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# Contribution of the submarine groundwater discharge (SGD) to sessile bivalve production; estimate by the carbon stable isotope ratio recorded in the shell

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# Introduction

Submarine groundwater discharge (SGD) has been shown to be an important pathway between land and sea for the transport of terrestrial materials [1-3]. SGD results in various biogeochemical changes in the coastal environments, such as coastal primary production [4], eutrophication [5], and benthic production [6]. Therefore, it is important to investigate the ecological significance of SGD.

Although respired  $CO_2$  and ambient inorganic carbon both contribute to mollusk shells [7], McConnaughey and Gillkin [7] suggested that aquatic animals build their carbonates from mainly ambient inorganic carbon. Since the  $\delta^{13}C$  value of underground water is much lower than that of sea water [8], it can be used as proxy of SGD signal. In the present study we investigated two subjects 1) whether the  $\delta^{13}C$  of ambient water reflect the proportion of fresh water flow rate in SGD, 2) whether the  $\delta^{13}C$  recorded in the shell of the sessile bivalve reflect that of the ambient water.

# Materials and methods

The SGD rate and the proportion of fresh water flow rate in SGD were measured by the seepage meter at Kamaiso beach along the Mt. Chokai volcanic coast in Yamagata prefecture Japan in June and September 2016. The seepage meter consists of one liter bucket that is fitted with a sample port and a plastic collection bag. The bucket is inserted open end down into the sediment. The volume of water in the bag over a measured time provides the flux measurements. The Radon 222 (<sup>222</sup>Rn) concentration that is a useful tracer of SGD at Kamaiso Beach and adjacent 3 areas (Mega, Takinoura, Torisaki) was measured (Fig. 1). The rock-oyster (*Crossostrea* 



nippona) was also sampled at 4 areas (Fig. 1).

The measurement of  $\delta^{13}$ C of ambient water ( $\delta^{13}$ C<sub>DIC</sub>) was conducted by an elemental analyzer-isotope ratio mass spectrometer (Thermo Finnigan Gas-Bench 2-Delta V Plus). The edge of the oyster shell was grinded by micro drill and  $\delta^{13}$ C of carbonate powders was measured. Results are relative to VPDB by calibration to the NBS-19 limestone reference standard ( $\delta^{13}$ C = +1.92‰ VPDB).

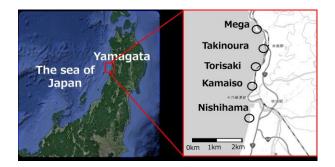


Fig. 1. Map showing the sampling area of this study around foot of the Mt. Chokai, Yamagata Prefecture, Japan.

# **Results and discussion**

Judging from the results of seepage meter survey, Kamaiso beach was clearly divided into two areas, high SGD rate and high freshwater ratio area (Kamaiso A) and low SGD rate and low freshwater ratio area (Kamaiso B). The <sup>222</sup>Rn concentration was high at Mega and Kamaiso A and comparative low at Torisaki and Kamaiso B.

There was a positive significant relationship between salinity and the  $\delta^{13}C_{DIC}$  of ambient water (p<0.01). In order to estimate the fresh water ratio in

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the ambient waters, we used the classical two end member mixing model [9] incorporating DIC concentration of both sea water and fresh underground water :  $\delta^{13}C_{DIC} = (\delta^{13}C_{SW} \times Conc_{DICSW} \times Rt \ s_W + \delta^{13}C_{GW} \times Conc_{DIC}\ s_W \times (1 - Rts_W)) / (Conc_{DIC}\ s_W \times Rts_W + Conc_{DIC}\ s_W \times (1 - Rts_W))$ , where  $\delta^{13}C_{SW}$  and  $\delta^{13}C_{G}$  are  $\delta^{13}C$  of sea water and fresh groundwater, respectively, and  $Conc_{DICSW}$  and  $Conc_{DICGW}$  are DIC concentration of sea water and fresh groundwater, respectively.  $Rt\ s_W$  is ratio of sea water in ambient water. We incorporate DIC concentration into the two source model, because the relation between the  $\delta^{13}C_{DIC}$  of ambient water and chlorinity (namely ratio of sea water) was better fitted (Fig 2).

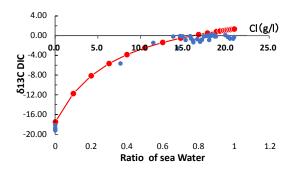


Fig. 2. The relationship between  $\delta^{13}C_{DIC}$  and chlorinity (ratio of sea water in the ambient water). Red line indicate the estimate curve by the two end member mixing model incorporating DIC concentration of both sea water and fresh underground water

The  $\delta^{13}$ C of the shell ( $\delta^{13}$ C<sub>shell</sub>) was high at high <sup>222</sup>Rn area We individually estimated the  $\delta^{13}$ C<sub>DlC</sub> of ambient water around rock oyster by the McConnaughey's model:  $\delta^{13}$ C<sub>DlC</sub> =  $100 \times \delta^{13}C_{shell} - 100 \times \varepsilon_{cal-b-} CM \times \delta^{13}C_{POM}$ , where  $\varepsilon_{cal-b}$  is enrichment factor between bicarbonate and calcite (+0.9‰) and  $\delta^{13}C_{POM}$  is  $\delta^{13}C$  of particulate organic matter. In order to estimate the ratio of fresh SGD, we used the classical two end member mixing model incorporating DIC concentration of both sea water and fresh underground water again. The estimated average fresh water flow rate in SGD ranged from 4% (Torisaki) to 35% (Mega). These results estimated from stable isotope model was consistent with the results <sup>222</sup>Rn concentration.

#### Conclusions

We could estimate the fresh water ratio in the ambient waters from the  $\delta^{13}C_{DIC}$  by using the classical two source model incorporating DIC concentration of sea water and fresh underground water. Moreover, the carbon stable isotope ratio of rock-oyster shell can provide the ratio fresh water ratio in SGD. This is the first study to estimate the fresh water ratio in SGD quantitatively from the animal. However, the estimated

values from rock-oyster shell were higher than those estimated from the  $\delta^{13}$ C of ambient water (1.3% Torisaki and 18.1% Mega). The difference of these results are seems to be the difference of local SGD environment around rock-oyster.

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