

## Utility of Nd isotope ratio as a tracer of marine animals: regional variation in coastal seas and causal factors

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**Abstract.** Isotopic compositions of animal tissue are an intrinsic marker commonly used to trace animal origins and migrations; however, few isotopes are effective for this purpose in marine environments, especially on a local scale. The isotope ratio of the lanthanoid element neodymium (Nd) is a promising tracer for coastal animal migrations. Neodymium derives from the same geologic materials as strontium, well known as an isotopic tracer ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) for terrestrial and anadromous animals. The advantage of the Nd isotope ratio ( $^{143}\text{Nd}/^{144}\text{Nd}$ , expressed as  $\epsilon_{\text{Nd}}$ ) is that it varies greatly in the ocean according to the geology of the neighboring continents, whereas oceanic  $^{87}\text{Sr}/^{86}\text{Sr}$  is highly uniform. This study explored the utility of the Nd isotope ratio as a marine tracer by investigating the variation of  $\epsilon_{\text{Nd}}$  preserved in tissues of coastal species, and the causes of that variation, in a region of northeastern Japan where the bedrock geology is highly variable. We measured  $\epsilon_{\text{Nd}}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  in seawater, river water, and soft tissues of sedentary suspension feeders: the mussels *Mytilus galloprovincialis* and *Mytilus coruscus* and the oyster *Crassostrea gigas*. We also measured concentrations of three lanthanoids (La, Ce, and Pr) in shellfish bodies to determine whether the Nd in shellfish tissue was derived from solution in seawater or from suspended particulates. The  $\epsilon_{\text{Nd}}$  values in shellfish tissue varied regionally (−6 to +1), matching the ambient seawater, whereas all  $^{87}\text{Sr}/^{86}\text{Sr}$  values were homogeneous and typical of seawater (0.7091–0.7092). The seawater  $\epsilon_{\text{Nd}}$  values were in turn correlated with those in the adjacent rivers, linking shellfish  $\epsilon_{\text{Nd}}$  to the geology of river catchments. The depletion of Ce compared to La and Pr (negative Ce anomaly) suggested that the Nd in shellfish was derived from the dissolved phase in seawater. Our results indicate that the distinct Nd isotope ratio derived from local geology is imprinted, through seawater, on the soft tissues of shellfish. This result underscores the potential of  $\epsilon_{\text{Nd}}$  as a tracer of coastal marine animals.

**Key words:** animal migration; catchment geology; Ce anomaly; coastal sea; mussel; Nd isotope ratio; oyster; river water; seawater; shellfish; tracer.

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## INTRODUCTION

Tracing the migrations of free-ranging marine animals in coastal areas has been a challenge for ecologists, despite the importance of migration patterns for conservation and stock management of fishery resources. Coastal areas are important reproductive habitats for marine animals as well as being the most heavily exploited part of the ocean (e.g., Sundblad et al. 2011, Sundblad and Bergström 2014). Therefore, understanding how marine organisms use the nearshore area is important for management of marine resources. However, little is known about the migrations and connectivity of marine organisms (Cowen et al. 2007). Although the use of artificial markers has yielded migration information for some marine species (e.g., Parsons et al. 2003, Block et al. 2005), it is restricted to larger individuals, whose behavior and mortality are nevertheless inevitably affected.

The isotopic composition of body tissues has been used as an intrinsic marker in animal studies. Intrinsic markers have several advantages over tagging techniques in that their application is not restricted by body size, they avoid the need to tag captured animals and recapture them after tagging, and they do not affect the behavior and mortality of the studied animals (e.g., Rubenstein and Hobson 2004, Hobson et al. 2010, McMahon et al. 2013). The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio is a well-known intrinsic marker for investigating the migration of terrestrial animals and anadromous fishes (e.g., Vogel et al. 1990, Chamberlain et al. 1997, Kennedy et al. 1997, Bentley 2006). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in water and soil varies widely with the bedrock geology (Capo 1998), and physiologic mass-dependent fractionation is rendered negligible by normalizing measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios by the theoretical value (0.1194) of the stable isotope ratio  $^{86}\text{Sr}/^{88}\text{Sr}$  (Graustein 1989). Thus, it is possible to characterize the habitat area of animals with high precision. However, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is an ineffective tracer in marine environments because the concentration of Sr in seawater (7.74 mg/L) is orders of magnitude greater than in average river water (0.070 mg/L), and thus,  $^{87}\text{Sr}/^{86}\text{Sr}$  is essentially uniform ( $0.70918 \pm 0.00001$ ) in all oceanic areas (Faure and Mensing 2005).

On the global scale, isoscapes have been established in marine environments for stable isotope

ratios of light elements (including  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{18}\text{O}$ ) at the base of the food web or in seawater (e.g., McMahon et al. 2013). These isoscapes are of growing usefulness for inferring the movements of highly migratory species (e.g., Graham et al. 2010, Ceriani et al. 2014). However, on the local scale, variations of these isotope ratios are usually too small to distinguish different habitats. In addition, although several studies have documented local variations of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  of organisms in marine coastal environments (e.g., Carlier et al. 2007), such variations reflect not only geographic variation but also differences in the food sources and trophic levels of the organisms. Straightforward estimation of habitats from the isotope ratios of light elements is difficult because physiologic mass-dependent fractionation of these elements creates offsets between the isotopic values of animal tissues and ambient materials.

The neodymium (Nd) isotope ratio,  $^{143}\text{Nd}/^{144}\text{Nd}$ , has potential as an intrinsic marker of marine organisms that may be useful at the local scale. Neodymium is a lanthanoid element included in the rare earth elements (REEs), which are remarkably similar in their chemical and physical characteristics. The  $^{143}\text{Nd}/^{144}\text{Nd}$  of environmental materials reflects the local geology, much as  $^{87}\text{Sr}/^{86}\text{Sr}$  does (Faure and Mensing 2005). Although some provenance studies have used Nd isoscapes to infer the origin of geological materials, mainly for archeological purposes (e.g., Brems et al. 2013), none to our knowledge has used them for ecological applications. The advantage of the Nd isotope ratio in ecological studies is that, as with the Sr isotopic ratio, physiologic fractionation of Nd can be rendered negligible by normalization with respect to the theoretical value (0.7219) of the stable isotope ratio  $^{146}\text{Nd}/^{144}\text{Nd}$ . The  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio is conventionally expressed in epsilon units, in which  $\epsilon_{\text{Nd}}$  represents the relative deviation of  $^{143}\text{Nd}/^{144}\text{Nd}$  in the sample from that of the present chondritic uniform reservoir (0.512638), in units of  $10^{-4}$ . Previous studies have shown that  $\epsilon_{\text{Nd}}$  in seawater varies widely among oceanic regions and water masses (e.g., Amakawa et al. 2000, 2004a, b, Lacan et al. 2012). Because the oceanic variation originates from the differing values in neighboring continents (Lacan et al. 2012),  $\epsilon_{\text{Nd}}$  in seawater should be highly variable in coastal seas, which adjoin the continents.

Because the Nd concentration in seawater (10–12 ng/L) is almost equivalent to that of river water (Lacan et al. 2012), variations in  $\epsilon_{Nd}$  of river water should lead to  $\epsilon_{Nd}$  variations in coastal seawater and consequently in the bodies of organisms inhabiting coastal seas.

Although the Nd concentration in seawater is rather low, the element can become concentrated in biological settings. Because REEs are similar in ionic radius to the calcium ion and higher in valence, REE ions tend to displace  $Ca^{2+}$  by preferentially occupying sites where  $Ca^{2+}$  is adsorbed onto biomembranes (Brown et al. 1990). Also, Nd tends to accumulate in a few specific organs, including the gills, kidney, and liver, where other heavy trace elements such as Cu, Zn, Mn, Cr, Ni, Cd, and Pb are known to accumulate (e.g., Pourang 1995, Al-Yousuf et al. 2000, Malik et al. 2010).

In this paper, in arguing for the utility of the Nd isotope ratio as a tracer of marine animal migration in coastal seas, we show, first, that the Nd isotope ratio in coastal seawater takes distinct values characteristic of the region and, second, that these values are well preserved in the bodies of animals living there. To do this, we measured isotope ratios of Nd and Sr in the soft tissues of bivalves, in the seawater at their locations, and in the water of rivers in the nearby hinterlands. We selected the Pacific coast of the Tohoku district, northeast Japan, as the study site because the wide variety of bedrock in that region was expected to create large variations in Nd isotope ratios in coastal ecosystems. Three species of benthic, suspension-feeding shellfish (the mussels *Mytilus galloprovincialis* and *Mytilus coruscus* and the oyster *Crassostrea gigas*) were examined as representative animals of nearshore ecosystems to ensure that the Nd in their tissues came only from their local seawater.

To determine whether Nd in shellfish tissues was derived from suspended matter or from solution in seawater, we examined the cerium (Ce) anomaly, the excess or depletion in Ce concentration compared to other lanthanoides (e.g., Lipin and McKay 1989), of shellfish tissues and suspended materials. Although the lanthanoides have very similar chemical behavior, the behavior of Ce is exceptionally dependent on redox conditions (e.g., Elderfield 1988). As a result, Ce is commonly enhanced in suspended matter and depleted in seawater (e.g., Elderfield et al. 1990,

Piepgras and Jacobsen 1992, Sholkovitz et al. 1994). Therefore, the Ce anomaly should provide insight into the origin of Nd in shellfish tissues.

## MATERIALS AND METHODS

### Study area

To ensure a wide range of Nd isotopic variation, our study area was the Pacific coast of the Tohoku district, Japan, a complicated coastline with a number of small bays. Rivers originating in the Kitakami or the Ou Mountains are expected to discharge water with Nd isotope ratios influenced by the geology of their watersheds (Fig. 1a). The northern and southern Kitakami Mountains are composed mainly of Paleozoic to Mesozoic sedimentary rocks, whereas the central part of the range is composed mainly of Cretaceous volcanic and plutonic rocks. The Ou Mountains are composed mainly of Cenozoic volcanic rocks. Cenozoic sedimentary rocks are widely distributed at the base of the Ou Mountains.

Three ocean currents also may affect the Nd isotope ratios of seawater in this area (Amakawa et al. 2004a, Fig. 1b). The cold Oyashio Current brings water of high  $\epsilon_{Nd}$  (more than  $-3$ ) southward from the Arctic Ocean to the Sanriku coast. The extension of the warm Kuroshio Current, with low  $\epsilon_{Nd}$  (approximately  $-6$ ), commonly reaches the Sanriku coast from the south. The Tsugaru Warm Current, which is derived in the Japan Sea from the northward flowing Tsushima Current with  $\epsilon_{Nd}$  approximately  $-8$ , exits the Japan Sea via the Tsugaru Strait and then flows southward along the Sanriku coast (Yasuda 2003).

### Sampling and pre-treatment of shellfish samples

Living shellfish, consisting of 12 oysters (*Crassostrea gigas*) and 26 mussels (*Mytilus coruscus* and *Mytilus galloprovincialis*), were collected in June 2015 and April 2016 at 13 sites along the Sanriku coast, chilled, and brought to the laboratory. We selected these sedentary, suspension-feeding species to minimize any effect of feeding preference. Thus, elements in shellfish soft tissues could be derived only from solution or from suspended particulates in seawater. Under the assumption that the uptakes of Nd by *M. coruscus* and *M. galloprovincialis* were similar, the two mussel species were not treated separately. In the laboratory, the soft bodies of the shellfish were



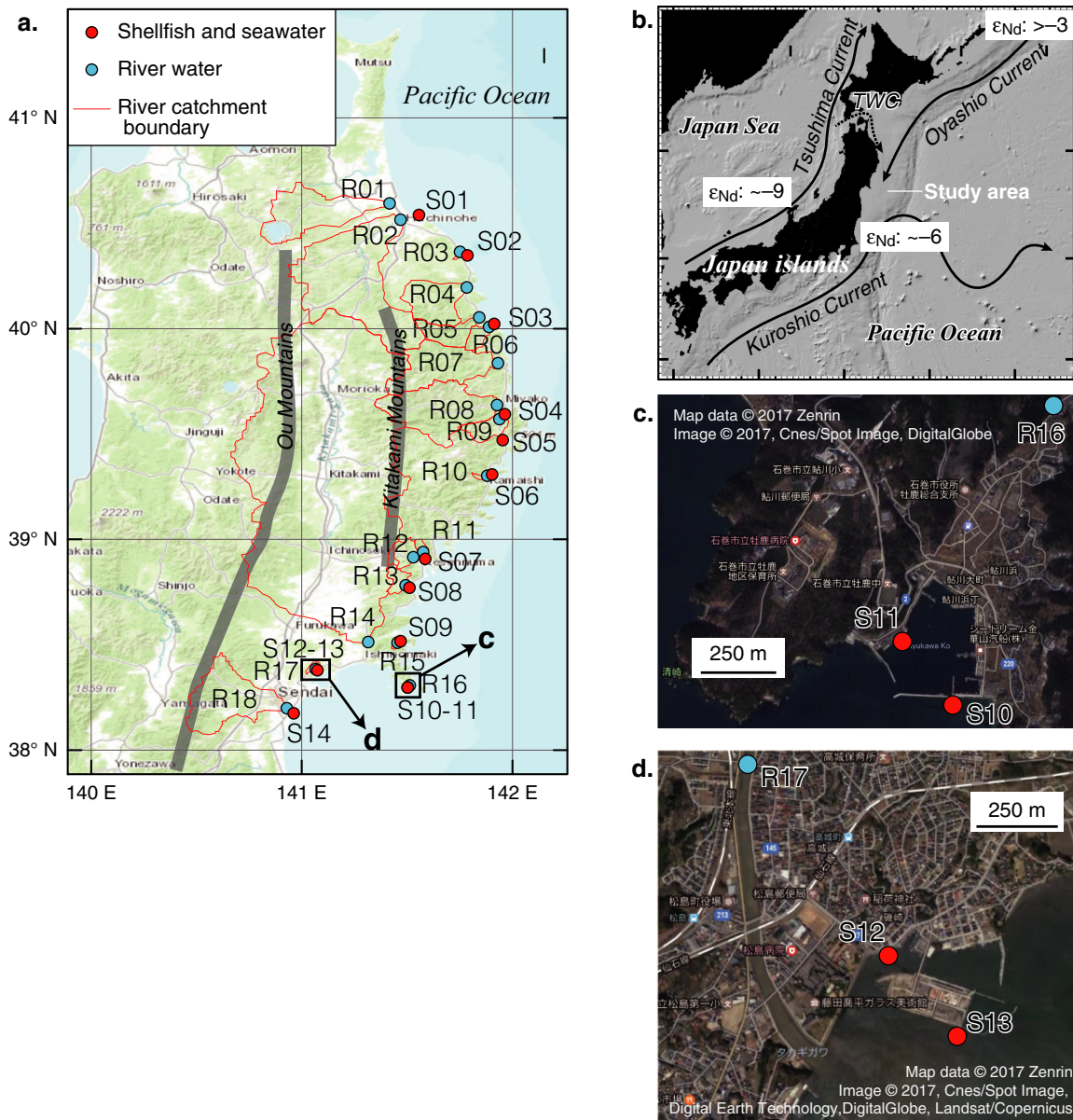


Fig. 1. (a) Map showing locations where shellfish and seawater samples were taken (red circles), and river water samples were taken (blue circles). Red lines indicate the boundaries of river catchments. (b) Ocean currents around Japan and the study area and typical  $\epsilon_{Nd}$  values (Amakawa et al. 2000, 2004a, b). TWC, Tsushima Warm Current. (c) Satellite image showing sampling sites S10, S11, and R16. (d) Satellite image showing sampling sites S12, S13, and R17.

extracted and dissected to remove digestive organs and gills, which can concentrate suspended particles with considerable amounts of Nd. The remaining tissues were then carefully rinsed with ultrapure water and dried in an oven at 105°C. After drying, each of the 38 samples

was ground to powder individually. Finally, we prepared 38 powdered samples with dry weights of 30–1000 mg for the analysis.

Each dried sample was placed in a capped Teflon bottle, completely digested in a 4:1 mixture of concentrated  $HNO_3$  and  $HClO_4$  on a hotplate

at 180°C following a commonly applied protocol to digest organic materials (e.g., Al-Yousuf et al. 2000, Canli and Atli 2003), and then evaporated to dryness with the cap removed. The dried sample was then re-dissolved in 2 mL of 2 mol/L HNO<sub>3</sub>. An aliquot of 0.05 mL of this solution was used for elemental analysis by quadrupole inductively coupled plasma mass spectrometry (ICP-MS).

For isotopic analyses, Sr and Nd were purified using a common chromatographic method briefly described as follows. The remaining 2M HNO<sub>3</sub> solution was dried again, re-dissolved in 0.3 mL of 3.5 mol/L HNO<sub>3</sub>, and loaded onto a column filled with Sr resin (Eichrom Technologies, Lisle, Illinois, USA). The Nd-containing fraction was first extracted by elution with 0.5 mL of 3.5 mol/L HNO<sub>3</sub> followed by 0.5 mL of 7 mol/L HNO<sub>3</sub>, and then, the Sr fraction was extracted by elution with 1.8 mL of 0.05 mol/L HNO<sub>3</sub>. The Nd-containing fraction was dried and then re-dissolved in 2 mL of 2.5 mol/L HCl, and the solution was loaded onto a column filled with AG 50 W-X12 resin (Bio-Rad Laboratories, Hercules, California, USA). The REE fraction was extracted by elution with 3.5 mL of 7 mol/L HNO<sub>3</sub> after elution with 2 mL of 2.5 mol/L HCl, followed by elution with 8 mL of 2 mol/L HNO<sub>3</sub>. The REE fraction was dried and re-dissolved in 0.2 mL of 0.25 mol/L HCl and then loaded onto a column filled with Ln resin (Eichrom Technologies). The Nd fraction was extracted by elution with 3 mL of 0.25 mol/L HCl after the elution with 4 mL of 0.25 mol/L HCl.

#### *Sampling of river water and seawater and sample pre-treatment*

Water samples were taken in April 2016. Coastal seawater samples were collected at the 13 sites at which shellfish samples had been collected and at two additional sites. River water samples were collected from the lower reaches of 18 rivers, 11 of which debouch near the seawater sampling sites. The sampling sites at rivers were above the tidal range, except for site R17. The surface geology in the catchment of each sampled river was characterized in the ESRI ArcGIS software environment by overlaying geologic map data provided by the Geological Survey of Japan, AIST (2015), on catchment boundaries that were extracted from topographic maps.

Waters were collected in pre-cleaned 4-L polyethylene bottles and then filtered through a

membrane with a pore size of 0.02 μm at the laboratory within a few days. pH and EC were measured at each sampling site. The membrane filters were stored in a freezer for the leaching experiment.

A few to several tens of milliliters of filtered water was subsampled for Sr isotope analysis and evaporated to dryness. Sr was extracted by using a column filled with Sr resin (Eichrom Technologies) and the same procedure that was used for the shellfish samples. Because the Nd concentration in the water samples was very low, an iron hydroxide precipitation technique (Amakawa et al. 2000) was employed to concentrate and extract Nd from seawater and river water. The filtered water sample was acidified with 10 mL of 6 mol/L HCl. Then, 0.1 g of Fe<sup>3+</sup> (pre-purified by isopropyl ether extraction) was added, and the solution was stirred vigorously. The solution was allowed to stand for at least 1 d, and then, an ammonia solution was added with stirring to raise the pH of the solution to 7.5–8.0 and form an iron hydroxide precipitate. After 3 d, the precipitate was collected into a 50-mL centrifuge tube. The sample tube was filled with ultrapure water, stirred, and centrifuged, and then, the supernatant was discarded. This washing process was performed three times.

The cleaned precipitate was dissolved in 6 mol/L HCl, and the solution was loaded onto an anion exchange column filled with 8 mL of Bio-Rad AG1-X8 resin to remove Fe. The effluent and the additional elution with 16 mL of HCl were recovered, evaporated to dryness, and re-dissolved in 2.5 mol/L HCl. Nd was further purified by the same procedure used for the shellfish samples by using first a column filled with AG 50 W-X12 resin (Bio-Rad Laboratories) and a second one filled with Ln resin (Eichrom Technologies). The Nd content of a blank sample was acceptably low (~50 pg) compared to the amount in samples (20–80 ng).

#### *Leaching of suspended materials in seawater*

In order to compare the Ce anomaly of each fraction of suspended material with that of shellfish tissues, the suspended material trapped on the membrane filters was sequentially leached basically following the protocol described by Bayon et al. (2002). Vacuum-dried filters were soaked in 8 mL of 10% (v/v) acetic acid (AcOH),

sonicated for 120 min, and then allowed to stand for a day to extract trace elements adsorbed onto the particulate surfaces (exchangeable ions) and those contained in carbonates. Next, the filters were rinsed three times with Milli-Q water, and elements scavenged from the seawater by iron and manganese oxides were leached from the rinsed filters with 10 mL of 1 mol/L hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) in 25% (v/v) acetic acid (HH) on a hotplate at 80°C. The membranes were again rinsed with Milli-Q water three times, and then, to extract trace metals that were more strongly bound to mineral particles or were present in organic compounds, they were leached with 15 mL of 7 mol/L  $\text{HNO}_3$ . Finally, the membranes were rinsed with Milli-Q water three times, and the remaining suspended material, which was considered the silicate fraction,

was digested in a mixture of 1 mL concentrated HF and 1 mL concentrated  $\text{HNO}_3$  on a hotplate at 120°C.

### Measurements

Elemental concentrations in shellfish samples and in filter leachates were measured by quadrupole ICP-MS (7500cx; Agilent Technologies, Waldbronn, Germany). Indium was added inline as an internal standard to correct for drift. External standard curves were drawn by using properly diluted multi-element standard solutions XSTC-622 and XSTC-1 (SPEX CertiPrep, Metuchen, New Jersey, USA). Concentrations of Al, Sr, and four LREEs (La, Ce, Pr, and Nd) were measured with a precision smaller than 10%. All reagents used were of ultrahigh purity, and the blank contribution was  $\ll 1\%$  of the analyte.

Table 1. Isotope ratios and concentrations of Sr and Nd and Ce anomaly in water samples.

Site	Contents	$^{87}\text{Sr}/^{86}\text{Sr}$	SE	$^{143}\text{Nd}/^{144}\text{Nd}$	SE	$\epsilon_{\text{Nd}}$	Sr ( $\mu\text{g/L}$ )	Nd ( $\mu\text{g/L}$ )	Ce anomaly
R01	River water	0.705332	0.000004	0.512713	0.000019	1.5	33.2	0.014	-0.22
R02	River water	0.706329	0.000005	0.512441	0.000010	-3.8	33.1	0.011	-0.21
R03	River water	0.706172	0.000004	0.512393	0.000035	-4.8	38.6	0.011	-0.28
R04	River water	0.708625	0.000004	0.512372	0.000005	-5.2	91.9	0.021	-0.28
R05	River water	0.708377	0.000004	0.512210	0.000013	-8.4	56.7	0.005	-0.58
R06	River water	0.705480	0.000004	0.512569	0.000020	-1.3	64.4	0.015	-0.42
R07	River water	0.708196	0.000005	0.512239	0.000006	-7.8	35.8	0.007	-0.43
R08	River water	0.707778	0.000004	0.512348	0.000017	-5.6	30.2	0.010	-0.39
R09	River water	0.707857	0.000004	0.512478	0.000006	-3.1	40.5	0.010	-0.47
R10	River water	0.708002	0.000004	0.512245	0.000008	-7.7	32.5	0.004	-0.58
R11	River water	0.707011	0.000004	0.512587	0.000011	-1.0	62.6	0.003	-0.73
R12	River water	0.705268	0.000004	0.512523	0.000015	-2.2	84.8	0.007	-0.48
R13	River water	0.706472	0.000004	0.512625	0.000019	-0.3	58.0	0.007	-0.26
R14	River water	0.706782	0.000005	0.512617	0.000009	-0.4	47.4	0.013	-0.21
R15	River water	0.707490	0.000004	0.512412	0.000015	-4.4	36.8	0.004	-0.65
R16	River water	0.707842	0.000004	0.512227	0.000004	-8.0	85.2	0.014	-0.72
R17	River water (brackish)	0.709167	0.000005	0.512520	0.000018	-2.3	5588.6	0.005	—
R18	River water	0.707215	0.000004	0.512720	0.000005	1.6	78.8	0.009	-0.43
S01	Seawater	0.709172	0.000004	0.512520	0.000006	-2.3	7219.7	0.007	—
S02	Seawater	0.709167	0.000005	0.512414	0.000013	-4.4	8769.3	0.007	—
S03	Seawater	0.709178	0.000004	0.512358	0.000010	-5.5	8783.7	—	—
S04	Seawater	0.709163	0.000004	0.512465	0.000005	-3.4	4797.9	0.014	—
S05	Seawater	0.709168	0.000004	0.512494	0.000008	-2.8	8993.1	—	—
S06	Seawater	0.709185	0.000005	0.512429	0.000006	-4.1	8924.3	—	—
S07	Seawater	0.709142	0.000004	0.512553	0.000008	-1.7	2862.6	0.006	—
S08	Seawater	0.709172	0.000005	0.512559	0.000008	-1.5	8896.8	0.007	—
S09	Seawater	0.709175	0.000004	0.512553	0.000004	-1.7	8479.2	0.013	—
S10	Seawater	0.709179	0.000004	0.512459	0.000015	-3.5	8814.8	0.006	—
S11	Seawater	0.709171	0.000004	0.512201	0.000008	-8.5	8928.1	0.011	—
S12	Seawater	0.709161	0.000004	0.512623	0.000010	-0.3	5315.2	—	—
S13	Seawater	0.709165	0.000005	0.512520	0.000025	-2.3	7237.0	0.004	—
S14	Seawater	0.709125	0.000004	0.512706	0.000005	1.3	2100.7	—	—

The Ce anomaly was quantified by assuming that the logarithms of the concentrations of La, Ce, and Pr normalized by their concentrations in chondrite (Anders and Grevasse 1989) had an inverse linear relationship with the atomic numbers of these elements. We calculated the anomaly as follows, using the equation of Akagi and Masuda (1998):

$$\text{Ce anomaly} = \frac{\log(\text{Ce}_n) - \log(\text{La}_n)/2 - \log(\text{Pr}_n)/2}{1} \quad (1)$$

where the subscript n indicates concentrations normalized by the chondritic value.

Sr and Nd isotope ratios were measured with a thermal ionization mass spectrometer (Finnigan Triton, Thermo Fisher Scientific) installed at the Research Institute for Humanity and Nature, Kyoto, Japan. Measured Sr and Nd isotope ratios were normalized to  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$  and  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ , respectively. Repeated analyses of standards NIST SRM 987 and JNdi-1 yielded an average  $^{87}\text{Sr}/^{86}\text{Sr}$  of  $0.710244 \pm 15$  ( $2\sigma$ ) ( $n = 19$ ) and  $^{143}\text{Nd}/^{144}\text{Nd}$  of  $0.512106 \pm 8$  ( $2\sigma$ ) ( $n = 13$ ), respectively. The Sr and Nd isotope ratios of samples were corrected by using  $^{87}\text{Sr}/^{86}\text{Sr} = 0.710250$  for NIST SRM 987 and  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512115$  for JNdi-1 (Tanaka et al. 2000), respectively. Nd isotopic data are reported as  $\epsilon_{\text{Nd}}$  on the basis of the following equation:

$$\epsilon_{\text{Nd}} = \left[ \frac{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{sample}}}{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}}} - 1 \right] \times 10^4 \quad (2)$$

where CHUR is the chondritic uniform reservoir value, which at present is 0.512638 (Jacobsen and Wasserburg 1980).

## RESULTS

### Concentration and isotope ratio of Sr and Nd in water

In coastal seawater, the Sr concentration ranged from 2.1 to 9.0 mg/L (average, 7.3 mg/L) and was about 100 times the river water concentration, which ranged from 30 to 90  $\mu\text{g/L}$  (average, 54  $\mu\text{g/L}$ ), except at an intertidal site, R17, where it was 5.6 mg/L. No correlation was observed between seawater and river water Sr concentrations (Table 1).

The Nd concentration of seawater ranged from 4 to 14 ng/L, although the concentration could not be measured for five samples owing to technical difficulties. For ICP-MS measurements of element concentrations, seawater samples had to be diluted too much to adequately quantify ultratrace elements, including Nd. No correlation was observed with the Nd concentration of the river water samples, which ranged from 3 to 21 ng/L (Table 1).

The variation of  $^{87}\text{Sr}/^{86}\text{Sr}$  in coastal seawater was very small (0.70912–0.70919), or about

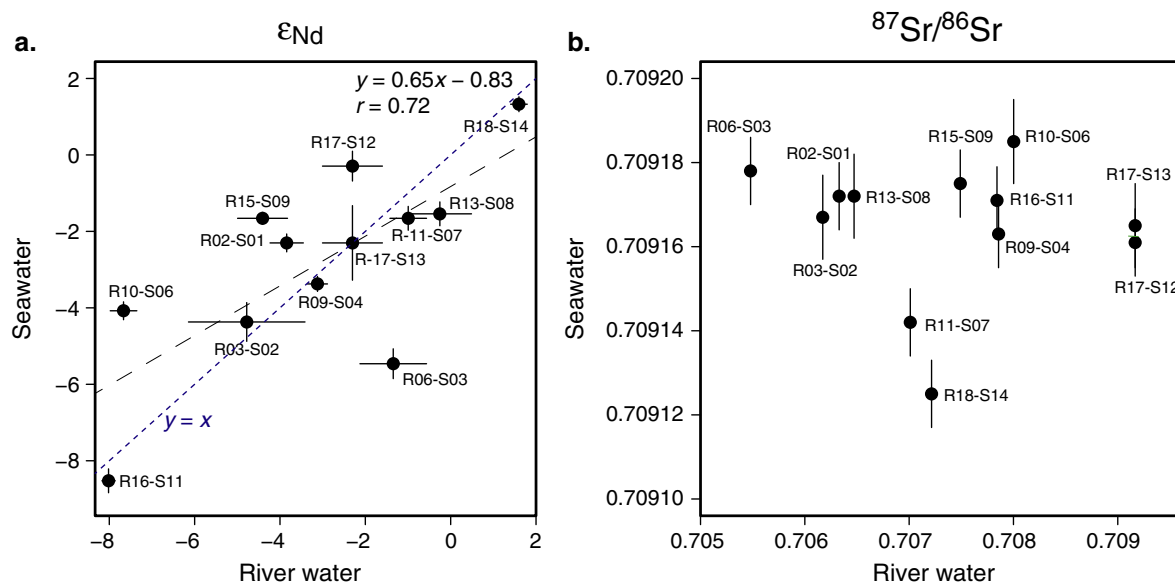


Fig. 2. Relationships of (a)  $\epsilon_{\text{Nd}}$  and (b)  $^{87}\text{Sr}/^{86}\text{Sr}$  between seawater and river water. Error bars indicate 2 SE.



one-fiftieth of that in river water (0.70527–0.70863, except for 0.70917 in a brackish sample from R17) (Fig. 2b, Table 1).  $^{87}\text{Sr}/^{86}\text{Sr}$  values were not correlated between seawater and river water. In watersheds larger than 10 km<sup>2</sup>,  $^{87}\text{Sr}/^{86}\text{Sr}$  values of river water showed a significant positive correlation ( $r = 0.78$ ,  $P < 0.001$ ) with the area ratios of Mesozoic sedimentary rocks, which are mainly accretionary prism rocks of Jurassic age (Fig. 7b, c).

The range of  $\epsilon_{\text{Nd}}$  values in coastal seawater was large (−8.5 to +1.4) and comparable to that in river water (−8.4 to +1.6). (Fig. 2a, Table 1). In addition, the  $\epsilon_{\text{Nd}}$  of seawater was significantly correlated

with the  $\epsilon_{\text{Nd}}$  of samples collected at adjacent river water sites ( $r = 0.72$ ,  $P = 0.008$ ). In contrast to  $^{87}\text{Sr}/^{86}\text{Sr}$ , the  $\epsilon_{\text{Nd}}$  values in river water showed a significant negative correlation ( $r = -0.82$ ,  $P < 0.001$ ) with the area ratios of Mesozoic sedimentary rocks in watersheds larger than 10 km<sup>2</sup>.

#### Concentration and isotope ratio of Sr and Nd in shellfish tissues

The range of Sr concentrations in the mussel tissues (16–101 mg/L) were of the same order of magnitude as those in the oyster tissues (5–154 mg/L) (Table 2). The difference in Nd

Table 2. Isotope ratios and concentrations of Sr and Nd and Ce anomaly in shellfish samples.

Site	Taxon	$^{87}\text{Sr}/^{86}\text{Sr}$	SE	$^{143}\text{Nd}/^{144}\text{Nd}$	SE	$\epsilon_{\text{Nd}}$	Sr (μg/L)	Nd (μg/L)	Ce anomaly
S01	Mussel	0.709148	0.000004	0.512567	0.000030	−1.4	29	0.063	−0.14
S01	Mussel	0.709135	0.000004	0.512563	0.000025	−1.5	28	0.130	−0.18
S01	Mussel	0.709175	0.000005	0.512556	0.000010	−1.6	87	0.152	−0.24
S01	Mussel	0.709167	0.000004	0.512614	0.000020	−0.5	8	0.023	−0.34
S01	Mussel	0.709154	0.000004	0.512595	0.000012	−0.8	18	0.051	−0.11
S02	Mussel	0.709163	0.000004	0.512451	0.000008	−3.7	26	0.275	−0.06
S02	Mussel	0.709163	0.000005	0.512562	0.000030	−1.5	18	0.048	−0.18
S02	Mussel	0.709166	0.000004	0.512580	0.000018	−1.1	24	0.048	−0.37
S02	Mussel	0.709167	0.000004	0.512466	0.000015	−3.4	24	0.046	−0.19
S02	Mussel	0.709178	0.000005	0.512488	0.000033	−2.9	24	0.053	−0.13
S02	Mussel	0.709162	0.000004	0.512480	0.000031	−3.1	38	0.084	−0.30
S02	Mussel	0.709183	0.000004	0.512463	0.000023	−3.4	18	0.039	−0.18
S02	Mussel	0.709168	0.000004	0.512476	0.000015	−3.2	21	0.074	−0.12
S02	Mussel	0.709168	0.000004	0.512462	0.000021	−3.4	22	0.047	−0.09
S03	Mussel	0.709126	0.000005	0.512564	0.000010	−1.4	25	0.040	−0.31
S03	Mussel	—	—	0.512545	0.000022	−1.8	62	0.099	−0.12
S03	Mussel	0.708973	0.000004	0.512616	0.000017	−0.4	51	0.115	−0.18
S03	Mussel	0.709067	0.000005	0.512603	0.000014	−0.7	76	0.100	−0.17
S04	Oyster	0.709176	0.000006	0.512522	0.000023	−2.3	26	0.224	−0.20
S04	Oyster	0.709177	0.000004	0.512460	0.000007	−3.5	27	0.150	−0.21
S05	Oyster	0.709180	0.000005	0.512555	0.000006	−1.6	31	0.052	−0.40
S05	Oyster	0.709177	0.000005	0.512567	0.000007	−1.4	25	0.053	−0.28
S06	Mussel	0.709150	0.000005	0.512534	0.000006	−2.0	44	0.306	−0.02
S07	Mussel	0.709180	0.000005	0.512580	0.000006	−1.1	26	0.188	−0.30
S07	Oyster	0.709178	0.000006	0.512502	0.000017	−2.7	68	0.135	−0.13
S07	Oyster	0.709165	0.000007	0.512582	0.000007	−1.1	154	0.095	−0.22
S07	Oyster	0.709176	0.000004	0.512589	0.000007	−1.0	5	0.044	−0.32
S08	Mussel	0.709191	0.000005	0.512560	0.000006	−1.5	31	0.405	−0.07
S09	Mussel	0.709170	0.000006	0.512536	0.000012	−2.0	47	0.295	−0.08
S09	Oyster	0.709169	0.000006	0.512529	0.000005	−2.1	30	0.086	−0.20
S11	Mussel	0.709171	0.000005	0.512342	0.000015	−5.8	30	0.063	−0.09
S11	Mussel	0.709172	0.000004	0.512410	0.000008	−4.4	52	0.076	−0.30
S11	Mussel	0.709171	0.000004	0.512401	0.000018	−4.6	40	0.062	−0.23
S12	Oyster	0.709155	0.000005	0.512648	0.000004	0.2	27	0.156	−0.09
S12	Oyster	0.709162	0.000005	0.512628	0.000006	−0.2	42	0.250	−0.10
S14	Mussel	0.709160	0.000005	0.512704	0.000010	1.3	100	0.207	−0.27
S14	Oyster	0.709148	0.000006	0.512675	0.000007	0.7	18	0.084	−0.10
S14	Oyster	0.709125	0.000005	0.512682	0.000008	0.8	23	0.105	−0.08



concentration between the two taxa was also slight ( $0.06\text{--}1.87\text{ L}^{-1}$  in mussels,  $0.04\text{--}0.27\text{ L}^{-1}$  in oysters), although the concentration tended to be slightly higher in mussels than oysters at sites S07, S09, and S14 (Fig. 3).

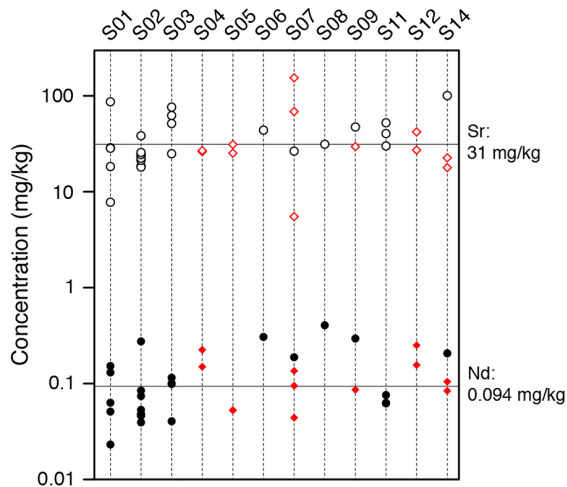


Fig. 3. Concentrations of Sr (open symbols) and Nd (closed symbols) in shellfish soft tissue samples. Mussel samples are indicated by black circles and oyster samples by red diamonds.

In the shellfish tissues,  $^{87}\text{Sr}/^{86}\text{Sr}$  varied only slightly, from 0.70912 to 0.70919, within the same range as  $^{87}\text{Sr}/^{86}\text{Sr}$  in the coastal seawater samples, except at site S03 where it ranged from 0.70897 to 0.70912 (Fig. 4b). Therefore, the range was much narrower than that in river water samples (Fig. 5b).  $^{87}\text{Sr}/^{86}\text{Sr}$  was not correlated between shellfish and either seawater or river water.

In contrast,  $\epsilon_{\text{Nd}}$  in the shellfish samples varied widely, from  $-5.6$  to  $+1.3$ ; this range is slightly narrower than the range in the seawater samples (Fig. 4a). We recognized no difference between mussel and oyster at any of the sites.  $\epsilon_{\text{Nd}}$  was significantly correlated between the shellfish and seawater samples ( $r = 0.78$ ,  $P < 0.001$ ; Fig. 4a), although at sites S03 and S11,  $\epsilon_{\text{Nd}}$  was notably higher in mussel than in seawater. At site S03,  $\epsilon_{\text{Nd}}$  in the shellfish corresponded to its value in river water (Fig. 5a).

#### Cerium anomaly of shellfish and suspended particles

The Ce anomalies of most of the shellfish samples were lower than  $-0.15$ . No difference in the anomaly was apparent between oysters and mussels (Fig. 6, Table 2, Appendix S1).

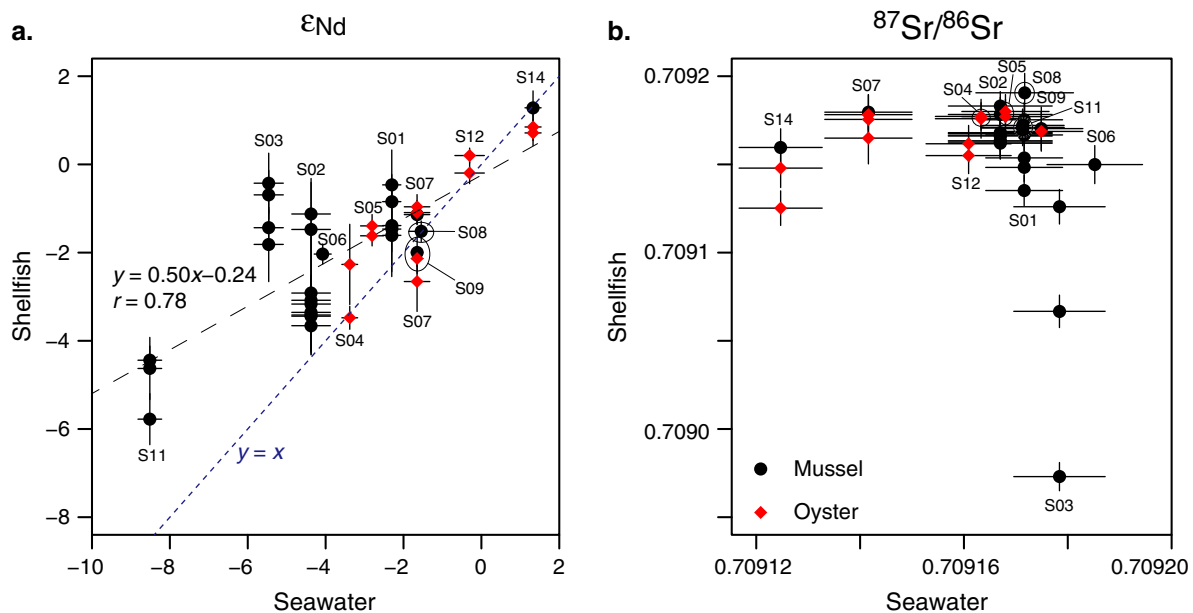


Fig. 4. Relationships of (a)  $\epsilon_{\text{Nd}}$  and (b)  $^{87}\text{Sr}/^{86}\text{Sr}$  between shellfish soft tissues and seawater. Mussel samples are indicated by black circles and oyster samples by red diamonds. Error bars indicate 2 SE.

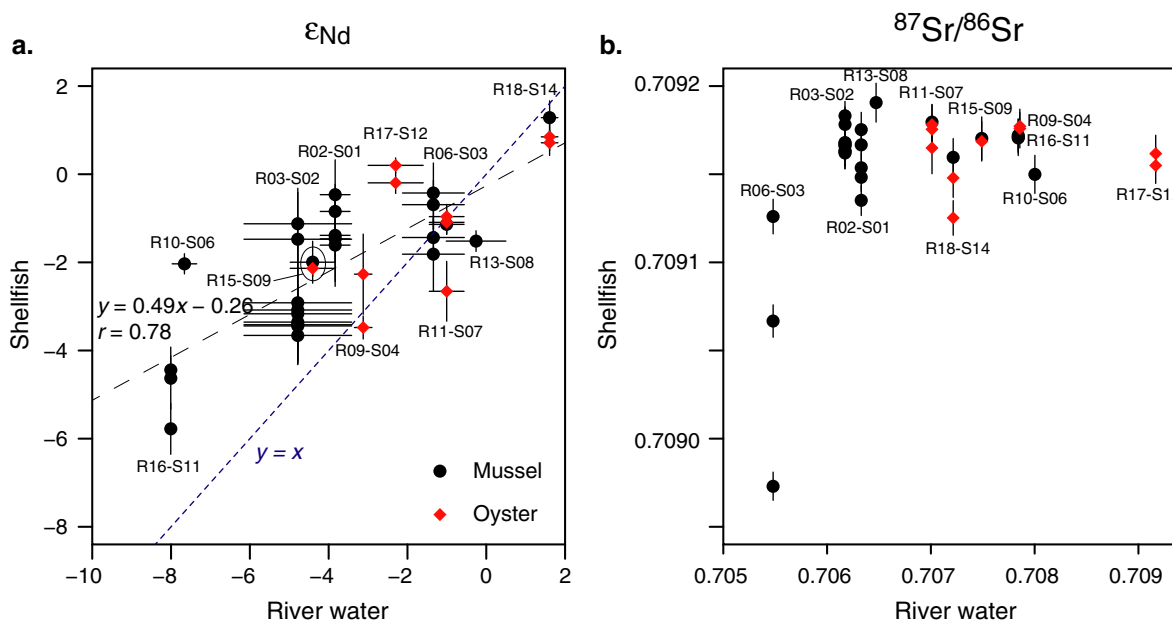


Fig. 5. Relationships of (a)  $\epsilon_{Nd}$  and (b)  $^{87}Sr/^{86}Sr$  between shellfish soft tissues and river water. Mussel samples are indicated by black circles and oyster samples by red diamonds. Error bars indicate 2 SE.

Ce anomalies of the AcOH-extractable fraction of the suspended materials were negative, but they were less negative than the anomalies in shellfish soft tissues (Fig. 6). In contrast, the anomalies in the HH-extractable fraction of most samples (excepting samples from sites S03 and S08) were positive and higher than 0.1. Ce anomalies of the  $HNO_3$ -extractable fraction were also positive, but less positive than those of the HH-extractable fraction. Ce anomalies of the HF-decomposed silicate fraction were close to zero. The total Ce anomaly of each suspended material sample was either close to zero or somewhat positive.

## DISCUSSION

### Origin of Nd and Sr in river water

The common dependence of the Nd and Sr isotope ratios of river water on the geology of the river catchment indicates that these elements are largely derived from bedrock (e.g., Peucker-Ehrenbrink et al. 2010). Accordingly, the Sr-Nd isotopic compositions of river water samples in this study also reflected the bedrock of the river catchments (Fig. 7a). Thus, as expected, the Sr and Nd isotope ratios of river water were regionally distinctive in the Tohoku district.

### Origin of Nd and Sr in seawater

The positive correlation between seawater and river water  $\epsilon_{Nd}$  values (Fig. 2a) indicates that the Nd dissolved in seawater at the coastal sites is derived largely from the Nd in water from the adjacent river. A few disagreements between  $\epsilon_{Nd}$  in seawater and water of the nearest river can be explained by contributions from offshore seawater or from water of a larger, more distant river. For example, the much lower  $\epsilon_{Nd}$  value in seawater at site S03 ( $-5.5$ ) compared with the river water value at the adjacent R06 site ( $-1.3$ ) suggests a considerable contribution of Tsugaru Warm Current water, which has a very low  $\epsilon_{Nd}$  value ( $-8$ ). As another example, the higher  $\epsilon_{Nd}$  value in seawater at site S06 ( $-4.1$ ) compared with the river water value at the adjacent R10 site ( $-7.7$ ) can be accounted for by input of Nd from the Oyashio Current ( $\epsilon_{Nd} > -3$ , Fig. 1B). As a third example, the  $\epsilon_{Nd}$  value of seawater ( $-1.7$ ) at site S09 is much higher than that of both the adjacent river water ( $-4.4$  at R15) and the Oyashio Current ( $-3$  to  $-2$ ; Amakawa et al. 2004a). One plausible source of Nd to site S09 is the Kitakami River (site R14;  $\epsilon_{Nd} = -0.4$ ), which discharges large amounts of water ( $391 \text{ m}^3/\text{s}$  in annual mean) to Oppa Bay, north of site S09. It is

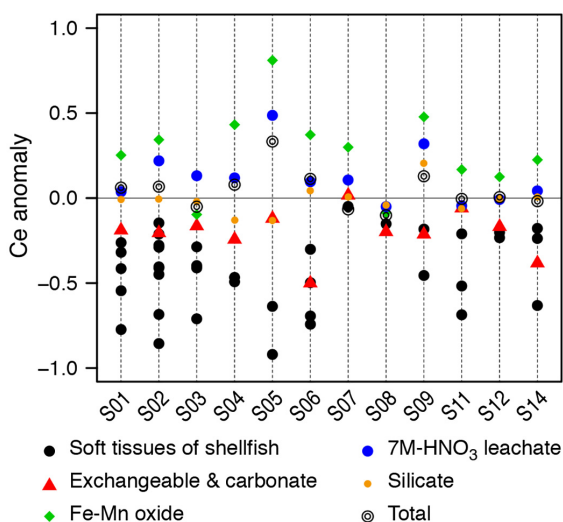


Fig. 6. Ce anomalies in shellfish soft tissue samples (black circles) and in each fraction of suspended particulate matter: AcOH extractable (exchangeable and carbonate) (red triangles), HH extractable (on surfaces of Fe and Mn oxides) (green diamonds), 7 mol/L  $\text{HNO}_3$ -extractable (strongly bound to mineral particles or organic compounds) (blue circles), and residue after digestion with concentrated  $\text{HF-HNO}_3\text{-HClO}_4$  (silicate) (small circles of orange color). Total (black double circles) indicates the weighted sum of the Ce anomalies of each fraction.

likely that Nd from that river is transported beyond Oppa Bay and carried to site S09 by southward-flowing coastal currents (Fig. 8).

Even though offshore water greatly influences  $\epsilon_{\text{Nd}}$  values of the coastal seawater at these few sites, the  $\epsilon_{\text{Nd}}$  values of seawater and adjacent river water were positively correlated (Fig. 2a). In general, then,  $\epsilon_{\text{Nd}}$  in coastal seawater is controlled by that of nearby river water, which is controlled in turn by the catchment geology (Fig. 9).

The highly homogeneous  $^{87}\text{Sr}/^{86}\text{Sr}$  values of coastal seawater ( $0.709166 \pm 0.000031$ ,  $2\sigma$ ) that we obtained are consistent with reported values for modern seawater ( $0.70918 \pm 0.00001$ , mean  $\pm 2\sigma$ ; Faure and Mensing 2005). Because the Sr concentration of seawater (about 7.7 mg/L for a salinity of 35) is much higher than the concentration in river water, the Sr contribution of the rivers to the seawater Sr isotope ratio is effectively masked.  $^{87}\text{Sr}/^{86}\text{Sr}$  values of coastal seawater were slightly

lower at sites S04, S07, and S14, where low electrical conductivity ( $<2000$  mS/m) indicates a considerable contribution of river water. In contrast, despite high conductivity ( $\sim 5000$  mS/m) indicating little contribution of freshwater,  $\epsilon_{\text{Nd}}$  values in coastal seawater at sites S08 and S11 were consistent with those in the adjacent rivers at sites R13 and R16, respectively. It appears that a complicated interaction between dissolved REEs and REEs in the suspended particulates discharged from rivers (Sholkovitz and Szymczak 2000) plays an important role in the formation of dissolved Nd in coastal seawater.

#### *Incorporation of Nd dissolved in seawater into shellfish soft tissue*

The positive correlation of  $\epsilon_{\text{Nd}}$  between shellfish and seawater (Fig. 4a) suggests that the Nd in soft tissues of the shellfish is derived from the seawater in which they live. The Ce anomaly provides information on the origin of REEs, including Nd, in shellfish tissues. It is well known that Ce is depleted in the dissolved phase of seawater, compared with the other REEs, giving rise to a negative Ce anomaly (Elderfield et al. 1990, Piepgras and Jacobsen 1992). Most REEs behave as trivalent ions, but Ce can assume a valence state of +4 or +3, depending on redox conditions. In fully oxidized seawater, dissolved Ce(III) is oxidized to Ce(IV) and adsorbed onto  $\delta\text{-MnO}_2$  (Ohta and Kawabe 2001). As a result, seawater is depleted in dissolved Ce relative to other REEs (negative Ce anomaly) (e.g., Elderfield et al. 1990, Piepgras and Jacobsen 1992). Conversely, among REEs adsorbed onto suspended materials, the Ce anomaly is either positive or less negative than in the dissolved phase (e.g., Sholkovitz et al. 1994). Although we could not calculate the actual Ce anomaly for our seawater samples, because Pr concentrations were not determined, we can assume that it should be negative in all seawater samples because the Ce anomaly in river water samples, which is typically higher than in seawater (Elderfield et al. 1990), was lower than  $-0.2$  (Table 1). The Ce anomaly in the shellfish samples was also consistently negative. Therefore, we inferred that the REEs in the shellfish soft tissues were mainly derived from REEs dissolved in seawater. In contrast, the HH-extractable and  $\text{HNO}_3$ -extractable fractions of the suspended material showed positive Ce anomalies, whereas the

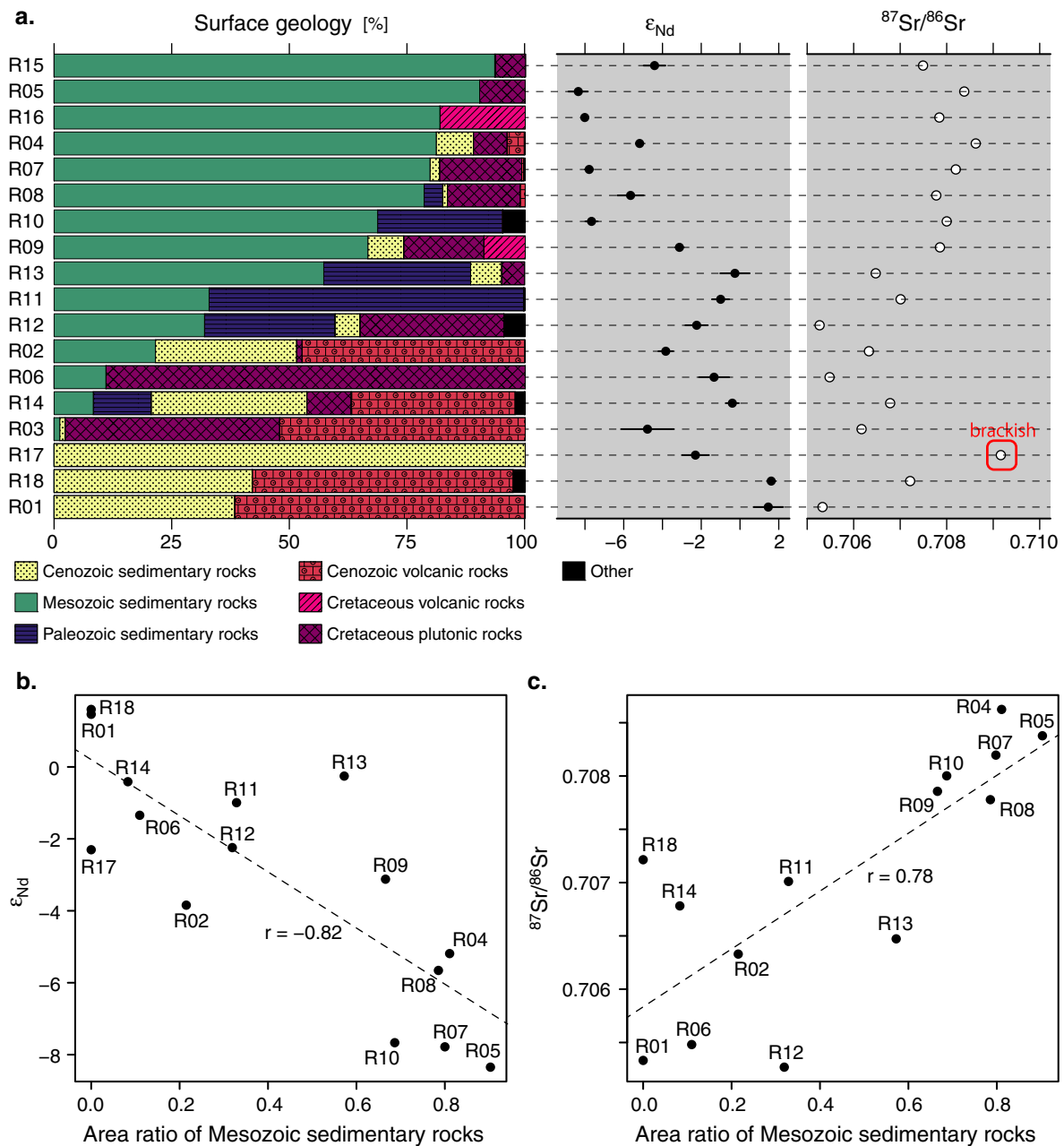


Fig. 7. (a) Characterization of river waters by catchment bedrock lithology,  $\epsilon_{Nd}$ , and  $^{87}Sr/^{86}Sr$ , and relationships between catchment lithology and (b)  $\epsilon_{Nd}$  and (c)  $^{87}Sr/^{86}Sr$  in river water samples.

silicate fraction did not show any Ce anomaly (Fig. 6). This result indicates that the suspended component made a negligible contribution to the shellfish soft tissues. Although the Ce anomalies of the AcOH-extractable fraction were negative, because REE concentrations in marine carbonates

are very low (Bayon et al. 2004), the REEs in this fraction are considered to have existed as exchangeable ions in equilibrium with seawater. Thus, we conclude that Nd in the shellfish soft tissues was derived from Nd dissolved in seawater.





Fig. 8. Map showing the inferred path of Nd from the Kitakami River to site S09 (dashed white line). Black arrows indicate dominant direction of coastal currents. Map based on Google Maps.

#### *Time scale of Nd accumulation in shellfish tissues*

Because Nd in seawater can vary with changes in the balance between riverine and oceanic processes, such as tides, waves, and ocean currents, it is important to evaluate the time of Nd accumulation in shellfish soft tissues. The enrichment in Nd in shellfish soft tissue relative to seawater (Fig. 3) suggests that the  $\epsilon_{Nd}$  value in shellfish reflects the average of long-term changes in seawater rather than short-term fluctuations. Consistent with this

supposition, the  $\epsilon_{Nd}$  values in the shellfish samples fell in a much narrower range than in seawater samples (Fig. 4a).

Although bioaccumulation of neodymium has not been well studied, Wang et al. (1996) investigated the uptake of other metals dissolved in seawater by a mussel (*Mytilus edulis*) and estimated absorption efficiencies of Ag, Am, Cd, Co, Se, and Zn ranging from 0.03% (Co) to 1.53% (Ag). If the absorption efficiency of Nd is similar to that

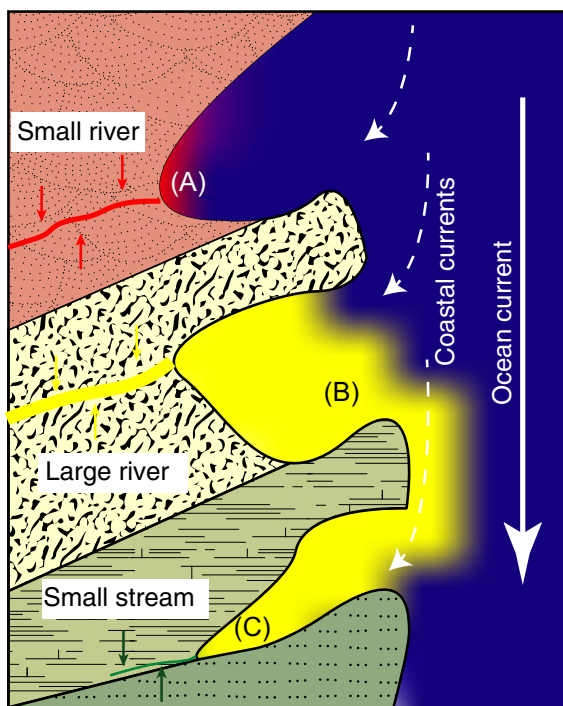


Fig. 9. Schematic view of coastal distribution of Nd derived from rivers of different scales. A small river influences seawater Nd only near its outlet (A), whereas Nd from a large river influences neighboring bays (B), and a small stream has little or no influence even at its outlet (C). Colored arrows represent the influence of catchment geology.

of these metals, then the time required for the Nd concentration to reach the concentrations we measured in the shellfish tissue samples would be 5–300 d: that is, the Nd concentration of the shellfish samples ( $\sim 100$  ng/g) divided by the product of the mussel filtration rate ( $\sim 120$  L $\cdot$ g $^{-1}\cdot$ d $^{-1}$ ; Widdows et al. 1995), the Nd concentration in seawater ( $\sim 10$  ng/L), and the absorption efficiency (0.03–1.5%). This estimate is rather conservative because in this study we discarded the digestive organs and gills, where ingested materials are likely to be concentrated, before measuring Nd in the shellfish tissues.

Given these considerations, it is possible that at site S03, where  $\epsilon_{\text{Nd}}$  of the shellfish samples ( $-1.8$  to  $-0.4$ ) differed considerably from that of seawater ( $-5.5$ ) but was similar to that of the adjacent river water ( $-1.34$ ), Nd derived from river water rather than seawater was the dominant long-term influence over Nd in the shellfish tissues at that

site. Consistent with this interpretation, the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the shellfish samples from that site was lower (0.70897–0.70913) than that from other sites, indicating a large contribution of Sr from nearby river water ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.70548$ ). Assuming that the Sr in coastal seawater at site S03 is formed by simple mixing of river water at site R06 and typical seawater, the concentration of Sr in the mixed water,  $C_{\text{mix}}$  is expressed as

$$C_{\text{mix}} = f \times C_{\text{rw}} + (1 - f) \times C_{\text{sw}}, \quad (3)$$

where  $f$  ( $0 \leq f \leq 1$ ) is the volume ratio of the river water and  $C_{\text{rw}}$  and  $C_{\text{sw}}$  are Sr concentrations in river water at R06 and typical seawater (7.7 mg/L). Then, the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the mixed water,  $\delta_{\text{mix}}$ , is expressed as

$$\delta_{\text{mix}} = (f \times C_{\text{rw}} \times \delta_{\text{rw}} + (1 - f) \times C_{\text{sw}} \times \delta_{\text{sw}}) / C_{\text{mix}}, \quad (4)$$

where  $\delta_{\text{rw}}$  and  $\delta_{\text{sw}}$  are the  $^{87}\text{Sr}/^{86}\text{Sr}$  in river water at R06 and typical seawater (0.70918), respectively (e.g., Faure and Mensing 2005). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the shellfish samples at S03 are comparable to  $\delta_{\text{mix}}$  with a 64–88% proportion of river water (Fig. 10), consistent with the long-term dominance of river water at the site. The  $\epsilon_{\text{Nd}}$  of shellfish samples at S03 ( $-1.09 \pm 1.2$ ), which was likewise close to the value of river water at site R06 ( $-1.34$ ), supports this interpretation. The  $\epsilon_{\text{Nd}}$  of the seawater sample at site S03 ( $-5.5$ ), which was lower than that of the shellfish samples, might reflect the ephemeral dominance of the Tsugaru Warm Current water at the time of sampling.

#### Use of $\epsilon_{\text{Nd}}$ as a tracer of animal migration in marine habitats

Our results showed that  $\epsilon_{\text{Nd}}$  varies widely in coastal seawater, and this is reflected in shellfish soft tissues. Thus, like the Sr isotope ratio in terrestrial animals and anadromous fishes,  $\epsilon_{\text{Nd}}$  can be a habitat indicator for marine animals, at least in coastal seas, and  $\epsilon_{\text{Nd}}$  may be applicable to animals in further offshore regions considering its wide variation in ocean currents. Commercially,  $\epsilon_{\text{Nd}}$  may be highly useful in authenticating the provenance of shellfish and coastal fish species. Ecologically, isotopic measurements of organs with different turnover rates (e.g., bone, muscle, liver) may be useful in tracing the recent migration history of an individual. The greatest weakness of Nd isotope ratios is the scarcity

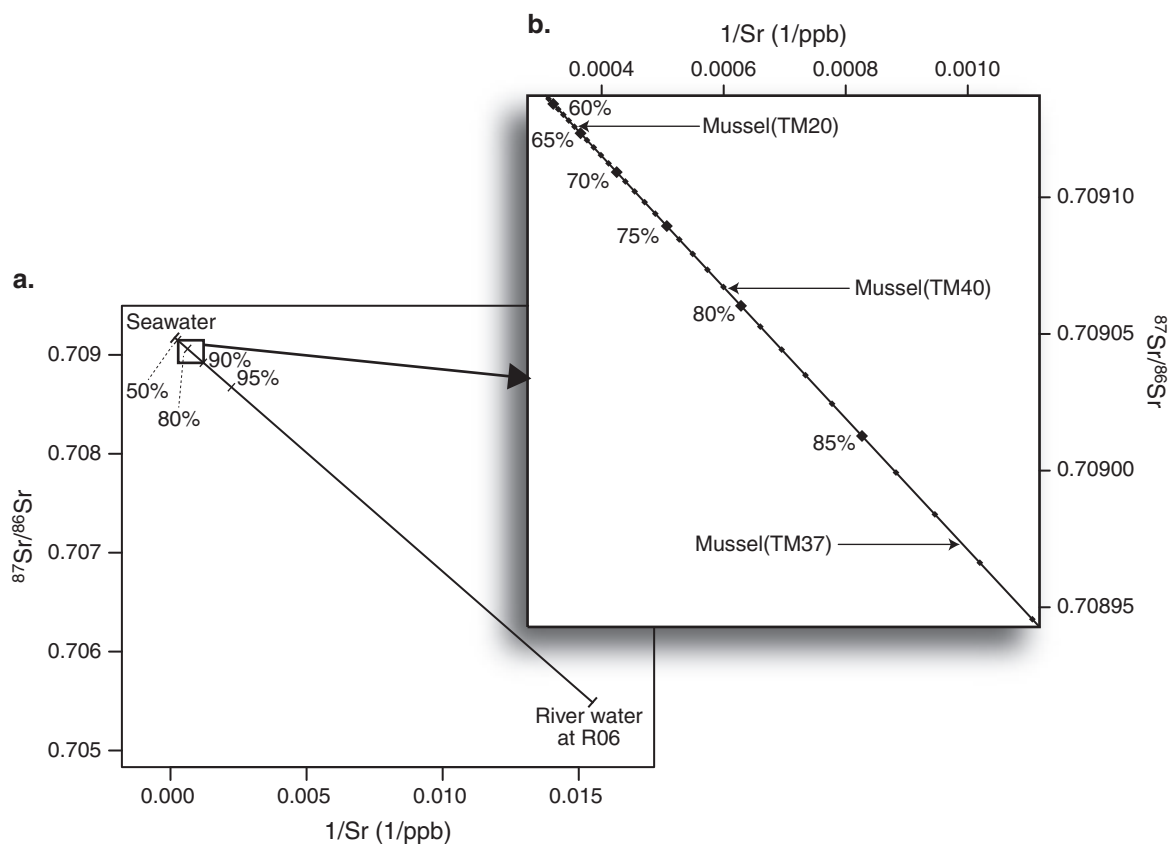


Fig. 10. (a) Hypothetical example of  $^{87}\text{Sr}/^{86}\text{Sr}$  calculations assuming two-component mixing between river water at site R06 and typical seawater, in relation to the reciprocal of Sr concentration calculated for the same mixture. Percentages indicate the contribution of river water. (b) Detail of (a) showing positions of shellfish samples along the mixing line.

of Nd, which necessitates special care to avoid contamination (e.g., sample processing in cleanroom environments, using reagents of ultrahigh purity). Although it is well known that otoliths, which grow by apposition, preserve chronological information about the habitats of an individual in the form of geochemical properties such as Mg/Ca and Sr isotope ratios (e.g., Kennedy et al. 2002), otoliths are too small to yield enough Nd for isotopic measurements. However, a method using vertebral centra (Matsubayashi et al. 2017), which also grow by apposition like otoliths, may make it possible to retrieve Nd isotopic information from the juvenile to adult life stages of marine organisms.

## CONCLUSION

We showed that the spatial variation of  $\epsilon_{\text{Nd}}$  in coastal seawater was well preserved in shellfish

soft tissues, and, because it reflects local geology through the influence of river water, it is distinctive among regions. Negative Ce anomalies showed that the Nd in shellfish tissues was mainly derived from the Nd dissolved in seawater. The Nd concentration in shellfish tissues is cumulative such that  $\epsilon_{\text{Nd}}$  in shellfish reflects the long-term seawater value. These findings indicate that  $\epsilon_{\text{Nd}}$  has potential as a tracer of animal migration in coastal environments, where the Sr isotope ratio is not useful.

## ACKNOWLEDGMENTS

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