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Seasonal and spatial variations of rare earth elements in rainwaters, river waters and total suspended particles in air in South Korea

J.S. Ryu [a,d], K.S. Lee [a,*], S.G. Lee [b], D. Lee [c], H.W. Chang [d]

[a] Division of Isotope Geoscience, Korea Basic Science Institute, Eoeun-dong 52, Yuseong-gu, Daejeon 305-333, Republic of Korea
[b] Groundwater and Geothermal Researches Division, Korea Institute of Geoscience and Mineral Resources, Gajeong-dong 30, Yuseong-gu, Daejeon 305-350, Republic of Korea
[c] Department of Atmospheric Sciences, Yonsei University, Seoul 120-749, Republic of Korea
[d] School of Earth and Environmental Sciences, Seoul National University, Seoul 151-742, Republic of Korea

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Abstract

In order to investigate the seasonal and spatial variations of rare earth element (REE) concentrations in natural waters in the central part of South Korea, rain and river waters were collected during 2003–2004. Total suspended particles (TSP) in air were also sampled to investigate the effect of the Asian dust (the Yellow sand) on the chemistry of rainwaters. All samples showed that the absolute concentrations of the light REEs (LREEs) were higher than those of the heavy REEs (HREEs). The post-Archean Australian shale (PAAS)-normalized REE patterns indicate that the REEs in TSP and rainwaters were affected by Asian dust and anthropogenic contaminant, whereas those of river waters were mainly controlled by the geology of their drainage basin and seasonal changes in water regime. The calculated fluxes and yields of total REEs (REEs plus Y) in the South Han River were much greater than those in the North Han River due to the more widespread distribution of sedimentary rocks in the drainage area and more efficient chemical weathering.

Keywords: Rare earth elements; Seasonal and spatial variations; Rainwaters; River waters; Total suspended particles; South Korea

1. Introduction

Rare earth elements (REEs), lanthanum to lutetium (atomic numbers 57–71), have very similar physicochemical properties, and thus they form a chemically coherent group of elements. Yttrium also shows a similar chemistry to that of REEs, and is sometimes included with them in descriptive accounts [1]. With increasing applications of REEs to agricultural and industrial fields, the significant growth of interest in REE geochemistry has come out because accurate quantitative analysis for them is now possible even at very low concentration level (∼ng/l) [2].

Because the chemical compositions of dissolved components in river waters reflect various processes controlling their chemistries, such as weathering of rocks and soils, atmospheric inputs and anthropogenic disturbances, chemical data of river waters provide important informations about these processes [3]. In particular, the dissolved REEs in waters are relatively immobile during water–rock interaction, and thus they have been used as a good tool to trace water movement in surface and subsurface environments [4–6].

The REE concentrations of 5 world's major rivers and 15 Japanese rivers have been reported in the previous literatures [6,7]. The REE abundance patterns of river waters and its implications on weathering processes were mainly reported in their studies. However, seasonal sampling of water samples was not carried out, and atmospheric inputs were not dealt in their studies.

To date, no REE data of river and rainwaters have been reported in South Korea. In this study, we carried out a systematic investigation of the seasonal and spatial variations of REEs in the Han River, South Korea. The REE contents of the total suspended particles (TSP) in air and rainwaters were also monitored to estimate the effect of atmospheric inputs on the river water chemistry. This study focuses on two aims: (1) to investigate the seasonal and spatial variations of REE abundances in TSP in air, rain and river waters; (2) to determine the major

* Corresponding author. Tel.: +82 42 865 3447; fax: +82 42 865 3963.
E-mail address: kslee@kbsi.re.kr (K.S. Lee).

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processes and factors controlling their variations in natural environments.

2. The study area

The Han River, with a length of 481.7 km and a drainage area of 26,018 km^2, is the largest river in South Korea and supports a variety of agricultural and industrial activities. It has been used as the drinking water source for more than 20 million inhabitants living in the central part of the Korean Peninsula. It consists of two major (the North and the South Han Rivers) and many small tributaries (Fig. 1). The North Han River drains an area of 10,834 km^2 with a length of 317.5 km and the South Han River has a drainage area of 12,154 km^2 with a length of 375 km (data from the Han River Flood Control Office, http://www.hrfco.go.kr/).

The Han River originates at an altitude of more than 1300 m above sea level in the Taeback Mountains, which run subparallel to the eastern coast of South Korea. The river flows E and traverses the mid-western parts of the Korean Peninsula before flowing into the Yellow Sea. Most catchments of the Han River are in mountainous terrain. About 50% of its area has a slope exceeding 400 m/km and only 10% has a gradient of less than 140 m/km. The North and the South Han Rivers are joined at Paldang dam, and then form the main channel of the Han River (Fig. 1).

The North Han River basin mainly consists of Precambrian gneisses and Mesozoic granites. On the contrary, Ordovician carbonates and Permo-Carboniferous coal-bearing sedimentary rocks are widely distributed in the northeastern part of the South Han River basin (Fig. 1).

In the study area, about two thirds of the annual precipitation occurs during summer monsoons from June to September (Korea Meteorological Administration, http://www.kma.go.kr/). The 30-year (1971–2001) annual average of precipitation amount is 1344 mm.

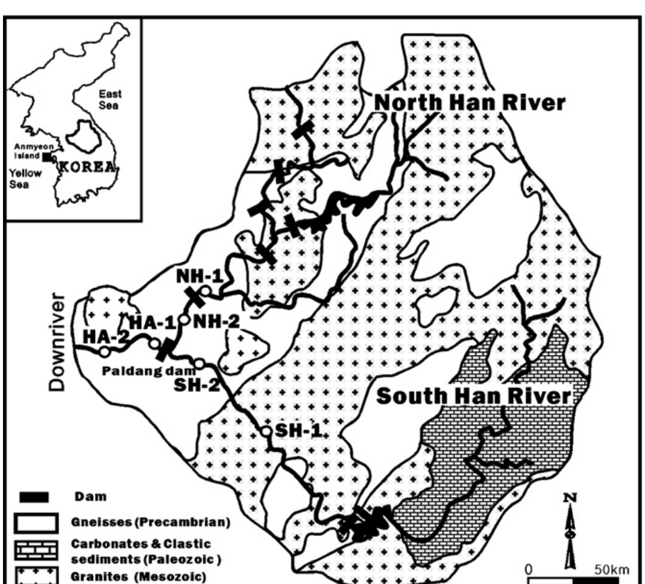

Fig. 1. A map showing the sampling sites and lithological characteristics of the study area.

3. Materials and methods

To investigate the seasonal and spatial variations of REE concentrations in the Han River, 24 water samples were seasonally collected from 6 sites along the main channel of the Han River and 2 major tributaries (the North and the South Han Rivers) during a hydrological year (2003–2004). Monthly composites of rainwater samples were collected at the Korea Global Atmosphere Watch Observatory (KGAWO) in Anmyeon Island (located in Yellow Sea), Chungnam province. To estimate the effect of the Asian dust, TSP samples were collected daily at the same place of the island. TSP samples were collected on cellulose membrane filters exposed for 24 h using high-volume samplers (Andersen) at the average flow rate of 1.1 m^3/min.

The TSP loading filters were cut into appropriate size for acid dissolution (40 mm × 60 mm). The sampling filter was placed into a 60 ml Teflon container, then 5 ml of mixed acid (HNO_3:$HClO_4$ = 4:1) and 1 ml of HF was added to dissolve it completely. All the acids used in the dissolution procedure were reagent grade (Merck, Germany) and were two bottle-distilled. An inductively coupled plasma mass spectrometer (ICP-MS; X-7, Thermo Elemental) at Korea Basic Science Institute (KBSI) was used for REE analysis.

The pH of river waters was measured using electronic meters in the field prior to sampling. For the analysis of cations and REEs, water samples were filtered in the field using a hand-held syringe with 0.45 μm membrane filters. Then, two bottle-distilled HNO_3 was added to the samples to prevent the adsorption to the container surface and precipitation of ions. REEs in river waters were analyzed by ICP-MS (ELAN 6100, Perkin-Elmer) at Korea Institute of Geoscience and Mineral Resources. Detection limit for REE analysis was <0.1 ng/l.

4. Results and discussion

The absolute concentrations of several selected REEs in TSP, rain and river waters are shown in Fig. 2 as box and whisker plots. The geometric mean concentrations of REEs in rainwaters are much lower than those in river waters except for La and Ce. The concentrations of REEs in TSP samples show the largest variation. In particular, during the Asian dust period, the REE concentrations in TSP are at least eight times higher than the average REE concentrations of TSP (Table 1), indicating that the Asian dust (the Yellow sand) which originates from northern and northwestern China is a major source for mineral aerosol particles and various trace elements in the North Pacific region [8].

The REE concentration range of the Han River waters is somewhat narrower than that of rainwaters. The concentrations of the light REEs (LREEs) are much higher than those of the heavy REEs (HREEs) in all samples. The geometric mean concentrations of LREEs (from La to Sm) are 0.35–5.13 ng/m^3, 25.3–232.9 ng/l and 31.7–308.9 ng/l in TSP, rain and river waters, respectively, whereas those of HREEs (from Gd to Lu) are 0.02–0.32 ng/m^3, 20.8–35.9 ng/l and 12.5–54.9 ng/l, respectively. These values of river waters are similar to the world average [6] and the values in Japanese rivers [7]. The concentrations of La and Yb are inversely related to pH [4], while less sensitive to [Na + Ca] (Fig. 3).

The post-Archean Australian shale (PAAS)-normalized REE patterns of average TSP, rain and river waters are shown in Fig. 4 [9]. Most TSP and rainwater samples have patterns that are mod-