Lithium isotope fractionation in the Ganges–Brahmaputra floodplain and implications for groundwater impact on seawater isotopic composition

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A B S T R A C T

Lithium isotopes are a promising proxy for reconstructing past weathering processes, but unraveling the seawater record requires a comprehensive understanding of the magnitude and isotopic composition of Li fluxes to the oceans, and of how these change over time. Little information is available on the role of floodplain sediments and groundwater systems in setting the Li isotope signature of the dissolved flux delivered from the continents to the oceans. Here we investigate the Li dissolved fluxes of river waters and groundwaters in the Ganges–Brahmaputra floodplain. The data suggest that a maximum of 3.1×10^8 and 1.5×10^8 moles Li/yr are carried to the Bay of Bengal by Ganges–Brahmaputra rivers and groundwaters, respectively. The riverine flux has a significantly heavier Li isotope composition (average δ^7Li: 26‰) than the groundwater flux (average δ^7Li: 16‰) and increases downstream across the floodplain. δ^7Li in both river waters and shallow groundwater can be explained by Li scavenging by Quaternary floodplain sediments following a Rayleigh fractionation process, with preferential removal of ^{6}Li. On the other hand, deep groundwaters (>40 m) contributing to submarine groundwater discharge to the Bay of Bengal are enriched in ^{6}Li at depth, likely due to the dissolution of floodplain sediments releasing Li with a light isotope composition. Similarly low δ^7Li has been reported in other large sedimentary aquifers. The deep groundwater values are close to the average isotope composition of the global Li inputs to the ocean (~15‰), so groundwater submarine discharge has only a minor influence on the assessment of the modern Li isotope budget of the ocean. Our analysis further suggests that groundwater discharge of Li has probably played at most a small and secondary role in past changes in the isotope composition of the total continental flux of Li to the ocean.

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1. Introduction

The stable isotope composition of lithium (δ^7Li) is a potentially powerful geochemical tool that can provide quantitative information about Earth processes such as sediment recycling (Elliott et al., 2004; Dellinger et al., 2014), global chemical weathering and its role in the carbon cycle (Hathorne and James, 2006; Misra and Froelich, 2012), hydrothermal alteration (Tomascak et al., 2003; Négrel et al., 2012), and groundwater evolution (Pogge von Strandmann et al., 2014). Accurately reading the clues from Li isotopes relies on understanding the processes that drive Li isotope frac-

tionation in the Earth surface system. The δ^7Li isotopic record of seawater in the geologic past shows significant changes during the Cenozoic, including a pronounced ~9‰ increase since 55 Ma (Hathorne and James, 2006; Misra and Froelich, 2012). Such changes could reflect shifts in the weathering system on the continents, potentially shedding light on the weathering fluxes that regulate the global climate system over geologic time. Although Li is predominantly associated with silicate mineral weathering and thought to be minimally complicated by sources from carbonates or other minor lithologies, which influence other isotope systems such as Sr and Os, Li isotopes are still not a direct proxy for the silicate-derived fluxes of Ca and Mg that are primarily relevant for the geologic carbon cycle. There is still considerable uncertainty in using Li isotopes to infer how global silicate weathering fluxes relate to potential tectonic and climatic forcing (Misra and Froelich, 2012; Bouchez et al., 2013; Li and West, 2014; Wanner et al., 2014;

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Vigier and Godderis, 2014) and information about Li fractionation during modern weathering processes is vital to untangle such questions.

Several studies have explored the dissolved δ^7Li of rivers. Globally, the correlation between dissolved δ^7Li and Si/(total cation) concentration ratios suggests a first-order link between δ^7Li and the 'intensity' of chemical weathering (Huh et al., 1998), i.e. the extent to which a given mass of rock, soil or sediment is chemically depleted during continental weathering. Studies of the Orinoco (Huh et al., 2001) and the Amazon (Dellinger et al., 2015) systems support the notion that Li isotope composition may be related to the interaction of physical and chemical erosion processes that set the 'weathering regime'. However, across many other studies of dissolved δ^7Li in river systems, it is not straightforward to find universal first-order relationships between δ^7Li and total chemical weathering fluxes, total concentrations of major ions, the ratio of chemical weathering to physical erosion, or the concentration of dissolved Li (e.g., Kisakürek et al., 2005; Vigier et al., 2009; Pogge von Strandmann et al., 2010; Millot et al., 2010). Comprehensive understanding of what sets the flux and isotopic composition of the continental dissolved Li thus remains incomplete.

To date, pieces of the Li puzzle that have received relatively little attention are the influence of chemical transformation during material transport across floodplains and in the large groundwater systems that release submarine groundwater discharge (SGD) directly to the oceans. Both floodplain and groundwater processes are generally recognized for their important contributions to the dissolved fluxes of many elements delivered from the continents to the oceans (e.g., for floodplain weathering: West et al., 2002; Lupker et al., 2012; Bouchez et al., 2012; Fontorbe et al., 2013; for groundwater weathering: Moore and Church, 1996; Dowling et al., 2003; Paul et al., 2010). Recent studies have reported heavy dissolved δ^7Li in floodplains of the Amazon (Dellinger et al., 2015) and New Zealand (Pogge von Strandmann and Henderson, 2015), motivating further investigation of floodplain fractionation as these observations contrast with the pattern of generally higher dissolved δ^7Li at high compared to low elevations within eroding, upland mountainous systems (e.g., Huh et al., 2001; Kisakurek et al., 2005; Dellinger et al., 2015).

Meanwhile, groundwater discharge from the Ganges–Brahmaputra system is isotopically distinct from the associated riverine flux for dissolved strontium (Basu et al., 2001) and silicon (Georg et al., 2009), and groundwater fluxes may also be important for the Os marine budget (Paul et al., 2010). Existing δ^7Li measurements from continental groundwaters suggest these are often characterized by values distinct from that of surface waters, but most previous studies have focused on specific continental systems that are not representative of global fluxes (e.g., saline, evolved groundwaters, brines and hydrothermal fluids: Bottomley et al., 2003; Meredith et al., 2013; or anthropogenically disturbed systems: Hogan and Blum, 2003).

If floodplain and groundwater processes impart specific δ^7Li to the dissolved flux delivered to the oceans, they could significantly influence present-day seawater isotopic mass balance, and changes in the magnitude of associated fluxes could influence the long-term evolution of seawater chemistry. The goals of this study are to improve understanding of the effect of floodplain weathering on dissolved δ^7Li and to characterize the isotopic composition of SGD from a large continental system. This work focuses on one of the globally important, well-studied floodplain systems, the Ganges–Brahmaputra river system (Basu et al., 2001; Dowling et al., 2003, 2003; Paul et al., 2010; Fontorbe et al., 2013). Understanding the evolution of dissolved δ^7Li in this system additionally helps shed light on the set of processes that control dissolved δ^7Li in weathering systems more generally.

2. Sampling and analytical techniques

2.1. Sampling

River waters were collected from the Ganges and Brahmaputra river catchments (Fig. 1) during the dry season, between January and May 1999. Groundwaters were sampled from monitoring and domestic wells in the Bengal Basin (Fig. 1b) in May 1999 and January 2000. All samples were filtered at 0.2 μm, acidified with distilled HNO_3 and stored refrigerated in polypropylene bottles prior to analyses. Seawater samples stored for 10 years under similar conditions reproduced present-day seawater δ^7Li. Detailed sampling protocols can be found in Basu et al. (2001) and Dowling et al. (2002, 2003).

2.2. Concentration and isotope ratio measurements

All standards and samples were prepared using MQ water and distilled HCl and HNO_3. Na and Mg concentrations in river waters and Li concentrations in river and groundwater samples were measured at the University of Southern California using a Thermo Finnigan Element 2 ICP-MS with external calibration. Machine drift was corrected by repeated measurements of a calibration standard. The external reproducibility determined by repeated measurements of seawater was $<5\%$ (1σ, $n = 8$).

Aliquots for Li isotope measurements were evaporated to dryness in teflon (PFA) beakers and digested with distilled aqua regia. Li was separated from the sample matrix by passing through a cation exchange column filled with 4 mL of Biorad AG50WX-12 (200–400 mesh) resin; the Li fraction was eluted with 0.5 M HCl, dried down and subsequently taken up in 5% HNO_3 for spectrometric analyses (protocol adapted from Misra and Froehlich, 2009).

Li isotope measurements were carried out at the Water Quality Center at Trent University using a Nu Attom High Resolution ICP-MS. Instrument operating parameters are given in Table 1. Under these conditions, typical ^{7}Li signal intensities were 2M cps/ppb. The magnitude of the $^{14}N^{2+}$ and $^{12}C^{2+}$ interferences on ^{7}Li and ^{6}Li respectively were $<0.05\%$ of the Li signal (measured using a mass resolution of 600). The interfering doubly-charged ions were generally not observed for RF powers <850 W. However, lower RF powers were associated with a decrease in the mass bias stability. Therefore, isotope data were acquired using a RF forward power of 1000 W to minimize interferences whilst maintaining an acceptable level of mass bias stability. Samples were introduced using an ESI Apex Q and a PFA nebulizer, with nominal uptake rate of 200 μl min^{-1}. Measurements were performed in fast electrostatic peak jumping mode, using a dwell time of 5 ms per isotope (Newman and Georg, 2012). Each analysis consisted of 25 cycles, with 1000 sweeps per cycle and on-peak blank correction ($\sim 6\%$ of the total Li intensity). The total amount of Li consumed per analysis was ~ 1.13 ng. Each sample was measured in triplicate. Total procedural blanks were negligible ($< 0.5\%$). Instrumental mass bias was corrected by sample-standard bracketing using a concentration matched L-SVEC standard (Flesch et al., 1973). Li isotopic compositions are reported as the per-mil deviation relative to the L-SVEC standard, where: $\delta^7\text{Li} = [((^7\text{Li}/^6\text{Li})_{LSVEC}/(^7\text{Li}/^6\text{Li})_{LSVEC}) - 1] \times 1000$. The external repeatability, determined on repeated measurements of seawater solutions, was 1.4‰ (2σ, $n = 30$). Seawater was used as a reference material to test the accuracy of the measurements, and the results (30.5 ± 1.4‰, 2σ, $n = 30$) were in good agreement with previously published values (e.g., Hathorne and James, 2006; Misra and Froelich, 2012).