]. This method best suits for older fish or lower resolution data (i.e., weekly or yearly averages). However, the width of daily circuli in juvenile salmon otoliths is ~1.5–2.0 μm, and the resolution achievable with these approaches is, therefore, inadequate for measuring daily variability in the otolith chemistry. The approach described by McFarlane & Luo [2012], incorporating a rotating rectangular slit into the laser ablation system, allows increasing the spatial resolution to 2 μm still preserving the sensitivity of the analysis by ablating a large area (~200 μm^2). This approach allows a narrow ablation zone (2–4 μm) which is comparable to the width of a daily circulus. Stocks with coauthors [Stocks, 2012; Stocks et al., 2014] applied this laser ablation method to daily growth circuli to do a pilot analysis of the coastal migration duration in juvenile sockeye salmon. That study was based on a small data set of 19 otoliths with a focus on the largest juveniles caught at the mouth of the coastal inlet and, thus, requires further validation.

There are several elemental ratios that can be used to trace movements of fish between different environments. Strontium (Sr) is commonly used marker of movement of diadromous fish between fresh and saline waters as its concentration is by one to two orders of magnitude higher in marine environments [Campana, 1999; Secor & Rooker, 2000; Ruggerone & Volk, 2003; Wells et al., 2003; Elsdon et al., 2008; Yokouchi et al., 2011; Freshwater et al., 2015]. However, various studies have demonstrated that there may be a lag between the day of marine entry and the appearance of the Sr signal [Miller & Simenstad, 1994; Yokouchi et al., 2011]. Barium (Ba) is another trace element used as an indicator of transition between freshwater and marine environments, as Ba concentrations tend to be higher in fresh water due to inputs of Ba-rich sediments [Li & Han, 1979]. In many cases, the concentration of Ba in fresh water is twofold higher than in saline water [Bath et al., 2000; Elsdon & Gillanders, 2003; Wells et al., 2003*]*. Ba has several attractive features as a trace element of otolith for assessing changes in the environment. First, unlike Sr, Ba is accumulated independently of temperature variations [Bath et al., 2000; Khangaonkar et al., 2017], which significantly improves the correlation with other factors such as salinity and physiological condition. This is especially important when reconstructing the life history of fish moving through environments with different temperature regimes. Second, changes in Ba concentrations occur earlier than in Sr concentrations, possibly suggesting a short or no time lag of chemical signal compared to Sr, which potentially provides improved accuracy of marine entry point estimation [Hale & Swearer, 2008]. However, other studies report variable time lags and large individual variability in Ba profiles [Macdonald & Crook, 2010]. A combination of two elements (Sr:Ba ratio) was successfully used by Stocks et al. [2014] for fish that had resided in the marine environment longer than two weeks. In addition, Hammer et al. [2015] showed that the Sr:Ba ratio could be a more reliable proxy of the marine transition in environments with low calcium concentrations that alter the reliability of Sr:Ca signal. The Sr:Ba ratio may, however, be less reliable when fish spent only a few days in the marine environment mainly due to the variability of Ba signal [Egorova, 2016].

In this study we synthesize the findings of two independently conducted research projects focusing on the early marine stage of juvenile sockeye salmon in British Columbia by employing slightly different approaches. The primary objective of this study was to analyze two trace element profiles (Sr and Ba) in otoliths of anadromous juvenile salmon during the early marine stage with the highest (nearly daily) resolution and reliability of both elements for precise identification of marine entry point. Furthermore, the relative differences between marine entry points inferred from Sr and Ba profiles were analyzed across three stocks.

Materials and methods

Three wild sockeye salmon populations (stocks) were sampled for two research programs. The Rivers Inlet Ecosystem Study (RIES; 2008–2011) sampled Owikeno Lake sockeye and the Hakai Institute Juvenile Salmon Program (JSP; 2015–2016) sampled two Fraser River salmon stocks, Chilko and Lower Adams. For both programs, the care and use of experimental animals complied with the Scientific License issued under the authority of the Fisheries Act, R.S.C.1985, Chapter F-14 (License No: XR 126 2009 and XR 63 2019) animal welfare laws, guidelines and policies were approved by the University Animal Care Committee (UACC, Protocol No: 830S-07 for the Rivers Inlet and A19-0025 for the Hakai Juvenile Salmon Program). A total of 507 fish were sampled.

Sample collection and analysis. Rivers Inlet is a 45-km long fjord on the coast of British Columbia (Fig. 1). Juvenile sockeye salmon from the Owikeno Lake watershed migrate through this fjord on their way to the open ocean. Juvenile salmon (n = 146) were caught with a purse seine net during the Rivers Inlet Ecosystem Study surveys on board the MV Western Bounty, a fishing vessel operated by the Wuikinuxv First Nation, between May and early July of 2008–2011.

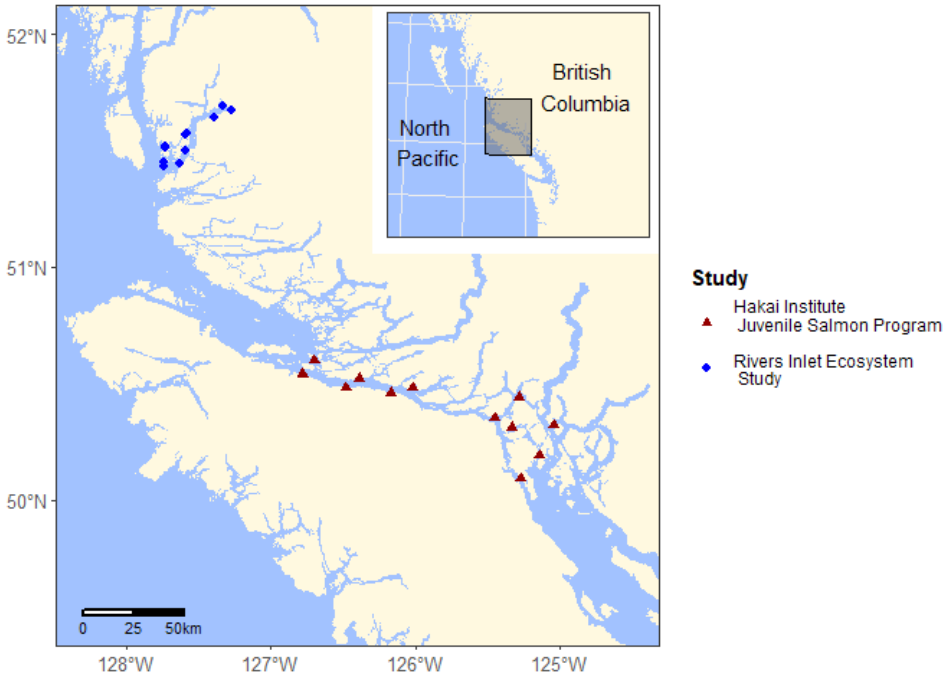


Fig. 1. Scheme of the Strait of Georgia and Rivers Inlet with sampling stations of the Hakai Institute Juvenile Salmon Program (▲) and the Rivers Inlet Ecosystem Study (♦)

Рис. 1. Карта прол. Джорджия и бухты Риверс с точками сбора проб по программам изучения молоди лососей (▲) и исследования экосистемы бухты Риверс (♦)

Juvenile Fraser River sockeye salmon were collected during the 2015 and 2016 outmigration seasons in the Discovery Islands and Johnstone Strait (Fig. 1). Fish were sampled from 6–8-m long outboard motor vessels using modified purse seine nets (bunt: 27 m × 9 m with 13 mm mesh; tow: 46 m × 9 m with 76 mm mesh). In addition, the Fraser River fish were genetically identified to stock using microsatellite markers [Beacham et al., 2005]. The fish from the Chilko (n = 161) and Adams (n = 169) stocks were analyzed for this study.

The specimens were frozen (in a freezer at –20°C for Rivers Inlet samples and at –80°C for Fraser River samples) for further analyses. In the laboratory, fish were defrosted, measured (standard, fork, and total lengths), weighed, and the pair of sagittal otoliths were extracted. The right sagittal otolith was generally used for microanalysis for the Rivers Inlet samples,

with the left otolith being a back-up in case the right otolith was broken or missing. For the Fraser River samples, the left sagittal otolith was used for the analysis, with the right otolith used as a back-up. There was no significant difference in weight between the otoliths in the pair (paired *t*-test, $p = 0.43$), so data was considered comparable.

The Rivers Inlet samples were mounted in 1-inch diameter epoxy pucks with ~10 otoliths per puck [Egorova, 2016]. Then the otoliths were progressively polished on the ventral side with 240, 400, and 600 grit abrasive paper rolls on a Buehler HANDIMET® II Roll Grinder instrument. For the Fraser River samples, the otoliths were cleaned, embedded in resin, transversely cut to expose the cores, and finely polished until the daily circuli could be visible. Then the Fraser River samples were attached to the microscope slides in groups of 18 to 30 for laser ablation.

LA-ICP-MS. The previously tested LA-ICP-MS method [Stocks et al., 2014] was adjusted to achieve a maximum resolution as close as possible to daily circulus width. A rectangular rotating slit was used in these studies to minimize the ablation area. The use of a rotating slit allowed for a sufficient ablation area and optimal slit dimensions to minimize the ablation of multiple circuli. The transverse sections of the Fraser River sockeye salmon otoliths allowed a 4 μm slit width and a 50 μm maximum slit length to be used without ablating curved circuli (which can cause a mixed signal), which yielded a 50 × 4 μm slit window (200 μm^2 ablation area). The Rivers Inlet samples were analyzed with a 2 × 142 μm rectangular slit window (280 μm^2 ablation area), which provided an area sufficient for element detection. The detection limits were below 230 ppb for ^{88}Sr and 3 ppb for ^{138}Ba in the Rivers Inlet study, while in the Fraser River study, the detection limits were higher: 426 ppb and 18 ppb for ^{88}Sr and ^{138}Ba, respectively. The concentrations of Sr and Ba were higher than the detection limits in both studies.

The Rivers Inlet otolith samples were ablated on the ventral side, which allowed maintaining a surface area sufficient for analysis. However, this technique is not optimal if a daily circulus count is needed, since circuli are harder to see over a long ablation path. In the Fraser River samples, transverse sections of otoliths were used, which significantly improved the visibility of daily circuli, but significantly reduced the surface area for laser ablation as the sections were thinner. The optimal set-ups of the instruments for both studies are listed in Tabl. 1.

The trace element profiles of the salmon otoliths were investigated using two different instruments. The Rivers Inlet otoliths were analysed on a Resolution M50-LR Ablation System (ASI, Australian Scientific Instruments, Australia) equipped with a Complex Coherent ArF (193 nm) laser and coupled to an Agilent 7700 x Quadrupole-ICPMS system (Agilent Technologies, Japan). The ablation path was set to start ~150–200 μm inwards from the edge, depending on the size of the otolith, and was run towards the edge of the otolith, perpendicular to the circuli (Fig. 2). The path did not end at the edge of the otolith but continued into the resin to ensure that the edge was covered (e.g., Fig. 2). The otoliths were run in blocks of 30 samples with standards bracketing every 3–5 samples. The samples and the standards were analyzed with an acquisition time of 0.331 s and a scan speed of 2 $\mu m \cdot s^{-1}$. Several samples ($n = 9$) were run at a slower scan speed of 0.25 $\mu m \cdot s^{-1}$, which allowed comparison of results obtained at different scan speeds.

For the Fraser River samples, the ablation was performed on a Thermo X-Series II ICPMS (Thermo Fisher Scientific) and Photon Machines Analyte G2 (Photon Machines, Bozeman, Montana, USA). The ablation started at approximately 50 μm from the outside edge of the otolith and moved toward the core of the otolith, with the slit oriented perpendicular to the daily circuli. The total length of the laser path varied from 150 to 200 μm, depending on the size of the otoliths and visible check marks.

Data reduction and analysis. For both studies, five isotopes were measured: ^{43}Ca, ^{44}Ca, ^{88}Sr, ^{137}Ba, and ^{138}Ba. Raw data obtained with the instrument were reduced using Iolite, a self-contained package for Igor Pro® (Wavemetrics Inc. of Lake Oswego, Oregon, USA) [Paton et al., 2011]. Concentrations and trace element ratios were determined by external

Table 1

LA-ICP-MS settings, operating conditions, and data acquisition parameters for multi-element analysis of otolith samples for the Rivers Inlet Ecosystem Study (RIES) and the Hakai Institute Juvenile Salmon Program (JSP)

Таблица 1

Настройки лазерной абляции и масс-спектрометра для многоэлементного анализа образцов отолитов по программам исследования экосистемы бухты Риверс (RIES) и изучения молоди лососей (JSP)

Laser Ablation Parameters:	**RIES set-up**	**JSP set-up**
Instrument Model	ASI Resolution M50-LR	Photon Machines Analyte G2
Wavelength, nm	193	
Ablation Gas	He	He
He Flow Rate, mL·min^{-1}	800	
Ablation Mode	Scan line with rotating slit	Scan line with rotating slit
Slit size, µm	2 × 142	4 × 50
Repetition Rate, Hz	5	15
Scan Rate, µm·s^{-1}	2 and 0.25	1
Fluence, J·cm^{-2}	1.8	6.9
ICP-MS Parameters:		
Instrument Model	Agilent Technologies 7700x Series	Thermo Scientific X-Series II
RF Power, W	1350	
Carrier Gas	Ar	Ar
Ar Flow Rate, L·min^{-1}	0.53	0.60
Additional Gas	N_2	–
N_2 Flow Rate, mL·min^{-1}	2.00	–
Isotopes Monitored	^{43}Ca, ^{44}Ca, ^{88}Sr, ^{137}Ba, ^{138}Ba	^{43}Ca, ^{44}Ca, ^{88}Sr, ^{86}Sr ^{138}Ba
Standards	SRM NIST 612, NIST 610	SRM NIST 612, NIST 610
Internal Standard Element	Ca	Ca

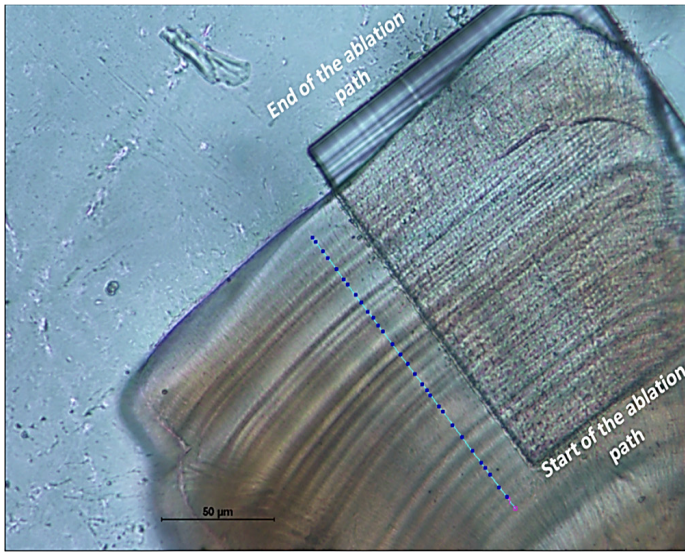


Fig. 2. An example of the ImageJ software window with the ObjectJ automatic ring detection option (light blue line with dark blue dots). On the right, the start and the end of the ablation path are shown. Tested otolith was embedded in epoxy resin (sulcus side up) and polished with 240, 400, and 600 grit Buehler CARBIMET® abrasive paper rolls until daily circuli were visible

Рис. 2. Пример окна программы ImageJ с опцией автоматического определения колец отолитов ObjectJ (*голубая полоса с синими точками*). Справа показаны начало и конец лазерной абляции. Исследуемый отолит был залит эпоксидной смолой (бороздкой вверх) и полировался абразивной бумагой Buehler CARBIMET® с зернистостью 240, 400 и 600 до проявления суточных колец

calibration using the synthetic silicate reference glass SRM NIST612 and SRM NIST 610. Instrument drift was corrected assuming Ca = 40% m/m as an internal standard for carbonates. The synthetic silicate glass SRM NIST 610 and the carbonate USGS reference material MACS-3 were monitored for quality control purposes. Using natural abundance values, the measured counts for each isotope were transformed into elemental counts, and element : calcium (Ca) ratios were calculated [Arrowsmith, 1987]. Here we refer to Sr:Ca and Ba:Ca ratios as the Sr and Ba signal, respectively. For the Rivers Inlet samples, element concentrations in ppm were calculated based on their known concentrations in the reference material (μg of the element to 1 g of calcium).

Ba and Sr breakpoint determination. To determine the breakpoint, segmented regression analysis (SRA) was performed using the R statistical software (R Core Team]. The package *segmented* was used to compute the summary of estimates of the slopes and the location of breakpoints [Muggeo, 2003, 2008], with some modifications as SRA requires a piecewise linear relationship between the response and an explanatory variable. The breakpoint was determined based on the change in Sr and Ba signals determined by SRA Protocol [Egorova, 2016]. It is important to note that Ba profiles were not piecewise linear along the ablation path with multiple peaks in the signal, and, therefore, it was important to crop the area on the ablation path with two linear segments before and after the final decrease in the signal.

Comparison of Ba and Sr profiles. To quantify and compare the changes in Ba and Sr profiles close to the breakpoint (± 100 μm from the breakpoint), we first assessed the behavior of the signals prior to and after the estimated breakpoints. In general, most of the Sr profiles at the transition between the environments were characterized by the stable levels of the signal prior to and a rapid increase after the breakpoint, plateauing at a higher level. Ba showed varying signal behaviors with the presence of multiple additional peaks in the profiles prior to the sharp increase in the signal before the breakpoint. Thus, we classified Ba signals into five different groups depending on the type of Ba signal behavior (Tabl. 2). The difference in the number of Ba peaks in fish otoliths with different origins was tested for the Chilko and Adams stocks. A chi-square test of goodness-of-fit was performed to determine whether the number of Ba peaks was similar between these stocks. A significant difference was attributed to p values of < 0.05. A similar procedure was performed to assess the difference between years within each stock. In addition, the width of Ba peaks was measured for the Fraser River samples to determine the approximate duration of elevated Ba signal.

Table 2

Classification of different patterns of Ba signal behavior prior to the breakpoint

Таблица 2

Классификация профилей бария перед переходом в морскую среду

Type	Ba signal behavior	Additional details
1	One prominent uniform peak in Ba:Ca ratio before abrupt decrease	A more than two-fold increase in ratio followed by a more than two-fold decrease
1.5	Two not clearly separated peaks	One peak is clearly visible but the second is not as high or present as a flat line followed by a decrease in element concentration
2	Two clearly separated peaks	Two peaks with approximately similar shapes
2.5	More than two but not clearly separated peaks	As in 1.5 but with more than two peaks
3	More than two clearly separated peaks	As in 2 but with three and more peaks

To assess the difference in the breakpoint estimates inferred from the two different elemental signals, the differences in breakpoint occurrence were calculated between Sr and Ba signals for the Rivers Inlet and Fraser River samples. The differences obtained were statistically compared between studies after testing the variables for normality of distribution. As data were not normally distributed even after the transformation, the non-parametric Wilcoxon signed rank tests were applied. A significant difference was attributed to p values of < 0.05.

Discussion of results

All the Sr profiles had a generally similar pattern, starting with low concentrations in the freshwater environment and increasing sharply after the marine entry (typical Sr profiles are shown in Fig. 3). The Ba signals, on the other hand, were not stable prior to the breakpoint, as demonstrated in other studies [Bath et al., 2000; de Vries et al., 2005; Martin et al., 2013], but increased immediately before the breakpoint (e.g., Fig. 3). In general, Ba increased sharply in the profiles before dropping as juveniles entered the marine environment. However, most samples (72% for both studies) had multiple peaks in Ba profiles. The peaks could overlap (Fig. 3, H), appear close to one another (Fig. 3, F,G) or far apart (Fig. 3, E). Overall, the Ba profiles were classified into five different patterns (Tabl. 2). The typical patterns for the types of Ba signal are shown in Fig. 4.

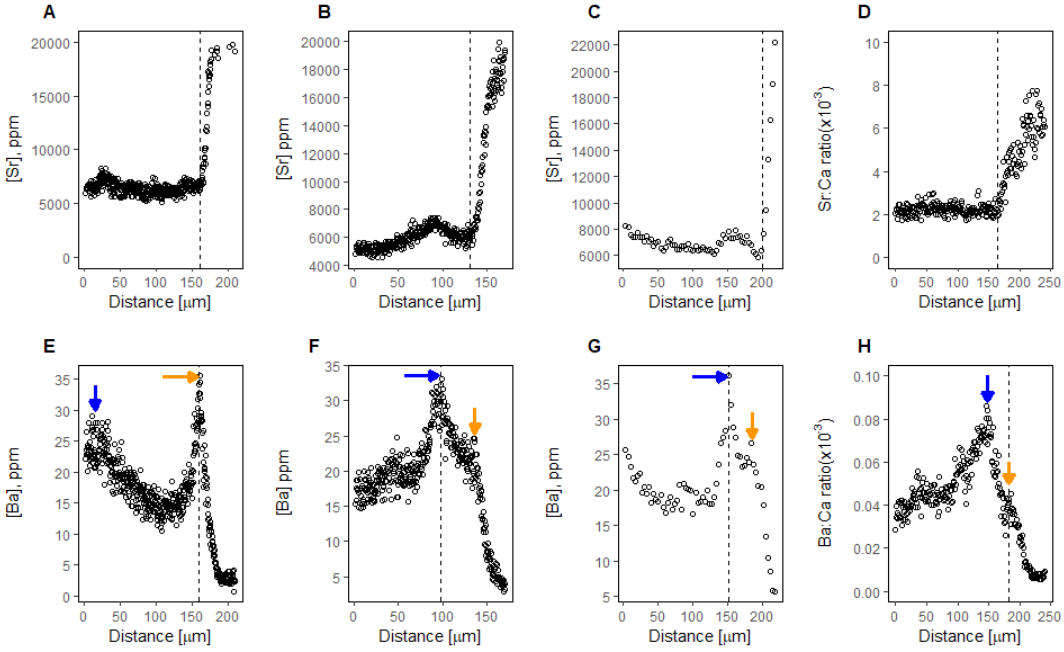


Fig. 3. An example of the change in Sr (**A, B, C, D**) and Ba (**E, F, G, H**) signals along the ablation path (ppm units for the Rivers Inlet study; Sr:Ca and Ba:Ca ratios for Hakai Institute program). *Arrows* indicate double peaks in the Ba profile: orange arrow — the peak associated with transition to the marine environment (determined on Sr profile); blue arrow — the event before the entry to the marine environment. *Dotted line* indicates the breakpoint determined by the segmented regression analysis. Zero on the X-axis corresponds to the start of the ablation path. Profiles **A, B, E, F** were obtained at a scan speed of 0.25 μm·s^{-1}; profiles **C** and **G** — 2.0 μm·s^{-1}, and profiles **D** and **H** — 1.0 μm·s^{-1}

Рис. 3. Примеры изменений сигналов стронция (**A, B, C, D**) и бария (**E, F, G, H**) в прорези отолита (в частях на миллион для проекта в бухте Риверс, соотношения Sr:Ca и Ba:Ca для проекта института Хакай в пр. Джорджия). *Стрелками* показаны двойные пики на профилях бария: оранжевой стрелкой — пик, связанный с переходом в морскую среду (точка перехода определена по профилю стронция), синей — пик перед переходом. *Пунктирная линия* показывает точку перехода, определенную методом кусочной регрессии. Ноль на оси абсцисс соответствует началу лазерной абляции. Профили **A, B, E, F** получены со скоростью сканирования 0,25 мкм/с; профили **C** и **G** — 2,0 мкм/с; профили **D** и **H** — 1,0 мкм/с

There was a distinct difference in the number of Ba peaks between the two Fraser River stocks, X^2 (2, N = 330) = 78, $p < 0.001$. Most of the Lower Adams fish (82%) had 1.5–2.5 peaks, while 81% of the Chilko fish had 1 or 1.5 peaks (Tabl. 3). No significant difference between years was observed for the Fraser River stocks. We also measured the width of Ba peaks to estimate the duration of the heightened Ba:Ca ratios. The average width of the elevated Ba:Ca ratios was approximately 70 μm (Fig. 5), which corresponds to a duration of ~35 days before entering the marine water (assuming daily circulus width to be 2 μm).

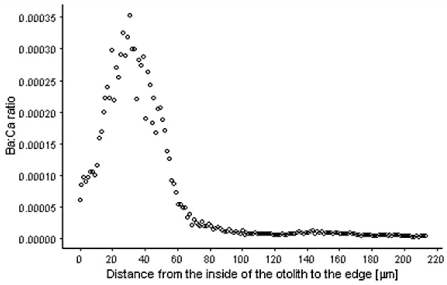
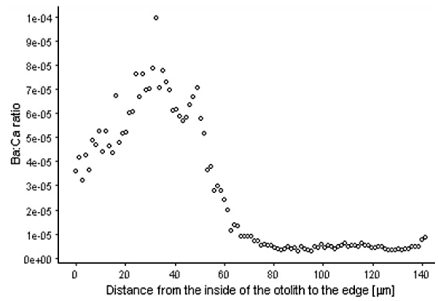
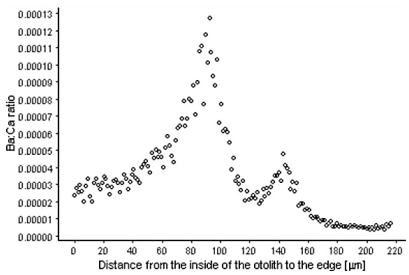
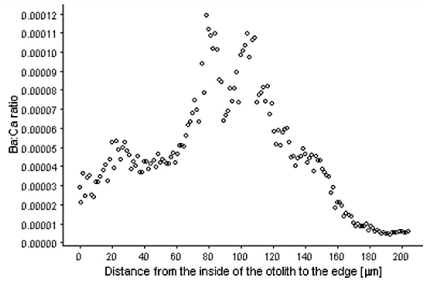
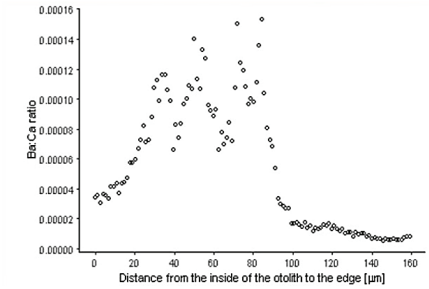
Type	Ba signal	Type	Ba signal
1	One prominent uniform peak in Ba:Ca ratio before abrupt decrease 	**1.5**	Two not clearly separated peaks 
2	Two clearly separated peaks 	**2.5**	More than two but not clearly separated peaks 
3	More than two clearly separated peaks 		

Fig. 4. Five behavior patterns of the Ba signal (refer to Tabl. 2 for the types description)

Рис. 4. Пять разных типов профилей сигналов бария (см. описания типов в табл. 2)

Table 3

Distribution of Ba peaks for the two Fraser River stocks, Chilko and Adams, sampled in 2015 and 2016

Таблица 3

Пики профилей бария для двух популяций р. Фрейзер: Чилко и Адамс (сборы 2015 и 2016 гг.)

Number of Ba peaks	Chilko		Adams	
	2015	**2016**	**2015**	**2016**
0	0	1	0	0
1	39	42	9	11
1.5	24	25	13	32
2	11	7	16	49
2.5	4	4	10	19
3	4	0	5	5

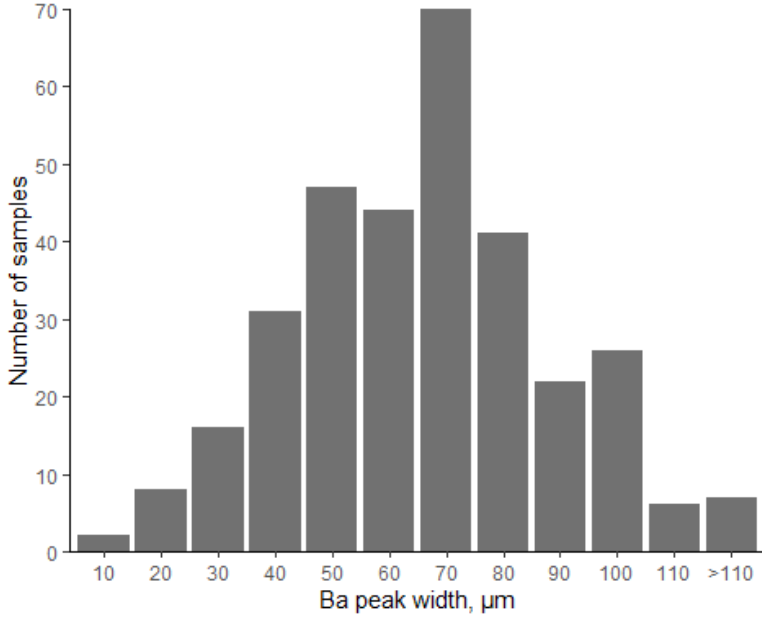


Fig. 5. Frequency distribution of the Ba peaks width, µm. The entire width of elevated Ba signal cannot be measured for some profiles that may explain the skewness of the graph to the left

Рис. 5. Частотное распределение ширины пиков профилей бария, мкм. Не все профили имели достаточную длину для измерения полной ширины последнего пика, что могло привести к асимметрии графика

In both studies, the breakpoint was calculated for each sample using the SRA analysis of two elemental signals, Sr and Ba. In comparison to the breakpoint estimated on the basis of Sr, the change in Ba signal occurred earlier in most cases (102/141 for the Rivers Inlet and 253/351 for the Fraser River samples): 11 µm earlier (10.5 ± 1.8 µm) for the Rivers Inlet sockeye and 3 µm earlier (3.04 ± 0.35 µm) for the Fraser River fish (Fig. 6). The difference in breakpoint estimates between the studies was significant ($p < 0.01$). Variability in breakpoint estimates was higher for the Rivers Inlet study.

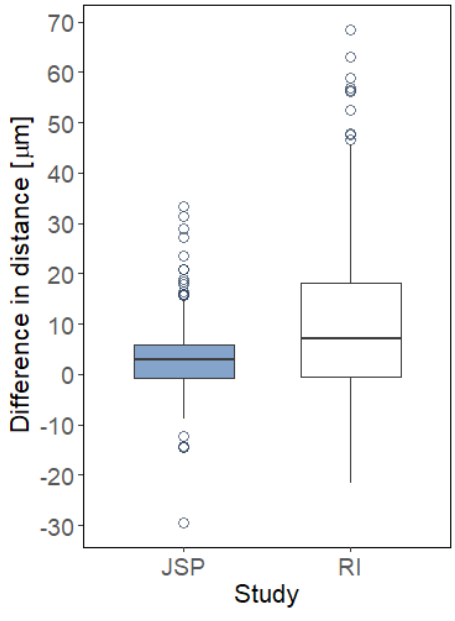


Fig. 6. Boxplots showing the deviation in the breakpoint location (in µm) between Sr and Ba profiles for the Hakai Institute Juvenile Salmon Program (JSP; *grey*) and the Rivers Inlet Ecosystem Study (RI; *white*). Median values are indicated by the *black solid horizontal lin*e, the interquartile range by the *box outline*, and the 95% confidence intervals by *whiskers*. Empty circles are outliers. Positive values indicate Ba-based breakpoint preceding Sr-based one.

Рис. 6. Разница (в микрометрах) в определении точки перехода в морскую среду по профилям стронция и бария в отолитах, отобранных в прол. Джорджия (JSP, обозначены *серым*) и бухте Риверс (RI, обозначены *белым*). Медианы показаны *черными горизонтальными линиями*, межквантильные расстояния — *«ящиками»*, 95 %-ные доверительные интервалы — «*усами*». Статистические выбросы обозначены *пустыми кружками*. Положительные значения соответствуют случаям, когда переход, определенный по профилю бария, опережает переход, определенный по профилю стронция

In this study, we considered commonly used Ba and Sr profiles inferred from an ultra-high-resolution LA-ICP-MS analysis of otoliths of juvenile sockeye salmon from three different stocks in order to evaluate how these elements in otoliths could be used to best estimate the marine entry point. These techniques are particularly relevant to studying juvenile diadromous species, especially when detailed information on the point of marine entry is required.

Behavior of Sr and Ba signals. The Sr signal in all cases followed the most common pattern, starting with low values in fresh water and rapidly increasing after entering the marine environment. Highly resolved measurements showed that the Ba signal was not as steady as expected and reached its maximum prior to decreasing permanently. In addition, multiple Ba peaks were present throughout the ablation area. Previously, the Ba signal was often discarded due to its high variability [Tabouret et al., 2011]. However, we demonstrated that the variability in exhibiting multiple peaks is not random and may provide valuable information on the fish physiology. In this study, we demonstrated that Ba peaks were significantly different between the two Fraser River stocks regardless of year. The first peak in the Ba signal often coincided with the edge of a distinct translucent zone (Fig. 7). It has been suggested that smoltification can be asociated with rapid changes in physiology and may take months to complete [Wedemeyer et al., 1980; Björnsson et al., 2011]. Indeed, elevated hormone levels accompanying smoltification have been observed over a 30–60-day period [Dickhoff et al., 1978]. Assuming that the elevated Ba concentration correspondes to the smoltification process, the width of the first Ba peak of 70 μm indicates an approximate duration of 35 days, which is well consisnent with previously reported estimates [Dickhoff et al., 1978]. However, it is possible that the Ba peaks may signal other physiological changes occurring at the onset of smoltification and are, thus, preserved in the chemical composition of the otolith. Alternatively, it may be due to a release of Ba from river-borne suspended matter during estuarine mixing [Coffey et al., 1997] .

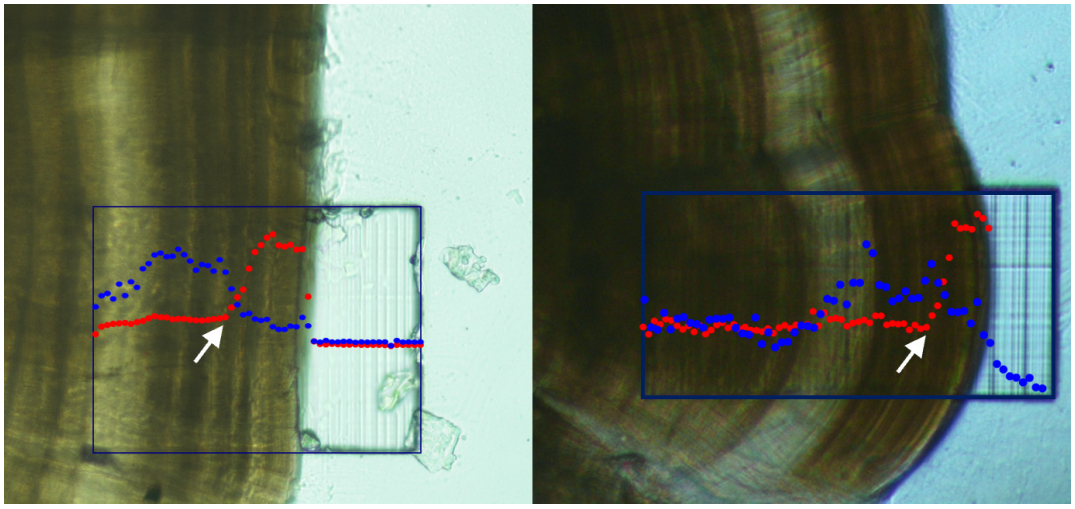


Fig. 7. Examples of the position of the “double” peaks in two otoliths. The *blue rectangle* represents the boundaries of the ablation path; *blue dots* are the Ba signal and *red dots* are the Sr signal; the white arrow indicates the point of marine entry

Рис. 7. Примеры двойных пиков на профилях для двух отолитов. Синий квадрат указывает границы лазерной абляции, *синими точками* показана концентрация бария, *красными точками* — концентрация стронция

Variability in breakpoint estimates. In 72% of samples, changes in the Ba breakpoint signal occurred earlier than those in the Sr signal, which is consistent with previous research [Hale & Swearer, 2008]. This may occur due to differences in uptake, metabolic turnover,

and reaction pathways for the incorporation of these two elements into the otolith [Bath et al., 2000; Elsdon & Gillanders, 2003; Tabouret et al., 2010; Braux et al., 2014; Stanley et al., 2015]. It is also possible that the breakpoint in the Ba signal may act as an indicator of the transition from a freshwater to an estuary-type environment, while the breakpoint in Sr signal marks a permanent transition to the marine environment [Limburg, 1995; Stecher & Kogut, 1999; Hale & Swearer, 2008]. This hypothesis may explain the earlier emergence of the breakpoint in the Ba signal than in the Sr one. In addition, substantial time-lags for both elements have been described from the Australian bass, *M. novemaculeata*, and the Japanese eel, *A. japonica* [Macdonald & Crook, 2010; Yokouchi et al., 2011]. In the Australian bass, it took ≤40 days for Sr:Ca and ≤30 days for Ba:Ca concentrations to reach equilibrium at a salinity of 0.5‰ in an experimental study [Macdonald & Crook, 2010]. This finding confirms the earlier appearance of Ba in wild sockeye samples. However, resolving the issue as to which signal shows the true point of marine transition is a subject for further laboratory investigation.

In <28% samples, the difference between the Sr and Ba breakpoint signals was negative, and the Ba signal occurred after the Sr signal (e.g., Fig. 3, B and F). This is likely an artefact of the analysis used, because a closer inspection of Ba profiles revealed that the delay in Ba signal was due to the presence of "multiple peaks" situated close to each other . If the first peak in Ba profiles occurred close to the second one, the segmented regression analysis identified the first larger peak as a breakpoint, while the "true" breakpoint was the second peak (assuming Sr shows the position of true breakpoint). Furthermore, the Sr signal was always "cleaner," as a minor change in the Sr concentration was never able to hide the true fresh water–saline water difference (Fig. 3). When multiple peaks in the Ba signal occurred far from each other (Fig. 3, E), the breakpoint was identified at the same locations using both elements (Sr and Ba). Thus, the proximity of Ba peaks may be an important factor in the identification of the breakpoint. It appeared that a large variation came from the misidentification of the Ba breakpoint when multiple peaks were present.

Some researches argue the Sr:Ba ratio can be used as a more efficient marker of the marine transition as the Sr:Ba ratio changes by a few orders of magnitude when fish move from fresh to saline water [Limburg, 1995; McCulloch et al., 2005; Walther & Limburg, 2012; Stocks et al., 2014]. This ratio was found to be useful in studies where the concentration of Ca varied significantly between fresh and marine systems, altering Sr:Ca and Ba:Ca signals [Hamer et al., 2015]. This signal showed a lower deviation from the mean than the Ba signal but was influenced by both the Sr and Ba concentrations, which allows for a smaller ablation area [Stocks et al., 2014]. On the other hand, the Sr:Ba ratio was shown to provide less information available for interpretation, as the ratio could be driven by fluctuations in either of those signals [Walther & Limburg, 2012]. Thus, the tendency for Ba concentration to increase right before the marine entry and the presence of multiple peaks in Ba profiles can affect Sr:Ba ratios and eventually result in erroneous marine entry identification. For instance, Egorova [2016] demonstrated how the large differences between Sr and Ba signals can make the marine entry point appear significantly later in a Sr:Ba signal compared to a Sr:Ca signal. Based on our findings, it may be suggested that the Sr:Ba signal, while remaining a robust proxy for fish that have spent more than two weeks in the marine environment [Stocks et al., 2014] or for older fish which does not require high daily resolution (e.g., investigations of annuli), is not as useful for determining the breakpoint in the case of fish that have only recently entered marine water.

Repeatability of breakpoint estimates. The advantage of the rotating slit in ultra-high daily resolution studies over the conventional spot analysis (or raster scan) was demonstrated in this study. Specifically, to record the changes in elemental signal during the early marine stage, is it important to observe changes in the signal daily, as the duration of the early marine stage is quite short. The conventional spot, or raster scan, analysis is too coarse to resolve the daily chemistry, as was previously recognized by Altenritter et al. [2018] who found that a

30-μm spot size would average the Sr concentration over a longer period that would result in a lower measured concentration for the peak. However, the use of a large spot size can also lead to another problem that is considered in this study and was not reported previously. Even with a smallest spot diameter (10 μm) used in otolith studies based on a raster scan (the offset of ½ of the diameter), the breakpoint appeared ~5 μm earlier than the actual signal. However, such small spot sizes are not common in otolith analysis due to high coefficients of variation (CVs) and low accuracy provides lower reliability of the 10 μm ablation line measurements [Chang et al., 2012]. Based on the results from this study, larger spot sizes (20–30 μm) produce an error as large as 10–15 μm which can be equivalent to ~5–7 days, assuming an average circulus width to be 2 μm. Hence, while the reported lags in the elemental signal can be the result of physiological difference [Freshwater et al., 2015], they may also be due to the low resolution of spot/raster scan analysis. Such artificial lag due to instrumental set-up should be taken into account when correlating environmental data and fish movements.

Artificial lags/offsets can also be induced by ablating multiple layers of otolith material [Hoover & Jones, 2013], which is common during a raster scan/spot analysis, but can be minimized by using slit. Two-slit configurations can be used (2 × 124 or 4 × 50) depending on the sample preparation (curvature of circulus will limit the length of the slit). As the slit width can be as low as 2 μm, which is similar to an average otolith circulus width, the averaging of the signal can be minimized. Since the breakpoint also appears earlier when using slit, the error in our analysis appeared to be much smaller and was ~1 μm from the "true" breakpoint.

To increase the accuracy of marine entry estimation on the basis of Sr signal, additional experimental research on the time lag in the Sr signal is needed. The high variability of data for different species and life stages necessitates validation for certain species and life stage of interest. The position of the "true" breakpoint requires further laboratory studies, as peaks in Ba signal appear generally earlier than a change in Sr signal (the last peak of Ba signal usually coinciding with the increase in Sr signal). Further research is expected to clarify whether the peaks in Ba signal indicate the beginning of marine transition or rather reflect physiological changes that occur before the marine entry.

Limitations. Incomplete profiles might influence the estimation of the magnitude of shift of concentrations before and after breakpoints. Due to the high cost of the daily resolved laser ablation, only the parts of the otoliths closest to the marine transition were ablated. The average duration of residence in the marine environment, calculated from previous studies, was taken into account when estimating the length of the ablation pass. In this study the length of the pass was 100 μm. In cases when no prominent marks (potential marine entry marks) were visible across the 100-μm range, the path was extended to 150 μm to increase the probability of overlapping with the marine entry zone.

Water chemistry data from environments under consideration would help to determine the best marker of marine transition. A comparison of actual Ba, Ca, and Sr concentrations in fresh and saline water in the migration zone during the sampling period would also contribute to the interpretation of the study results.

Conclusions

The use of the rotating slit allowed a high-resolution analysis of the otolith chemical composition by LA-ICP-MS. The width of the slit was very close to a daily circulus width of the otoliths (2 μm), which allowed recording the daily changes in elemental composition during the period of transition to the marine environment. This study indicates that the Sr signal is more reliable than the Ba one for determining the marine entry point. However, Ba has several advantages as a marker of marine transition. First, the breakpoint was generally detectable in the Ba signal prior to its appearance in the Sr signal. Second, Ba is less dependent on temperature, though this statement needs further verification. However, the complexity of Ba profiles makes it challenging to identify the point of marine transition. This

is also complicated by our finding that the number of Ba peaks can vary between stocks. The presence of multiple peaks in the Ba signal can also provire important information on fish condition prior to the marine entry, and this should be further investigated.

In cases where no data on metal concentrations in water are available, Sr would be a more reliable signal. The exception are cases with low Ca levels in freshwater habitats [Hamer et al., 2015], which could be addressed by applying Sr:Ba profiles, or where the introduced error is considered negligible. For Fraser River and Rivers Inlet sockeye salmon, the Sr:Ca ratio provided the best precision and the lowest variability in determining the marine entry point. Additional experimental data on the Sr signal time lag would allow for highly accurate and precise determination of the marine entry point in otoliths. The results of this study could be used as a decision-making outline when selecting the Sr:Ca or Ba:Ca profiles in otoliths of diadromous fish for the determination of their environment transition points.

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