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Submarine groundwater discharge as a main source of rare earth elements in coastal waters

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ABSTRACT

To evaluate the role of submarine groundwater discharge (SGD) as a source of rare earth elements (REEs) in the coastal ocean, we estimated the SGD associated discharge of REEs into two semi-enclosed coastal bays in the southern coast of Korean peninsula. The mass balances of REEs demonstrated that the REE fluxes through SGD were two to three orders of magnitude higher than those through the other sources, such as diffusion from bottom sediments and atmospheric dust fallout. The Nd inputs through the total SGD from the two small coastal bays, Gamak Bay (148 km^2) and Hampyeong Bay (85 km^2), were estimated to be 0.7×10^4–1.3×10^4 mol y^{-1}, which is 0.06–0.3% of the total Nd fluxes from global rivers. In this region, coastal seawater was observed to have a substantially higher middle REE (MREE), which appears to be due to a large discharge of groundwater that is highly enriched with MREE. High MREE bearing waters were observed over the entire shore of the southern coast of Korea, implying that such high SGD-driven REE fluxes are common in coastal area. Our results suggest that the SGD-driven REE fluxes may contribute considerably to the global budget of REEs in the ocean.

1. Introduction

Rare earth elements (REEs) and their isotopic compositions are commonly used for tracing various oceanic processes. REEs are useful for tracing oceanic water masses, since the relative abundance of REEs in the oceans is controlled by regional sources and biogeochemical removal rates (Elderfield et al., 1988). The fractionations of REEs arising from differences in particle reactivity of each element also have been used to investigate the particle/solution interactions of trace elements in seawater (Byrne and Kim, 1990). The variations in Nd isotopes are particularly valuable in paleoceanography to trace water-mass circulation in the ocean using ratios of $^{143}Nd/^{144}Nd$ recorded in authigenic and diagenic minerals (Abouchami et al., 1999; Holser, 1997).

Traditionally, river discharges have been believed to be the dominant source of REEs in the ocean (Goldstein and Jacobsen, 1988). However, in the global ocean, over 90% of the REE sources have been still unidentified, based on the Nd isotope mass balance, which is the so-called "missing Nd flux" (Lacan and Jeandel, 2005; Tachikawa et al., 1999). Recent studies (Johannesson and Burdige, 2007) documented that REE fluxes through "fresh" submarine groundwater discharge (SGD) may be the missing source of REEs in the global ocean water, which could be an order of magnitude higher than the river-driven fluxes.

SGD occurs as undersea springs and seeps across the seafloor from coastal aquifers, where the region of mixing between fresh- and salty water is defined as the subterranean estuary. However, in general, the marine fraction of SGD is larger than the terrestrial SGD, accounting for more than 90% of the total SGD to the oceans worldwide (Burnett et al., 2003; Kim and Swarzenski, 2010; Moore, 2006), and the magnitude of the total SGD is known to be comparable to that through rivers in the Atlantic Ocean (Moore, 2003; Moore et al., 2008; Taniguchi et al., 2002). Therefore, we have to evaluate the REE (e.g., Nd) fluxes from both fresh groundwater and recirculating seawater, which include large REE inputs from marine sediments. Since the oceanic Nd isotope budget cannot account for the inputs of marine Nd (e.g., those that are regenerated from marine sediments) through SGD, the actual total fluxes of Nd through SGD should be determined by extensive regional coastal flux studies.

In recent total SGD studies, Johannesson et al. (2011) reported that the net flux of Nd through SGD to the Indian River Lagoon was approximately seven times that from the local surface runoff to the coastal waters. Kim and Kim (2011) reported that SGD from a volcanic island, Jeju, is the dominant source of REEs in coastal waters and that REE fluxes through SGD from this small island are comparable with those through major rivers. In this study, we quantified the total SGD-associated flux of REEs into two coastal embayments, Gamak Bay and Hampyeong Bay, located on the southern coast of Korea. In these bays, the SGD was found to be the major nutrient sources for coastal and benthic production (Hwang et al., 2010; Waska and Kim, 2011). In addition, we observed

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REEs in shore waters along the entire southwestern coast of Korea in order to evaluate the role of SGD in general coastal waters (Fig. 1).

2. Materials and methods

2.1. Study area

Gamak Bay is a semi-enclosed bay in the southern sea of Korea and is one of the largest cultivation areas of shellfish (Fig. 1). Its mean depth is about 8 m, and its area is about 148 km^2 (Kang and Kim, 2006; Kim et al., 2006). The tide is semidiurnal, and the tidal fluctuation of the bay has an amplitude of ~1 m and ~4 m during neap and spring tides, respectively. The bottom sediments consist mainly of silt and clay in the northern part, whereas the coarse sediments predominate in the peripheral areas and at the mouth of the bay (Lee et al., 1995). The water exchange between the bay water and the open-ocean water is very active through two channels located in the northeastern and southern parts of the bay. The average annual precipitation is about 1170 mm, and most of the precipitation occurs during the rainy season, from June to September (Korea Meteorological Administration; KMA, 2001). The natural recharge rate of the groundwater is less than approximately 9% of annual precipitation (Hwang et al., 2010). The amount of freshwater entering the bay through streams and ditches ranges from 2.7×10^4 to 18×10^4 m^3 d^{-1} (avg. ~7.0×10^4 m^3 d^{-1}), with a large seasonal variation. Hwang et al. (2010) reported that the biological production of this farming bay is controlled by SGD-driven nutrients.

Hampyeong Bay is a mesotidal (mean tidal range: 3.5 m), semi-enclosed bay located in the southeastern Yellow Sea and is one of the largest tidal flat ecosystems worldwide. Toward the bay head, the tidal channel branches into an intertidal zone covering more than 50% of the total bay area (85 km^2). The tidal flat is composed of fine-grained sediments transported into Hampyeong Bay from the offshore Yellow Sea (Fig. 1). On the shoreline, sandy and gravelly-sandy beaches, which originate from weathering and erosion of terrestrial alluvial sediments and granite and gneiss bedrock, sit atop a mud layer (Lee et al., 1997; Ryu, 2003). The bay has an average depth of 4 m and a bay-mouth width of ~1.5 km. Owing to the narrow bay mouth and the large tidal amplitude, strong tidal currents can occur (>1 m s^{-1}) in the central tidal channel (maximum depth: 23 m) (Ryu, 2003) (Fig. 1). Since rainfall occurs mainly in the summer monsoon season (annual rainfall: 1125 mm) and no major rivers flow into the bay, SGD is probably the main continuous source of terrestrial material. Anthropogenic impacts on Hampyeong Bay are relatively small compared with those on other areas in South Korea; there is no major city along the coast. Waska and Kim (2011) showed that SGD contributed 50–70% of the nutrient fluxes into this bay, and thus fueled the substantial primary production in both the water column and the intertidal benthic environments.

Coastal water samples were collected along the rocky and sandy shore around the entire southwestern coast of the Korean peninsula (Fig. 1). The straight-line length of the shoreline is ~380 km from west to east, with a heavily indented ria coast and many surrounding islands. Mean annual precipitation is ~1560 mm, with most of it falling during the summer monsoon season. The tide is semidiurnal with an average tidal amplitude of ~2 m, even though this range has large variations depending on the semimonthly tidal movement. The eastward-flowing coastal water off this area is composed of Yellow Sea water, oligotrophic Kuroshio water, and low-salinity Yangtze River Diluted Water (Yang et al., 2000). Seomjin River, Youngsan River, and the several streams are the freshwater sources of this coastal region. Youngsan Dam sharply limits Youngsan River runoff (J. Kim et al., 2010).

2.2. Sampling

Water samples, which include fresh/brackish groundwater, coastal/open ocean seawater, and river/stream water, were taken during 2007–2009 from southwestern coastal regions of Korea to analyze concentrations of REEs. We collected groundwater samples that are seeping groundwater from shallow wells (depths > 20 cm and dimensions of >50 cm × 50 cm) in nearshore sediments during low tide. The recharge rate of groundwater in these shallow wells is fast enough (>20 cm/s) to allow the collection of freshly recharged groundwater within a few minutes (Jeong et al., 2012; Kim et al., 2011; Kim and Kim, 2011; Lee et al., 2010). Thus, it is easy to collect seeping groundwater from shallow pit wells. The sampling wells were located 5–10 m seaward from the mean tide line, and the samples were obtained during low tide after a few fills had been discarded. The salinities of the groundwater samples (avg. ± s.d.) ranged from 1.9 to 30.1 (avg. 21.6 ± 8.5, n = 17) and 5.9 to 30.0 (16.5 ± 8.0, n = 18) in Gamak Bay and Hampyeong Bay, respectively. Since general borehole samples may not reflect geochemical alteration during the seeping processes, we used this simple method to collect seeping groundwater with good spatial coverage.

Coastal seawater samples were collected from coastal embayments (Gamak Bay, Hampyeong Bay, and Youngsan River estuary in Korea) using a submersible pump on a ship. Open-ocean seawater samples were collected from the East/Japan Sea. Surface stream and river

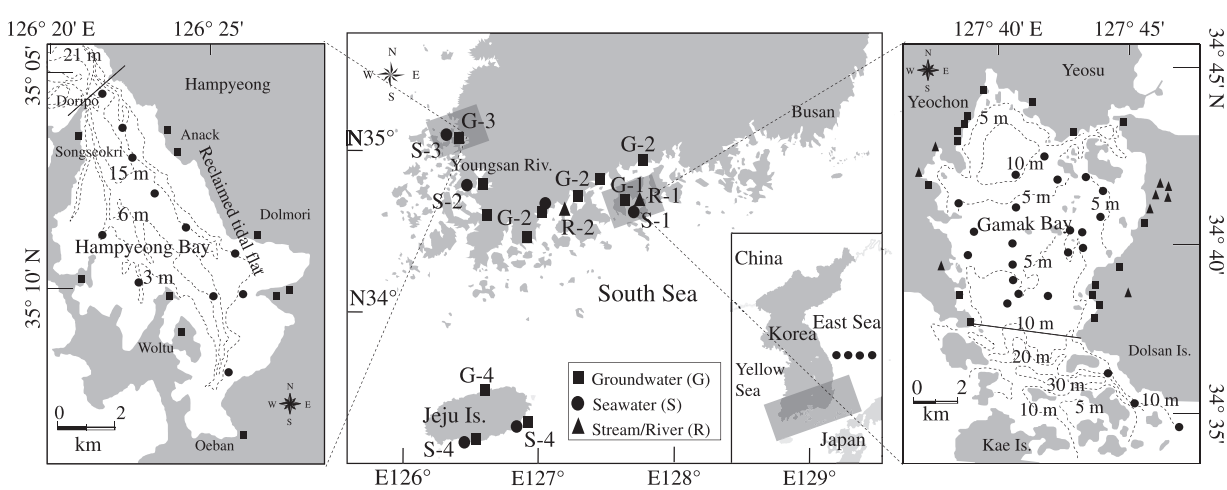

Fig. 1. Maps showing sampling locations of REEs in Gamak Bay (right side), Hampyeong Bay (left side). The dot indicates the site where the REE samples in coastal groundwater (brackish groundwater/meteoric groundwater) were collected. Groundwater (G-1 for Gamak Bay, G-2, G-3 for Hampyeong Bay, and G-4 for Jeju Island), coastal bay seawater (S-1 for Gamak Bay, S-2, S-3 for Hampyeong Bay, and S-4 for Jeju Island), local river water (R-1 for Gamak Bay and R-2 for Seomjin River) were also collected from various coastal sites along the southern part of the Korean peninsula. Open ocean water (OS) were collected from the East/Japan Sea.