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Magnesium isotope geochemistry in the Han River, South Korea

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ABSTRACT

Magnesium (Mg) isotopes can be a proxy for directly constraining the sources of riverine Mg, but the dominant controls on riverine Mg isotope ratios are still uncertain. Here, we report Mg isotope ratios for river waters, experimental leachates and digestions, bulk rocks, and fertilizers in the Han River (HR), South Korea. The HR is composed of two lithologically distinct tributaries: the North Han River (NHR) that flows over only silicate rocks, and the South Han River (SHR) that flows over silicate and carbonate rocks. The lithological differences between the NHR and SHR are reflected in major ion, $^{87}Sr/^{86}Sr$, and $\delta^{26}Mg$ geochemistry. In particular, the NHR has lower major ion concentrations but higher $^{87}Sr/^{86}Sr$ ratios and $\delta^{26}Mg$ values than the SHR. Simple mass balances and mixing equations indicate that if the riverine $\delta^{26}Mg$ values in the HR system are mainly controlled by conservative mixing between silicate and carbonate weathering, the average carbonate end-member $\delta^{26}Mg$ value should be unlikely lower than what are measured in this study. Although multiple process-related fractionations occur in the HR system, the enrichment of ^{24}Mg in river waters relative to silicate rocks they drain could be mostly controlled by either fractionation or mixing between isotopically distinct reservoirs, such as minerals or fractions (labile and structural Mg), during dissolution, while the little depletion of ^{24}Mg in the SHR waters relative to carbonate rocks they drain could be likely due to the input of groundwater with lower $\delta^{26}Mg$ value rather than fractionation. However, it is difficult to identify the contribution of anthropogenic inputs to riverine $\delta^{26}Mg$ because their effects are little. This study suggests that the potential of Mg isotopes for constraining Mg sources in a lithologically varied river basin can be enhanced with a better understanding of process-related fractionation.

1. Introduction

Magnesium (Mg), as one of the major elements in the continental crust, is closely related to various biogeochemical processes that are important to the carbon cycle (Berner and Berner, 2012). Because dissolved Mg is derived mainly from chemical weathering, many studies have tried to constrain Mg sources in solutions using indirect methods, such as mass balances and $^{87}Sr/^{86}Sr$ ratios (Gaillardet et al., 1999; Spence and Telmer, 2005). Recently, new technology using multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) has made it possible to constrain mineralogical sources of Mg and to trace the Mg cycle directly using Mg isotopes (Young and Galy, 2004; Ryu et al., 2011). Studies of terrestrial waters have investigated the Mg isotope systematics during chemical weathering (Tipper et al., 2006a,b; Brenot et al., 2008), controls on dissolved Mg isotope ratios (Pogge von Strandmann et al., 2008; Tipper et al., 2008a; Ryu et al., 2011), and Mg isotope fractionation during various processes, such as plant uptake, ion-exchange, and calcite precipitation (Black et al., 2006; Bolou-Bi et al., 2010; Higgins and Schrag, 2010; Jacobson et al., 2010). Although those studies have suggested several potential factors controlling dissolved Mg isotope ratios, such as mineral leaching, ion exchange, secondary mineral formation, and plant uptake, it remains unclear which factor most significantly controls the dissolved Mg isotope ratios. More information about Mg isotope fractionation during those processes is needed to allow for predictions.

The Han River (HR) is the largest river in South Korea and consists of two major tributaries draining different types of bedrock: the North Han River draining silicate rocks, and the South Han River draining carbonate rocks. This lithological difference between the two tributaries makes the HR an ideal place for studying the various geochemical processes that occur during chemical weathering (Ryu et al., 2008). Previous studies have examined the distinct elemental and isotope geochemistry between two tributaries (Ryu et al., 2007), calculated chemical weathering rates and associated CO_2 consumption rates using major ion mass balances (Ryu et al., 2008), and applied U isotopes to identify controls on dissolved solutes between two tributaries (Ryu et al., 2009). Their results suggest that the HR can be a useful study site for clarifying the dominant controls on riverine Mg isotope ratios.

In this study, we report Mg isotope data for river waters, experimental leachates and digestions, bulk rocks, and fertilizers. The data are interpreted using simple mass balances and Mg isotope mixing equations to examine lithological controls on riverine Mg isotope ratios in the HR system. The differences in $\delta^{26}Mg$ values between river waters

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and bulk rocks are also discussed in terms of process-related fractionation, such as fractionation during dissolution and carbonate precipitation, as well as anthropogenic input. The results suggest that the river waters draining silicate rocks are mainly controlled by either fractionation or mixing between isotopically distinct reservoirs, such as minerals or fractions (labile and structural Mg), while river waters draining carbonate rocks may be affected by the groundwater input with lower Mg isotopic compositions.

2. Material and methods

2.1. Study area

Detailed descriptions of the study area are given in previous studies (Ryu et al., 2007, 2008, 2009). In short, the HR is composed of two major tributaries, the North Han River (NHR) and South Han River (SHR), which merge at the Paldang dam to form the main channel of the river (Fig. 1). The length and drainage area of the HR are 564 km and 26,219 km^2, respectively. The annual discharge varies from 16.0 to 18.9 km^3. The climate is temperate and has four distinct seasons; the mean annual temperature is 12.3 °C, ranging from −5.7 °C in the winter to 27.3 °C in the summer (KMA, 2012). The mean precipitation is 1497 mm/year, about two-thirds of which occurs between June and September (KMA, 2012). The HR basin consists of Precambrian gneiss, Mesozoic granites, and Paleozoic carbonates, within which the NHR drains Precambrian gneiss and Mesozoic granites. The upper SHR flows through Paleozoic carbonates/clastic sediments and the lower SHR flows through Precambrian gneiss and Mesozoic silicates. Neither salt-bearing rocks nor evaporites occur in the study area.

2.2. Sample collection and field measurements

In June 2011 and 2012, 27 water samples in total were collected from 13 sites along a 414 km downstream transect between the river source and the Paldang dam (Fig. 1). All sampling sites were carefully selected to avoid anthropogenic contamination and direct influences from small tributaries. Temperature, pH, and electrical conductivity were measured in-situ using an ORION 5-STAR meter equipped with an ORION Combination epoxy pH electrode and DuraProbe 4-Electrode conductivity cells. Total alkalinity was measured using a Mettler Toledo T50A titrator with 0.1 M HCl acidimetric titration to an endpoint of pH = 4.5. Samples for dissolved cations and Sr and Mg isotope ratios were passed through 0.45 μm filters, collected in I-CHEM LDPE bottles, and acidified to pH = 2 using concentrated, ultrapure HNO_3. Samples for dissolved anions were passed through 0.45 μm filters and collected in Nalgene LDPE bottles. Nine silicate rocks (SR1–9) and five carbonate rocks (CR1–5) were collected from outcrops of the water sampling sites. Likewise, eight fertilizers (chemical and organic fertilizers) commonly used in the study area were purchased for

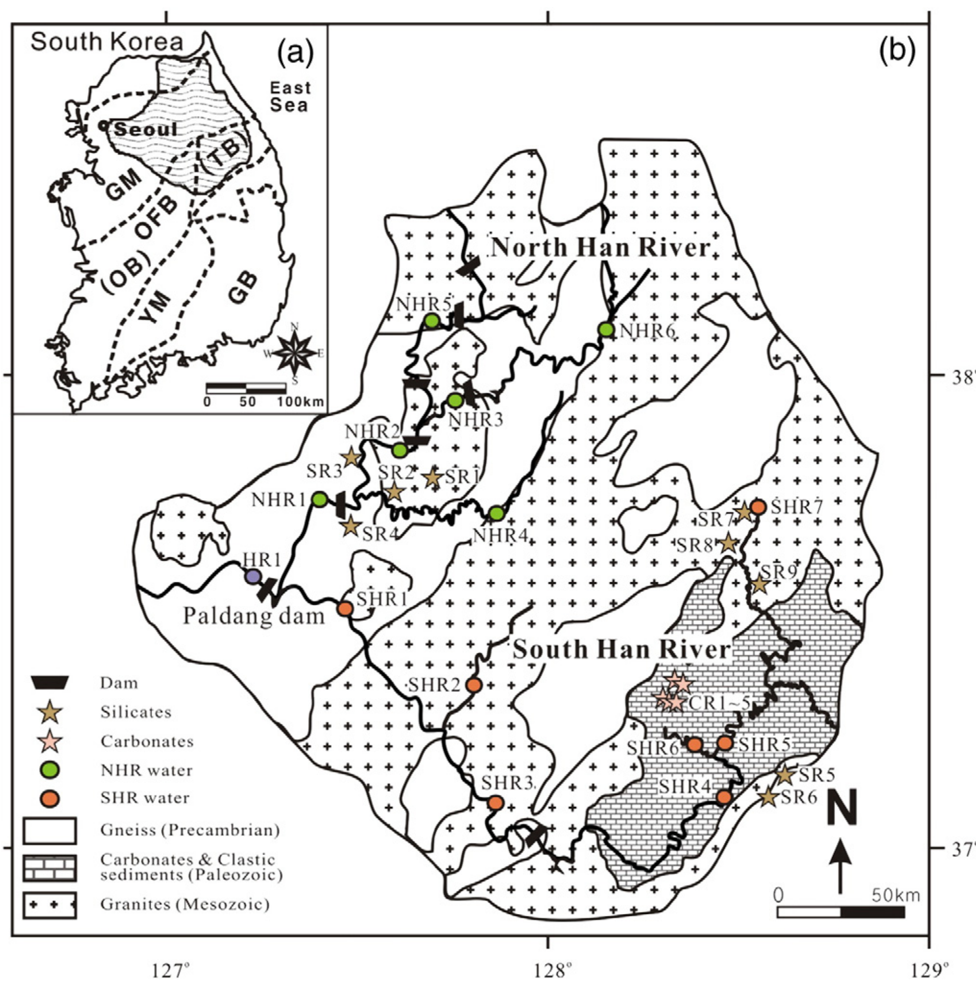

Fig. 1. Simplified map of the study area, geology and sample collection sites (Modified from Ryu et al., 2009; GM: Gyeonggi Massif, OFB: Ogcheon Fold Belt, OB: Ogcheon Basin, TB: Taebaeksan Basin, YM: Yongnam Massif, GB: Gyeongsang Basin).