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Processes controlling δ^7Li in rivers illuminated by study of streams and groundwaters draining basalts

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ABSTRACT

We evaluate the factors influencing the abundance, [Li], and isotopic composition of riverine Li delivered to the oceans through analyses and modeling of [Li] and δ^7Li in streams and groundwaters draining a single continental lithology, the Columbia River Basalts (CRBs). The streams were sampled in different climate zones that lie east (dry), and west (wet) of the Cascades Mountains, and during two different seasons (summer and late winter) in order to evaluate climatic and seasonal influences on Li isotopes in rivers. Dissolved Li ($\delta^7Li_{dis} = +9.3$ to $+30.4$) is systematically heavier than that of fresh or weathered CRBs (-4.7 to $+6.0$, Liu et al., 2013), suspended loads (-5.9 to -0.3), and shallow groundwaters ($+6.7$ to $+9.4$), consistent with previous studies showing that Li isotope fractionation is affected by equilibration between stream water and secondary minerals. However, the lack of correlation between δ^7Li_{dis} and climate zone, the uniform secondary minerals and bedrock, coupled with the highly variable (>20‰) δ^7Li_{dis} indicate that other factors exert a strong control on δ^7Li_{dis}. In particular, the heavier Li in streams compared to the shallow groundwaters that feed them indicates that continued isotopic fractionation between stream water and suspended and/or bed loads has a major influence on riverine δ^7Li. Seasonal δ^7Li variation is observed only for streams west of the Cascades, where the difference in precipitation rate between the dry and wet seasons is greatest. Reactive transport model simulations reveal that riverine δ^7Li is strongly controlled by subsurface residence times and the Li isotope fractionation occurring within rivers. The latter explains why there is no positive correlation between δ^7Li and traditional weathering proxies such as Si or normalized Si in rivers, as riverine Li isotope fractionation drives δ^7Li to higher values during transport, whereas the concentrations of major cations and anions are diluted. The varying residence time for groundwaters feeding the western streams in summer (long residence times, higher δ^7Li, greater weathering) and winter (short residence times, lower δ^7Li, less weathering) explains the observed seasonal variations. A global, negative correlation between δ^7Li and Li/Na for streams and rivers draining basaltic catchments reflects the overall transport time, hence the amount of silicate weathering. Based on our results, the increase of δ^7Li in seawater during the Cenozoic is unlikely related to changing climate, but may reflect mountain building giving rise to increased silicate weathering.

1. Introduction

Chemical weathering of silicate rocks on Earth's surface plays a critical role in regulating the global carbon cycle over geological time-scales (e.g., Berner et al., 1983). Basalt weathering, in particular, may significantly contribute to the global silicate weathering flux. For example, Gaillardet et al. (1999), suggested a minimum of 25% of the silicate weathering flux to the oceans derives from weathering of basalt. Attempts to illuminate chemical weathering processes using natural samples generally take two approaches: studies of river waters (e.g., Dessert et al., 2001; Gaillardet et al., 1999), and studies of weathering profiles or weathered regoliths (e.g., Brimhall et al., 1991; Nesbitt and Wilson, 1992). River chemistry is able to provide rate-related constraints, such as chemical weathering fluxes and CO_2 consumption rates (Gaillardet et al., 1999), although only for the present.

Li isotopes can potentially provide insights into the weathering flux from the continents over time (Liu and Rudnick, 2011), and changing climate, if the changes in δ^7Li in the seawater record (Misra and Froelich, 2012) can be deciphered. The Li isotopic

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composition in seawater is a function of the input of rivers and hydrothermal fluid, and the output into secondary minerals formed via low temperature basalt alteration and sediment clay authigenesis (referred to as "reverse weathering") (Chan et al., 1992). The dramatic (8‰) increase in δ^7Li in seawater through the Cenozoic has been interpreted to reflect the changing composition of riverine inputs that, in turn, reflect climatic and tectonic influences on continental weathering (Misra and Froelich, 2012). Assuming a constant hydrothermal input, the significant increase in δ^7Li through the Cenozoic may indicate increases in the riverine input (a greater flux and/or higher δ^7Li), an increased output flux of low δ^7Li, or both. Therefore, understanding the controls on riverine Li isotopes is a first-order requirement for understanding the secular evolution of seawater.

Li is contained mainly in silicates and is released, with attendant isotopic fractionation, during weathering (e.g., Huh et al., 2001, 1998; Kisakürek et al., 2005, 2004; Rudnick et al., 2004). Lithium's two stable isotopes, ^{7}Li and ^{6}Li, have great fractionation potential due to their 17% mass difference. Differences in Li isotopic composition are expressed as $\delta^7\text{Li}\ (‰) = ([^7\text{Li}/^6\text{Li}]_{\text{sample}}/[^7\text{Li}/^6\text{Li}]_{\text{standard}} - 1) \times 1000$, where the standard used is a lithium carbonate, L-SVEC (Flesch et al., 1973). Lithium is a water-soluble trace element, but neither primary basalt dissolution nor metamorphic dehydration appear to cause significant Li isotopic fractionation (Marschall et al., 2007; Pistiner and Henderson, 2003; Qiu et al., 2011a, 2011b, 2009; Teng et al., 2007; Wimpenny et al., 2010a). By contrast, Li isotopes fractionate significantly during incongruent continental weathering, due to the formation of secondary minerals, such as clays (e.g., Huh et al., 1998; Kisakürek et al., 2004; Pistiner and Henderson, 2003; Pogge von Strandmann et al., 2006; Rudnick et al., 2004; Teng et al., 2004). Lithium has a few more advantages as a potential geochemical tracer of weathering. Li has only one redox state (+1 charge), and is thus insensitive to changes in oxygen fugacity compared to Fe, Cr, Cu, Mo, etc. In addition, Li is not a nutrient, so its elemental and isotopic behavior is not directly influenced by biological processes (e.g., Lemarchand et al., 2010). Finally, Li is enriched in silicates and depleted in carbonates, so its abundance and isotopic composition in rivers mainly reflect continental silicate weathering (one caveat is that riverine Li can be significantly influenced by the presence of evaporites, e.g., Huh et al., 1998).

Studies investigating the use of δ^7Li as a weathering proxy (Huh et al., 2001, 1998; Millot et al., 2010; Pogge von Strandmann et al., 2006; Vigier et al., 2009) have not fully discerned why the Li isotope composition of rivers does not show consistent correlation with certain silicate weathering proxies. For instance, Huh et al. (1998) did not observe a clear correlation between $\delta^7\text{Li}_{\text{dis}}$ and ^{87}Sr/^{86}Sr, $\delta^7\text{Li}_{\text{dis}}$ and [Li] (using square brackets around elements to indicate concentration) as well as between $\delta^7\text{Li}_{\text{dis}}$ and Si/TZ$^+$ (Total cation charge, $\text{TZ}^+ = \text{Na}^+ + 2\text{Mg}^{2+} + \text{K}^+ + 2\text{Ca}^{2+}$ in 10^{-3} equivalents per liter, mEq/L) when compiling global river data. By contrast, for the Orinoco drainage basin a strong inverse correlation was observed between $\delta^7\text{Li}_{\text{dis}}$ and ^{87}Sr/^{86}Sr as well as between $\delta^7\text{Li}_{\text{dis}}$ and Si/TZ$^+$ (Huh et al., 2001). In addition, in some studies a correlation between δ^7Li and chemical weathering rates (in mass/area/time) was observed (Vigier et al., 2009), whereas in others no clear relationship could be identified (Millot et al., 2010). The lack of consistent correlation may reflect variations in climate (e.g., tropical vs. temperate climates), lithologies, hydrology, and sampling seasons encompassed in previous river studies. Here we seek to illuminate the causes of Li isotopic fractionation produced during weathering by studying surface waters draining a single lithology (basalt) as a function of climate, season, and groundwater residence time. The Columbia River Basalts (CRBs) afford this opportunity due to their large areal extent, which encompasses different climate zones and allows sampling within a single lithology having limited isotopic variability. Understanding the processes that control $\delta^7\text{Li}_{\text{dis}}$ will, in turn, afford greater insight into the changing δ^7Li observed in seawater with time.

2. Geological setting, climate and samples

The geological setting of the sampling area is described in Liu et al. (2013) and a brief account is provided here. The CRBs are continental flood basalts that erupted during the Miocene (between 17 Ma and 6 Ma) in the US Pacific Northwest, covering large parts of southern Washington, northeastern Oregon and parts of western Idaho (Fig. 1).

The CRBs crop out both east and west of the Cascade Mountain Range. The Cascades developed progressively from subduction zone magmatism since the Late Eocene, with topography increasing more or less steadily since the Late Oligocene (Kohn et al., 2002 and references therein). The mountains created two different climate zones that affected the CRBs via the rain shadow effect; regions west of the Cascades have high mean annual precipitation (MAP) (1500–2000 mm), whereas annual precipitation east of the Cascades is less than 300 mm (Kohn et al., 2002; Takeuchi et al., 2010). In addition, the monthly precipitation rates vary more in the west, where the mean monthly precipitation rate during the wet season (October–May) is up to 10 times greater than that during the dry season (June–September) (Fig. A1). By contrast, differences in monthly precipitation rates east of the Cascades are usually less than a factor of 2.

The advantages of studying streams and groundwaters in this area include: 1) The streams only drain a single lithology, the CRBs. 2) Sampling streams from different climate zones allows investigation of how annual precipitation rates, and thus climate, may have influenced riverine Li isotopic composition. 3) Due to the variable seasonal precipitation (Fig. A1), sampling in two seasons allow us to assess the effect of seasonally variable precipitation rates and corresponding variable surface runoff (Fig. A2) on Li isotopic compositions. 4) Sampling of groundwaters that are the potential sources of the streams allows distinction between Li isotope fractionation occurring in subsurfaces and fractionation occurring in rivers.

3. Samples and analytical methods

3.1. Sampling

Dissolved and suspended load samples from 10 CRB streams were collected in July 2010, and again in March 2012 to study possible seasonal variations; samples from the mouths of the much larger Deschutes and John Day rivers, which have lithologically diverse catchments, were also taken for comparison. In addition, five groundwater samples were collected in March 2012, as well as an additional stream (Mosquito Creek, R11) (Fig. 1).

At each site, pH, temperature, electrical conductivity, and total dissolved solids (TDS) were measured using a multi-meter (Hanna® Instruments) with analytical accuracy of ±0.05, ±0.5 °C, ±2% μS/cm, and ±2% ppm, respectively. All stream water samples were obtained using a peristaltic pump and filtered using a 142 mm filter holder system with 0.2 μm cellulose acetate filters. Filtered waters were collected in pre-cleaned Nalgene® bottles. Filters were placed in air-tight Ziploc plastic bags for transport back to the lab. The suspended loads of the stream waters were recovered from the filters in the clean lab. The sample tubing was pumped dry after each sample collection and one liter of deionized water was pumped through the system to clean it between each sampling event. At the start of sampling at a new site, a liter of sample water was first collected into the pre-cleaned bottles