



## RESEARCH LETTER

10.1002/2016GL067711

## Key Points:

- Dissolved Li isotope composition at mouth of the Congo River is controlled by hydrologic mixing
- Two contrasting dissolved  $\delta^7\text{Li}$  values in the Congo reveal two distinct weathering regimes
- Low late Paleocene seawater  $\delta^7\text{Li}$  value is not unequivocally generated by flat continents

## Supporting Information:

- Supporting Information S1

## Correspondence to:

S. Henchiri,  
henchiri@ipgg.fr

## Citation:

Henchiri, S., J. Gaillardet, M. Dellinger, J. Bouchez, and R. G. M. Spencer (2016), Riverine dissolved lithium isotopic signatures in low-relief central Africa and their link to weathering regimes, *Geophys. Res. Lett.*, 43, 4391–4399, doi:10.1002/2016GL067711.

Received 14 JAN 2016

Accepted 18 MAR 2016

Accepted article online 24 MAR 2016

Published online 6 MAY 2016

## Riverine dissolved lithium isotopic signatures in low-relief central Africa and their link to weathering regimes

Soufian Henchiri<sup>1</sup>, Jérôme Gaillardet<sup>1</sup>, Mathieu Dellinger<sup>1,2</sup>, Julien Bouchez<sup>1</sup>, and Robert G. M. Spencer<sup>3</sup>

<sup>1</sup>Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Université Paris Diderot, CNRS, Paris, France, <sup>2</sup>Department of Earth Sciences, University of Southern California, Los Angeles, California, USA, <sup>3</sup>Department of Earth, Ocean and Atmospheric Science, Florida State University, Tallahassee, Florida, USA

**Abstract** The isotopic composition of dissolved lithium ( $\delta^7\text{Li}$ ) near the Congo River mouth varied from 14‰ to 22‰ in 2010 and was negatively correlated to discharge. From the relationship between dissolved  $\delta^7\text{Li}$  and strontium isotopes, we suggest that this large variation is due to mixing of waters from two contrasting continental weathering regimes. One end-member (high  $\delta^7\text{Li} \approx 25\text{‰}$ ) represents waters sourced from active lateritic soils covering the periphery of the basin (Li highly sequestered into secondary mineral products) and another representing blackwater rivers (low  $\delta^7\text{Li} \approx 5.7\text{‰}$ ) derived from the swampy central depression where high organic matter content in water leads to congruent dissolution of the Tertiary sedimentary bedrock. This suggests that the lithium isotopic signature of tropical low-relief surfaces is not unique and traces the long-term, large-scale vertical motions of the continental crust that control geomorphological settings. This evolution should be recorded in the oceanic secular  $\delta^7\text{Li}$  curve.

### 1. Introduction

Chemical weathering of silicate rocks is a major geological process shaping the surface of our planet, forming the soil, mantling the continents, and playing a crucial role in the long-term evolution of the Earth's climate through the consumption of atmospheric carbon dioxide ( $\text{CO}_2$ ) [Berner *et al.*, 1983]. Therefore, weathering has influenced the Earth's habitability over time.

From a geochemical point of view, chemical weathering is the reaction between primary minerals, water, and an acid (usually  $\text{CO}_2$  or sulfuric acid). It leads to the release of the most soluble elements (e.g., Na) to the aqueous phase, while the insoluble elements are concentrated in residual solids that accumulate in soils and form river sediments (e.g., Al and Fe). The fraction of total mass (or of any element) weathered from the initial bedrock and transported as dissolved load in rivers is denoted as the weathering intensity and serves to characterize the chemical weathering regime. In regions featuring low physical erosion rates, solid material resides for long times in the soil and thus usually displays high weathering intensity [Stallard and Edmond, 1983].

Among soluble alkali elements, lithium (Li) and its isotopes are an ideal tracer of silicate weathering [Burton and Vigier [2011] for a review) and particularly of these weathering regimes [Dellinger *et al.*, 2015; Huh *et al.*, 2001]. Lithium is mainly hosted in silicate minerals, and the Li cycle is not substantially impacted by biological processes [Lemarchand *et al.*, 2010]. Moreover, during water-rock interactions, its isotopes ( $^7\text{Li}$  and  $^6\text{Li}$ ) are highly fractionated. The light isotope is preferentially incorporated into secondary solid weathering products like clays or iron oxides that form the soils. Conversely, the dissolved load is enriched in the heavy isotope. As a result, river waters usually have dissolved Li isotope composition ( $\delta^7\text{Li}$ ) values higher than the parent rocks [e.g., Huh *et al.*, 2001; Kisakurek *et al.*, 2005; Dellinger *et al.*, 2015; Wang *et al.*, 2015; Bagard *et al.*, 2015].

A 9‰ increase in the seawater  $\delta^7\text{Li}$  over the last 60 Myr has been reported [Hathorne and James, 2006; Misra and Froelich, 2012] (today  $\delta^7\text{Li}_{\text{seawater}} = 31\text{‰}$ ). The interpretation of this trend in terms of evolution of past riverine  $\delta^7\text{Li}$  and of paleoweathering conditions during the Cenozoic is not straightforward and highly debated. A first set of studies [Misra and Froelich, 2012; Bouchez *et al.*, 2013; Li and West, 2014; Wanner *et al.*, 2014] explain this trend by an increase in  $\delta^7\text{Li}$  of rivers during the Cenozoic, ultimately due to an increase in the global flux of materials deriving from the destruction of the continents. An alternative view suggested by Vigier and Godderis [2014] argues that this record reflects a large increase in the dissolved Li flux

with no change of the isotopic composition during the Cenozoic, corresponding to a decrease of both the amount of Li incorporated in clays and weathering rates due to global cooling. Notwithstanding, all these studies consider that the Paleocene environment ( $\delta^7\text{Li}_{\text{seawater}} = 22\text{‰}$ ) was characterized by deep laterite-type soils and high weathering intensity on essentially flat continents with low physical erosion rate and attribute very distinct riverine dissolved  $\delta^7\text{Li}$  for this Paleocene period (from  $+3\text{‰}$  to  $+25\text{‰}$ ). In order to test these models, here we report on the Li isotopic signature of continental regions characterized by high chemical weathering intensity, found in the tropical environments of the modern Earth. We focus on the dissolved load in the largely pristine Congo Basin [Spencer *et al.*, 2012] sampled over the entire hydrological cycle. The Congo River drains a low-relief continental area characterized by a very high chemical weathering intensity and exhibits very low suspended sediment concentrations in comparison to other major rivers systems [Gaillardet *et al.*, 1995; Dupré *et al.*, 1996], making it the perfect natural laboratory to constrain the Li isotope composition of rivers draining low-physical erosion rates settings and a suitable analogue for a “Paleocene Earth.”

## 2. Materials and Methods

### 2.1. Study Area and Sampling

The Congo River is the second largest river system on Earth in terms of water discharge ( $1200 \text{ km}^3/\text{yr}$ ) and surface area ( $3.7 \times 10^6 \text{ km}^2$ ). It comprises a large, ovoid, and relatively flat drainage area (“Cuvette Centrale”) surrounded by lateritic plateaux [Guillocheau *et al.*, 2015]. The bedrock is mainly composed of Archean and Proterozoic tonalitic to granodioritic gneisses (TTG) on the borders [de Wit and Linol, 2015], while the Cuvette Centrale is a sedimentary basin containing Mesozoic to upper Tertiary marine and continental deposits. The northwestern part of the Cuvette Centrale is a topographic low occupied by swamps, partly inundated with rivers having high dissolved organic matter concentrations (“blackwater rivers”) [e.g., Dupré *et al.*, 1996]. These rivers represent the regional base level and have particularly low dissolved and suspended loads. Geomorphologic analyses of the planation surfaces [Guillocheau *et al.*, 2015] indicate that the present-day topography of the Congo Basin derives from differential uplift, less pronounced in the central basin, and higher in the surrounding areas. Conversely, dynamic topographic models show that the Cuvette Centrale results from the subsidence of the Congo Basin over the past 30 Myr in response to mantle convective drawdown [Moucha and Forte, 2011].

As the Congo Basin straddles across the equator, the flow regime at Kinshasa (near the mouth) is characterized by two peaks (in December and May) due to the phase shift of the high and low water stages between the Northern and Southern Hemispheres [Spencer *et al.*, 2012] (Figures 1 and 2a). The major tributaries of the Congo River at Kinshasa are the Oubangui (draining the northern part of the basin), the Congo-Lualaba (draining the eastern and southern parts), the Kasai (from the southern part), and the Likouala-Sangha blackwater rivers (Figure 1) [Spencer *et al.*, 2014]. Overall, three types of ecosystems are represented: the rain forest is found predominantly around the equator, savannah vegetation characterizes the northern, and the southern parts of the basin and swamp areas (with inundated rain forest) are located in the central depression (Figure 1). Previous studies have highlighted the very different natures of the water flowing at the periphery of the Congo Basin and in the Cuvette Centrale [e.g., Dupré *et al.*, 1996]. While the rivers draining the Precambrian basement are white, dissolved organic carbon (DOC)-poor and relatively concentrated waters, rivers draining the central depression are black, DOC-rich and very dilute. Their cationic content ranges from 200 to  $220 \mu\text{eq/L}$  [Dupré *et al.*, 1996], lower than the global discharge-weighted average ( $1125 \mu\text{eq/L}$ ) [Meybeck, 2003]. Most of the watershed area is covered by lateritic formations which are ferrallitic soils (93%) and recent brown soils (7%). Podzols are associated with the central depression [Negrel *et al.*, 1993, and references within]. Due to the weakness of physical erosion processes, thick soils can accumulate leading to high intensity of chemical weathering.

Temporal monitoring of the Congo River was conducted at Kinshasa for the year 2010 (Figure 1). Samples were collected every 2 months from January to November 2010 and were filtered with preleached  $0.7 \mu\text{m}$  porosity membranes on site and stored unacidified. Other samples were collected during a cruise on the Congo River in November 1989 [Negrel *et al.*, 1993; Dupré *et al.*, 1996] between Bangui and Brazzaville (Figure 1). From the cruise, samples were filtered on site using  $0.2 \mu\text{m}$  porosity acetate cellulose filters and kept acidified under cold conditions. The blackwater rivers were sampled just before their confluence with the mainstream of the Congo River.

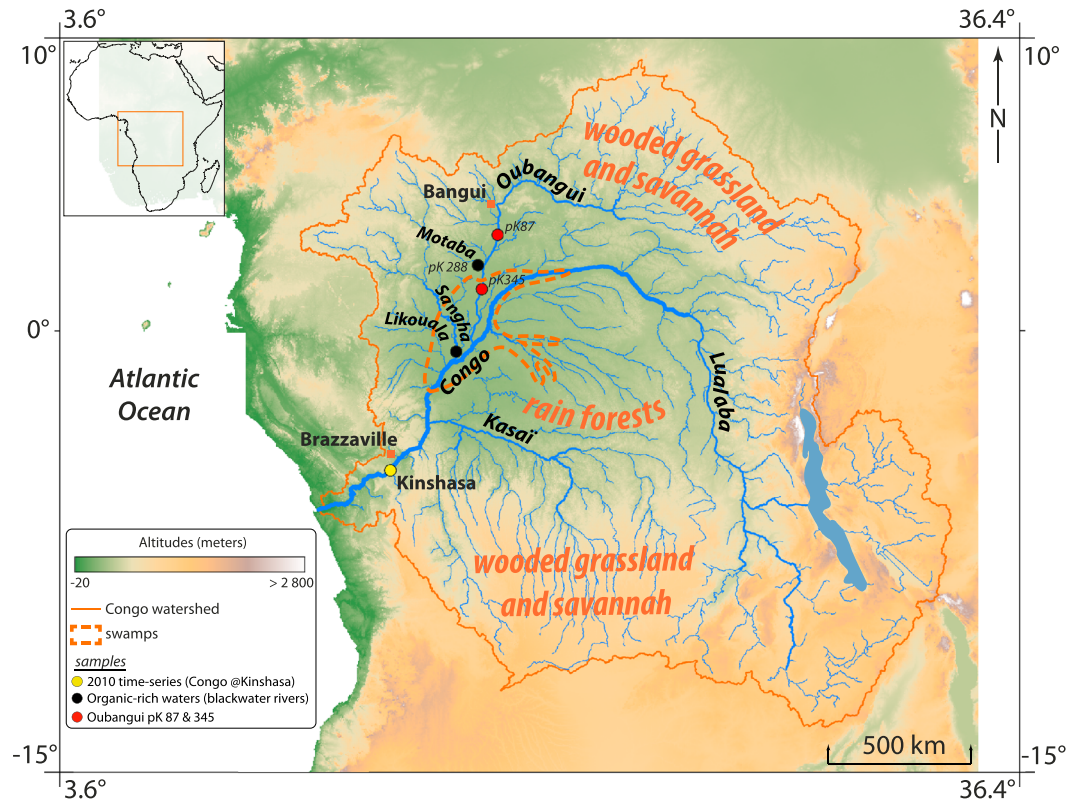


Figure 1. Map of the Congo River Basin with sample locations.

2.2. Analytical Methods

Analytical methods are described in Text S1 in supporting information. The Li isotope composition is expressed using the delta notation (in ‰) (normalization to the L-SVEC standard) [Flesch et al., 1973]:

$$\delta^7\text{Li} = \left( \frac{(^7\text{Li}/^6\text{Li})_{\text{sample}}}{(^7\text{Li}/^6\text{Li})_{\text{L-SVEC}}} - 1 \right) \times 10^3 \quad (1)$$

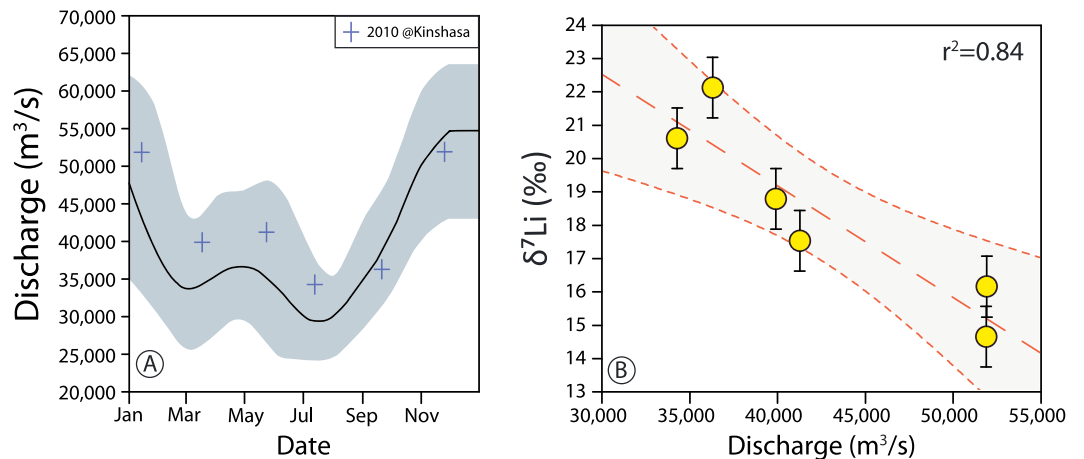


Figure 2. (a) Monthly discharge of the Congo River at Kinshasa (30 year average, 1977–2006): mean (solid black line) and maximum and minimum (gray area) (reproduced from Spencer et al. [2012]). The blue crosses represent the discharge at Kinshasa in 2010 at the time of sampling. (b) Relationship between dissolved  $\delta^7\text{Li}$  and discharge at mouth (Kinshasa) of the Congo River over the year 2010. Dotted lines and gray area delimited by stippled curves represent linear best fit and 95% confidence area, respectively.

The reproducibility of the Li chemical purification procedure was checked using the North Atlantic Surface Seawater standard reference NASS5 (long-term average  $\delta^7\text{Li} = 31.06 \pm 0.91\text{‰}$ ,  $2\sigma$ ,  $n = 34$  separations and measurements).

### 3. Results

Data are reported in Table S1. Despite the prevailing low relief and low erosion in the Congo Basin, dissolved  $\delta^7\text{Li}$  of the Congo River at Kinshasa over the year 2010 shows large temporal variations.  $\delta^7\text{Li}$  values in the Congo River range from 14.7‰ to 22.1‰ over the course of the hydrological cycle, clearly exceeding the analytical reproducibility (Figure 2b). For comparison,  $\delta^7\text{Li}$  values published for the dissolved load of rivers range from 1.2‰ [Dellinger *et al.*, 2015] to 43.7‰ [Pogge von Strandmann *et al.*, 2006]. A negative relationship between dissolved  $\delta^7\text{Li}$  and the discharge of the Congo River at Kinshasa is observed for the year 2010 (Figure 2b).

The two blackwater (organic-rich) rivers analyzed (Motaba and Sangha) exhibit the lowest dissolved  $\delta^7\text{Li}$  of this sample set (average of  $5.7 \pm 0.1\text{‰}$ ,  $n = 2$ ). These low values are comparable with those reported for the dissolved load of the Negro River, draining a similar geomorphological setting (1.3‰–6.5‰) [Dellinger *et al.*, 2015] in the Amazon Basin. By contrast, the Oubangui River sample (taken 87 km downstream from Bangui) exhibits the highest dissolved  $\delta^7\text{Li}$  value (25.8‰) (e.g., Figure 3). Such high  $\delta^7\text{Li}$  values are also found in Himalayan rivers, the Changjiang River system, the Ganges-Brahmaputra River system, rivers in west Greenland, the Mackenzie Basin, and in rivers draining volcanic areas [Kisakurek *et al.*, 2005; Wang *et al.*, 2015; Bagard *et al.*, 2015; Wimpenny *et al.*, 2010; Millot *et al.*, 2010; Henchiri *et al.*, 2014]. They are significantly higher than those reported for the lowland rivers of the Madeira Basin and for waters draining the Amazonian Shield in which dissolved  $\delta^7\text{Li}$  does not exceed 16‰ [Dellinger *et al.*, 2015], despite the fact that they drain similar lateritic settings.

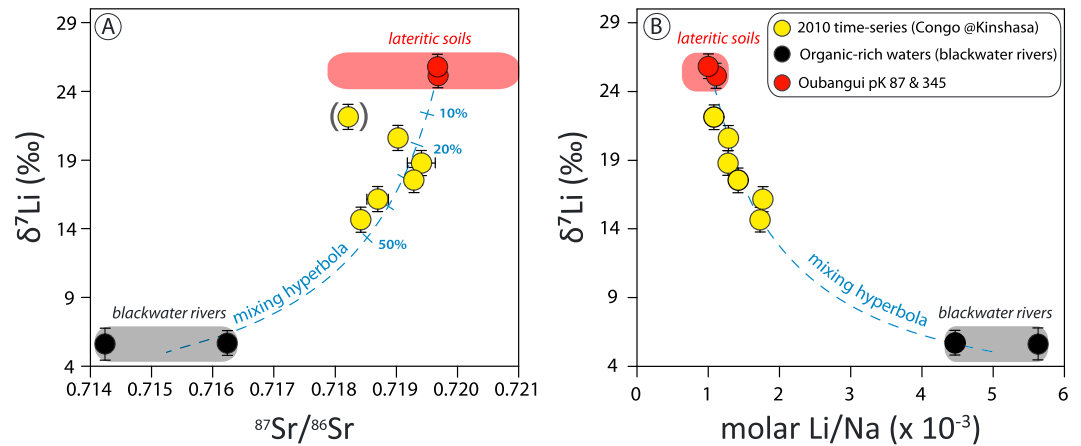
The  $^{87}\text{Sr}/^{86}\text{Sr}$  values of samples from the temporal observations at Kinshasa range from  $0.718215 \pm 0.000079$  (21 September 2010) to  $0.71941 \pm 0.00023$  (18 March 2010). Blackwater rivers have the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  values (average of  $0.7153 \pm 0.0026$ ,  $n = 2$ ), and the sample representing the northern part of the basin (C89 5a pK 87) has the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  value ( $0.719682 \pm 0.000029$ ) [Negrel *et al.*, 1993] (Figure 3a and Table S1). A positive relationship exists between  $\delta^7\text{Li}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  as shown in Figure 3a.

## 4. Discussion

### 4.1. Temporal Lithium Isotopic Signature Variations at Kinshasa Resulting From a Binary Hydrologic Mixing Process

We interpret the variations of  $\delta^7\text{Li}$  over the hydrological cycle at Kinshasa as the result of a mixing of two water masses exhibiting contrasting isotopic signatures and whose proportions are changing with time. Several arguments support this hypothesis which are detailed in the following.

The first argument is deduced from Figure 3a where dissolved  $\delta^7\text{Li}$  is plotted against  $^{87}\text{Sr}/^{86}\text{Sr}$ . In such a diagram, a mixing process leads to a hyperbola whose curvature depends on the relative values of the Li/Sr ratio in the two mixing water masses, assuming the conservative behavior of Sr and Li during mixture. Sr isotopes have been widely used as a conservative tracer in rivers [e.g., Palmer and Edmond, 1992]. The behavior of Li is less clear. Although Li isotopes in the Mackenzie and Amazon rivers are mostly conservative (i.e.,  $\delta^7\text{Li}$  does not change significantly along the course of the river) [Millot *et al.*, 2010; Dellinger *et al.*, 2015], recent work in New Zealand, on the Ganges River, and the Amazon River systems have shown that Li can be scavenged in floodplains and reincorporated in the solid load, most likely in oxides or clays [Pogge von Strandmann and Henderson, 2015; Bagard *et al.*, 2015; Dellinger *et al.*, 2015; Torres *et al.*, 2015]. Here the mixing process evidenced by the Sr-Li mixing curve strongly suggests that Li behaves conservatively in the Congo River and that the temporal variations of  $\delta^7\text{Li}$  at Kinshasa reflect mixing between two distinct water masses. The absence of significant floodplains, the quartz-dominated nature of the Congo River sediments, the low suspended sediment load and the low river pH [e.g., Dupré *et al.*, 1996; Spencer *et al.*, 2012] support a conservative behavior of Li in the Congo River between Bangui and Kinshasa. This is reinforced by calculations of mineral saturation indexes using Visual Minteq® that show that iron oxides cannot precipitate neither in Oubangui-like rivers nor in blackwater rivers.



**Figure 3.** (a) Relationship between dissolved  $\delta^7\text{Li}$  and dissolved  $^{87}\text{Sr}/^{86}\text{Sr}$ . This trend can be explained by the mixing between two end-members: one with high  $\delta^7\text{Li}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  and another with low  $\delta^7\text{Li}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ . The latter corresponds to the blackwater rivers (see text). The red limit corresponds to the lateritic soils end-member  $^{87}\text{Sr}/^{86}\text{Sr}$  data span reported for Oubangui, Kasai, and Congo-Lualaba by *Negrel et al.* [1993]. The values in blue indicate the proportion of the water mass originating from blackwater river systems calculated by a binary mixing model. (b) Relationship between dissolved  $\delta^7\text{Li}$  and molar Li/Na ratio (not corrected for atmospheric inputs).

Theoretical mixing curves from Figure 3a are calculated based on mass balance equations. For Li, the equation is

$$\delta^7\text{Li}_{\text{mix}}^t = \lambda_L^t \delta^7\text{Li}_L + (1 - \lambda_L^t) \delta^7\text{Li}_H \quad (2)$$

$$\text{where } \lambda_L^t = \frac{[\text{Li}]_L \gamma_L^t}{[\text{Li}]_L \gamma_L^t + [\text{Li}]_H (1 - \gamma_L^t)} \quad (3)$$

In these equations,  $\delta^7\text{Li}_{\text{mix}}^t$  is the Li isotope composition at any time  $t$  at Kinshasa;  $\lambda_L^t$  and  $\gamma_L^t$  are the mass fraction of Li and water supplied at time  $t$  by the end-member with low  $\delta^7\text{Li}$ , respectively.  $[\text{Li}]_L$  and  $[\text{Li}]_H$  are the concentrations of Li in waters of the end-member with low and high  $\delta^7\text{Li}$  values ( $\delta^7\text{Li}_L$  and  $\delta^7\text{Li}_H$ ), respectively. The same type of mixing equations can be written for Sr isotopes.

The two end-members necessary to explain the isotope composition of the samples from the time series at Kinshasa are in remarkable agreement with the samples measured at the periphery of the Congo Basin in the Oubangui River ( $\delta^7\text{Li} \approx 25\text{‰}$  and  $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.719682$ ) [*Negrel et al.*, 1993] and the samples of blackwater rivers collected in the permanently flooded swampy central part of the Cuvette Centrale ( $\delta^7\text{Li} \approx 5.7\text{‰}$  and  $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.714\text{--}0.716$ ). High Sr isotope ratios are typical of rivers draining the Archean and Proterozoic rocks constituting the border of the Congo Basin [*de Wit and Linol*, 2015]. By contrast, the low Sr isotope ratios are characteristic of the sedimentary region at the center of the Congo Basin [*Negrel et al.*, 1993; *Guillocheau et al.*, 2015]. One sample significantly deviates from the calculated mixing trend which can be attributed to the natural heterogeneity in terms of Sr isotope ratios of the Congo River tributaries draining the outer parts of the Congo Basin [*Negrel et al.*, 1993] (Figure 3a).

According to the binary mixing model described by equations (2) and (3), the proportion of dissolved Li at Kinshasa derived from the blackwater rivers ranges between 25 and 60% depending on the season. This corresponds to a contribution of organic-rich waters between 20 and 50% ( $[\text{Li}]_L \approx 0.6$  ppb and  $[\text{Li}]_H \approx 0.45$  ppb, equation (3)), depending on the sampling period. Highest contributions of the blackwater rivers from the swampy central depression are found when the water discharge at Kinshasa is the highest (Figures 3 and 2b). Discharge data for the individual tributaries of the Congo River are unfortunately not available. However, *Laraque et al.* [2009] have shown that the mean specific water discharge of the main organic-rich tributaries of the Congo Basin (Likouala aux Herbes, Sangha, and Likouala Mossaka), draining the western part of the Cuvette Centrale is  $12.3 \text{ L/s/km}^2$ . Considering that the permanently flooded swampy areas represent around 10% of the total surface of the Congo Basin and have the same specific discharge as the region investigated by *Laraque et al.* [2009], their average contribution to the total discharge at Kinshasa would not exceed 10%. This first-order mass balance calculation clearly demonstrates that Li supplies from the swampy area alone cannot explain the values of the dissolved  $\delta^7\text{Li}$  of the Congo River at Kinshasa, as the binary mixing model requires

that 20–50% of water at Kinshasa consists of this type of water. This most probably indicates that blackwater river-like low  $\delta^7\text{Li}$  signatures can be generated elsewhere than in the permanently flooded part of the Cuvette Centrale and particularly may extend to the seasonally inundated rain forest areas of the Cuvette Centrale [Mann *et al.*, 2014]. According to our binary mixing model, rivers with blackwater-like signatures have to cover around 30% of the total drainage area of the Congo Basin if the specific discharge of such rivers is similar to that of the Likouala region [Laraque *et al.*, 2009].

In the next section, we discuss the origin of the geochemical signatures of the two end-members required by the hydrologic mixing model. In the following, all concentrations are corrected for atmospheric inputs (see Text S2 for details). For Li isotopes, this correction is minor (Text S2 and Table S2).

#### 4.2. Origin of the Different Li Isotopic Signatures in the Congo River System

Several recent studies have shown that Li isotopes are a powerful proxy for constraining weathering processes at the watershed scale and have established the principles to use Li isotopes in water as an indicator of weathering regimes, i.e., the ratio of chemical weathering flux over total (chemical and physical) erosion flux [e.g., Huh *et al.*, 1998; Pogge von Strandmann and Henderson, 2015; Dellinger *et al.*, 2015]. Chemical weathering is classically described by a simple two-step process: dissolution of source minerals and precipitation of secondary phases that reincorporate poorly soluble (such as Li) and insoluble elements. While Li isotopes are likely not fractionated during mineral dissolution, the formation of secondary weathering products preferentially incorporates the light isotope ( $^6\text{Li}$ ) [e.g., Huh *et al.*, 2001; Millot *et al.*, 2010; Dellinger *et al.*, 2015]. If Li is not totally reincorporated in the new solid phases, the solution is expected to have a  $\delta^7\text{Li}$  value higher than the bedrock and is dependent upon the extent of the Li reprecipitation and the Li isotopic fractionation factor during precipitation. The isotope fractionation associated with secondary mineral formation is quantified by an isotopic fractionation factor,  $\varepsilon_{\text{sec-w}} = \delta^7\text{Li}_{\text{sec}} - \delta^7\text{Li}_w$  where  $\delta^7\text{Li}_w$  and  $\delta^7\text{Li}_{\text{sec}}$  are the Li isotopic signature of the residual dissolved phase and of secondary weathering products, respectively.

The Oubangui River, draining the northwestern periphery of the basin (Figure 1), exhibits the highest dissolved  $\delta^7\text{Li}$  ( $\approx 25\text{‰}$ ) and the lowest molar Li/Na (corrected for atmospheric inputs) of the sample set ( $\approx 1.43 \times 10^{-3}$ ) (Text S2 and Table S2). Relatively high  $\delta^7\text{Li}$  values are also found in similar tropical lateritic settings in the Amazon River Basin [Dellinger *et al.*, 2015] and in volcanic areas (e.g., Açores [Pogge von Strandmann *et al.*, 2010], Martinique [Rad *et al.*, 2013], Réunion, and Java [Henchiri *et al.*, 2014]). High dissolved  $\delta^7\text{Li}$  values associated with low dissolved Li/Na have been interpreted as produced by weathering regimes allowing pedogenetic reincorporation of Li [e.g., Henchiri *et al.*, 2014]. We observe that dissolved  $\delta^7\text{Li}$  measured in rivers draining lateritic regions of the Amazon range between 12 and 16‰ [Dellinger *et al.*, 2015] and are thus significantly lower (by 10‰) than in the Congo Basin. Similarly, low water  $\delta^7\text{Li}$  associated with low Li/Na ratios is also observed in some rivers draining tropical volcanic terrains (for which  $\delta^7\text{Li}$  values can be lower than 20‰, e.g., Martinique [Rad *et al.*, 2013] and Guadeloupe [Clergue *et al.*, 2015]). Lithology may explain part of the variability of dissolved  $\delta^7\text{Li}$ . Indeed, Archean terranes in the Congo Basin are likely to have higher  $\delta^7\text{Li}$  values (see Text S3 and references therein) than the Proterozoic-dominated bedrocks of the Amazon or basaltic and andesitic bedrocks of the volcanic settings [e.g., Burton and Vigier, 2011; Dellinger *et al.*, 2015; Liu and Rudnick, 2011]. Part of the variability between these settings may also be explained by a variation in the extent of Li reincorporation into secondary weathering products and/or with different isotope fractionation factors. The mineralogy of secondary minerals is indeed a function of multiple parameters such as climate, topography, and hydrology.

A more quantitative approach can be attempted. Simple mass balance models are displayed in the supporting information (Text S4 and Figures S1 and S2) for calculating the shift between the solution and the bedrock ( $\Delta\delta^7\text{Li}_{w\text{-bedrock}} = \delta^7\text{Li}_w - \delta^7\text{Li}_{\text{bedrock}}$ ) as a function of the extent of Li precipitation in secondary phases. These models allow us to predict the  $\delta^7\text{Li}$  value of a weathering solution under different assumptions and isotopic fractionation factor. Such a prediction is possible provided that the parent rock  $\delta^7\text{Li}$  is known. Bedrocks surrounding the Congo Basin (and drained by the Oubangui River) are dominated by TTG, mainly of Archean and Proterozoic ages [de Wit and Linol, 2015]. By considering that  $6 \pm 2\text{‰}$  constitutes a reasonable estimation for the  $\delta^7\text{Li}$  value of the TTG bedrock surrounding the Congo Basin (see Text S3 and references therein), we calculate a  $\Delta\delta^7\text{Li}_{w\text{-bedrock}}$  value of  $9 \pm 2\text{‰}$  for the Oubangui River. Arguments developed in Text S4 and Figure S1 and constraints on both the dissolved phase and solid weathering phases show that

$\Delta\delta^7\text{Li}_{\text{w-bedrock}} \approx 19 \pm 2\text{‰}$  can be explained by a distillation fractionation model and an isotopic fractionation factor  $\epsilon_{\text{sec-w}} \approx -20.7\text{‰}$ . The proportion of Li reincorporated into secondary weathering products forming laterite soils, independently estimated from dissolved Li/Na ratio (corrected for atmospheric inputs, Text S2) and bedrock Li/Na (Text S3), is  $60 \pm 10\%$  (see Text S4). A value of  $\epsilon_{\text{sec-w}} \approx -20.7\text{‰}$  is relatively large compared to that found in other large river basins [Dellinger *et al.*, 2015; Bagard *et al.*, 2015] but is in the range of values derived from studies on laterite profiles and small catchments, ranging from  $-28\text{‰}$  (Bidar laterite profile developed upon the Deccan Traps) [Kisakürek *et al.*, 2004] to  $-1\text{‰}$  (Icelandic rivers) [Vigier *et al.*, 2009]. Interestingly,  $\epsilon_{\text{sec-w}} \approx -20.7\text{‰}$  is close to the value of  $\epsilon_{\text{sec-w}}$  between  $\delta^7\text{Li}$  associated with iron oxyhydroxides and  $\delta^7\text{Li}$  in ultrafiltered river water from west Greenland (i.e.,  $-20\text{‰}$ ) [Wimpenny *et al.*, 2010]. Besides, we note that this value is consistent with the  $\epsilon_{\text{sec-w}}$  value ( $-20\text{‰}$ ) used by Wanner *et al.* [2014] in their reactive transport modeling approach for simulating Li isotopic fractionation during pedogenetic processes. Large uncertainties remain on the bedrock Li/Na ratio and  $\delta^7\text{Li}$  but to a first order, the relative enrichment in  $^7\text{Li}$  of the Oubangui waters (end-member with high  $\delta^7\text{Li}$ ) can be reasonably interpreted by the reincorporation of Li into secondary minerals. This result suggests that the lateritic regions covering the borders of the Congo River are still pedogenically active and that secondary weathering products are forming there.

This approach can also be applied to the second end-member, the dilute blackwater rivers from the swampy central depression. In the topographic lows of the Cuvette Centrale, the long residence time of water leads to suboxic conditions that preclude the remineralization of organic matter and favor the formation of humic-rich colored substances. Dupré *et al.* [1996] (in Congo) and Viers *et al.* [1997] (in Cameroon) have shown that African blackwater rivers are Al rich due to the complexation of Al (an insoluble element) by humic and fulvic acids. This in turn leads to very intense chemical weathering expressed through the quasi-congruent dissolution of the bedrock and the absence of secondary mineral formation. We thus expect that in such regions of high weathering intensity, the dissolved  $\delta^7\text{Li}$  will be close to that of the bedrock (or slightly higher if weak but significant reincorporation of Li occurs). The bedrock of the central part of the basin consists of Eocene and Paleocene sedimentary rocks ranging from claystones and silty claystones to grainstones of lacustrine origin (Mbandaka well) [Guillocheau *et al.*, 2015]. Their  $\delta^7\text{Li}$  value is not known, but it can reasonably be predicted to be close to values typical of shales ( $-0.5 \pm 2\text{‰}$ ) [Dellinger *et al.*, 2014]. The molar Li/Na of blackwater rivers, corrected for atmospheric contribution (e.g.,  $9.36 \times 10^{-3}$  for C89-44 Sangha) (Table S2) is relatively high and within the range spanned by molar Li/Na of sedimentary bedrocks ( $5.10^{-3}$  for the weighted average of chemical compositions of arenaceous rock types in central East China [Gao *et al.*, 1998] to  $17.10^{-3}$  for a typical shale [Dellinger *et al.*, 2014]). Despite large uncertainties due to the poor knowledge of the bedrock, isotope fractionation models indicate that the remaining fraction of Li in solution should be between 60 and 90% if we consider an isotopic fractionation factor  $\epsilon_{\text{sec-w}}$  of around  $-20.7\text{‰}$  (see Text S4 and Figures S1 and S2). In the Amazon Basin, blackwater rivers also have low  $\delta^7\text{Li}$  values ranging from 1.3 to 6.5‰ found in the Rio Negro [Dellinger *et al.*, 2015], likely comparable to the end-member inferred from the Congo data, reinforcing our interpretations.

Alternatively, it is possible that the  $\delta^7\text{Li}$  of organic-rich rivers corresponds to a mixture between dissolved Li derived from the congruent dissolution of a clayey and sandy bedrock (low  $\delta^7\text{Li}$ ) with no or little formation of secondary minerals and dissolved Li in waters deriving from surrounding lateritic soils. The latter solute source is characterized by high  $\delta^7\text{Li}$  inherited from Li reincorporation into secondary weathering products and feeds into the flooded area of the Cuvette Centrale.

## 5. Conclusions and Global Implications

The dissolved  $\delta^7\text{Li}$  of the Congo River near its mouth displays a large range of variation (14‰–22‰) over the course of the hydrological cycle. This variability is due to a shifting contribution of blackwater rivers from the central flooded depression to the total water discharge of the basin over the year. Indeed, in this singular area, congruent dissolution of the bedrock, due to poor remineralization of organic matter in soils, minimizes the reincorporation of Li into secondary minerals and leads to bedrock-like dissolved  $\delta^7\text{Li}$  values in blackwater rivers. These compositions are lighter than those of waters washing out from lateritic soils, covering the periphery of the basin, in which a large fraction of Li initially released from the dissolution of the bedrock is sequestered into secondary minerals ( $\approx 60\%$ ) with associated isotope fractionation. These conclusions, based on Li isotopes, are in line with those reached by Cardinal *et al.* [2010] using silicon isotopes.

Our study shows that Li isotopes can be viewed as a conservative tracer in the Congo River system and thus trace mixing processes. Li isotopes are confirmed as powerful tracers to identify chemical weathering processes leading to the signatures of the different mixing sources. As pointed out by *Cardinal et al.* [2010] for silicon isotopes, the  $\delta^7\text{Li}$  exported by the Congo to the Atlantic Ocean could be very sensitive to long-term hydrological variations in the Basin in relation to climate, topography, and ecosystem shifts. In particular, the current global changes could strongly affect the Congo dissolved  $\delta^7\text{Li}$ , and it would be relevant to monitor its changes in order to trace long-term pedogenetic shifts.

Returning to the initial question that motivated this study, we show that rivers draining low-relief continental settings typical of a “supply-limited” weathering regime [Stallard and Edmond, 1983; West et al., 2005] do not have a single and low  $\delta^7\text{Li}$  as assumed in *Misra and Froelich* [2012]. This also agrees with relatively high dissolved  $\delta^7\text{Li}$  inferred in rivers from the Cretaceous where continents were peneplained [Pogge von Strandmann et al., 2013]. At least two contrasting dissolved  $\delta^7\text{Li}$  values are generated in the Congo Basin and, by extension, in other low-relief tropical areas. Therefore, in the geological past, low-relief continents with high weathering intensity (dominated by a supply-limited weathering regime) were not unequivocally able to generate the low  $\delta^7\text{Li}$  in global runoff required to explain the low seawater  $\delta^7\text{Li}$  value observed during the late Paleocene and early Eocene, as suggested by *Froelich and Misra* [2014]. Our findings, together with those of *Dellinger et al.* [2015] on the Amazon River, show that blackwater rivers systematically exhibit low dissolved  $\delta^7\text{Li}$  due to the congruent dissolution of the bedrock in organic-rich environment. Consequently, during the hothouse climate period of the early Eocene, continental surfaces could have been dominated by tropical wetlands like the flooded part of the modern Cuvette Centrale (Sangha and Likouala swamps) drained by organic-rich rivers exhibiting low dissolved  $\delta^7\text{Li}$ .

The reason why large parts of the Cuvette Centrale in the Congo Basin are permanently or temporally flooded is that the uplift of central Africa over the Cenozoic has been faster in the outer parts of the basin than in the central part. The existence of the Likouala and Sangha wetlands where low  $\delta^7\text{Li}$  signatures are generated is thus the consequence of large-scale crustal deformation resulting from a long-term thermotectonic evolution following early Neoproterozoic rifting below the central part of the Congo Basin [Guillocheau et al., 2015]. Our study suggests that lithium isotopes in the ocean have recorded, in addition to climate, the long-term evolution of crustal vertical motions. Taken together with previous results from the Amazon Basin, this study highlights that Li isotopes are a powerful tracer of long-term geodynamic evolution of the continents.

#### Acknowledgments

The authors wish to express their sincere thanks to Pascale Louvat and Julien Moureau for their help with MC-ICPMS measurements. Dissolved elemental concentrations measurements and Sr purification were performed by Caroline Gorge. Alain Laraque, François Guillocheau, Cécile Robin, Eric Gayer, Laurent Longuevergne, Philippe Négrel, and Bernard Dupré are thanked for fruitful discussions. We thank José Wabakanghanzi for assistance with Congo River sampling at Kinshasa. This work has been funded by the French Ministry of Higher Education, Research and the Global Rivers Observatory Program (NSF-ETBC-0851101) and in part by the multidisciplinary program PARI of IGP/region Ile de France (SESAME Grant no. 12015908). Water discharge were collected by the HYBAM observatory (<http://www.ore-hybam.org>). Data are included as two tables in an supporting information file (Tables S1 and S3). The authors thank Philip Pogge von Strandmann and an anonymous reviewer for their constructive reviews. This is IGP contribution 3728.

#### References

- Bagard, M. L., A. J. West, K. Newman, and A. R. Basu (2015), Lithium isotope fractionation in the Ganges–Brahmaputra floodplain and implications for groundwater impact on seawater isotopic composition, *Earth Planet. Sci. Lett.*, *432*, 404–414.
- Berner, R. A., A. C. Lasaga, and R. M. Garrels (1983), The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years, *Am. J. Sci.*, *283*(7), 641–683.
- Bouchez, J., F. Von Blanckenburg, and J. A. Schuessler (2013), Modeling novel stable isotope ratios in the weathering zone, *Am. J. Sci.*, *313*(4), 267–308.
- Burton, K. W., and N. Vigier (2011), Lithium isotopes as tracers in marine and terrestrial environments, in *Handbook of Environmental Isotope Geochemistry*, pp. 41–59, Springer, Berlin Heidelberg.
- Cardinal, D., J. Gaillardet, H. J. Hughes, S. Opfergelt, and L. André (2010), Contrasting silicon isotope signatures in rivers from the Congo Basin and the specific behaviour of organic-rich waters, *Geophys. Res. Lett.*, *37*, L12403, doi:10.1029/2010GL043413.
- Clergue, C., M. Dellinger, H. L. Buss, J. Gaillardet, M. F. Benedetti, and C. Dessert (2015), Influence of atmospheric deposits and secondary minerals on Li isotopes budget in a highly weathered catchment, Guadeloupe (Lesser Antilles), *Chem. Geol.*, *414*, 28–41.
- de Wit, M. J., and B. Linol (2015), Precambrian basement of the Congo Basin and its flanking terrains, in *Geology and Resource Potential of the Congo Basin*, pp. 19–37, Springer, Berlin.
- Dellinger, M., J. Gaillardet, J. Bouchez, D. Calmels, V. Galy, R. G. Hilton, P. Louvat, and C. France-Lanord (2014), Lithium isotopes in large rivers reveal the cannibalistic nature of modern continental weathering and erosion, *Earth Planet. Sci. Lett.*, *401*, 359–372.
- Dellinger, M., J. Gaillardet, J. Bouchez, D. Calmels, P. Louvat, A. Dosseto, C. Gorge, L. Alanoca, and L. Maurice (2015), Riverine Li isotope fractionation in the Amazon River basin controlled by the weathering regimes, *Geochim. Cosmochim. Acta*, *164*, 71–93.
- Dupré, B., J. Gaillardet, D. Rousseau, and C. J. Allègre (1996), Major and trace elements of river-borne material: The Congo Basin, *Geochim. Cosmochim. Acta*, *60*(8), 1301–1321.
- Flesch, G. D., A. R. Anderson, and H. J. Svec (1973), A secondary isotopic standard for  $^6\text{Li}/^7\text{Li}$  determinations, *Int. J. Mass Spectrom. Ion Phys.*, *12*(3), 265–272.
- Froelich, F., and S. Misra (2014), Was the late Paleocene-early Eocene hot because Earth was flat? An ocean lithium isotope view of mountain building, continental weathering, carbon dioxide, and Earth’s Cenozoic climate, *Oceanography*, *27*(1), 36–49.
- Gaillardet, J., B. Dupré, and C. J. Allègre (1995), A global geochemical mass budget applied to the Congo Basin rivers: Erosion rates and continental crust composition, *Geochim. Cosmochim. Acta*, *59*(17), 3469–3485.
- Gao, S., T. C. Luo, B. R. Zhang, H. F. Zhang, Y. W. Han, Z. D. Zhao, and Y. K. Hu (1998), Chemical composition of the continental crust as revealed by studies in East China, *Geochim. Cosmochim. Acta*, *62*(11), 1959–1975.



- Guillocheau, F., R. Chelalou, B. Linol, O. Dauteuil, C. Robin, F. Mvondo, Y. Callec, and J. P. Colin (2015), Cenozoic landscape evolution in and around the Congo Basin: Constraints from sediments and planation surfaces, in *Geology and Resource Potential of the Congo Basin*, pp. 271–313, Springer, Berlin Heidelberg.
- Hathorne, E. C., and R. H. James (2006), Temporal record of lithium in seawater: A tracer for silicate weathering?, *Earth Planet. Sci. Lett.*, *246*(3), 393–406.
- Henchiri, S., C. Clergue, M. Dellinger, J. Gaillardet, P. Louvat, and J. Bouchez (2014), The influence of hydrothermal activity on the Li isotopic signature of rivers draining volcanic areas, *Proc. Earth Planet. Sci.*, *10*, 223–230.
- Huh, Y., L. H. Chan, L. Zhang, and J. M. Edmond (1998), Lithium and its isotopes in major world rivers: Implications for weathering and the oceanic budget, *Geochim. Cosmochim. Acta*, *62*(12), 2039–2051.
- Huh, Y., L. H. Chan, and J. M. Edmond (2001), Lithium isotopes as a probe of weathering processes: Orinoco River, *Earth Planet. Sci. Lett.*, *194*(1), 189–199.
- Kisakürek, B., M. Widdowson, and R. H. James (2004), Behaviour of Li isotopes during continental weathering: The Bidar laterite profile, India, *Chem. Geol.*, *212*(1), 27–44.
- Kisakürek, B., R. H. James, and N. B. Harris (2005), Li and  $\delta^7\text{Li}$  in Himalayan rivers: Proxies for silicate weathering?, *Earth Planet. Sci. Lett.*, *237*(3), 387–401.
- Laraque, A., J. P. Bricquet, A. Pandi, and J. C. Olivry (2009), A review of material transport by the Congo River and its tributaries, *Hydrol. Processes*, *23*(22), 3216–3224.
- Lemarchand, E., F. Chabaux, N. Vigier, R. Millot, and M. C. Pierret (2010), Lithium isotope systematics in a forested granitic catchment (Strengbach, Vosges Mountains, France), *Geochim. Cosmochim. Acta*, *74*(16), 4612–4628.
- Li, G., and A. J. West (2014), Evolution of Cenozoic seawater lithium isotopes: Coupling of global denudation regime and shifting seawater sinks, *Earth Planet. Sci. Lett.*, *401*, 284–293.
- Liu, X. M., and R. L. Rudnick (2011), Constraints on continental crustal mass loss via chemical weathering using lithium and its isotopes, *Proc. Natl. Acad. Sci. U.S.A.*, *108*(52), 20,873–20,880.
- Mann, P. J., et al. (2014), The biogeochemistry of carbon across a gradient of streams and rivers within the Congo Basin, *J. Geophys. Res. Biogeosci.*, *119*, 687–702, doi:10.1002/2013JG002442.
- Meybeck, M. (2003), Global occurrence of major elements in rivers, *Treatise Geochem.*, *5*, 207–223.
- Millot, R., N. Vigier, and J. Gaillardet (2010), Behaviour of lithium and its isotopes during weathering in the Mackenzie Basin, Canada, *Geochim. Cosmochim. Acta*, *74*(14), 3897–3912.
- Misra, S., and P. N. Froelich (2012), Lithium isotope history of Cenozoic seawater: Changes in silicate weathering and reverse weathering, *Science*, *335*(6070), 818–823.
- Moucha, R., and A. M. Forte (2011), Changes in African topography driven by mantle convection, *Nat. Geosci.*, *4*(10), 707–712.
- Negrel, P., C. J. Allègre, B. Dupré, and E. Lewin (1993), Erosion sources determined by inversion of major and trace element ratios and strontium isotopic ratios in river water: The Congo Basin case, *Earth Planet. Sci. Lett.*, *120*(1), 59–76.
- Palmer, M. R., and J. M. Edmond (1992), Controls over the strontium isotope composition of river water, *Geochim. Cosmochim. Acta*, *56*(5), 2099–2111.
- Pogge von Strandmann, P. A. P., K. W. Burton, R. H. James, P. van Calsteren, and S. R. Gislason (2010), Assessing the role of climate on uranium and lithium isotope behaviour in rivers draining a basaltic terrain, *Chem. Geol.*, *270*(1), 227–239.
- Pogge von Strandmann, P. A. P., and G. M. Henderson (2015), The Li isotope response to mountain uplift, *Geology*, *43*(1), 67–70.
- Pogge von Strandmann, P. A. P., H. C. Jenkyns, and R. G. Woodfine (2013), Lithium isotope evidence for enhanced weathering during Oceanic Anoxic Event 2, *Nat. Geosci.*, *6*(8), 668–672.
- Pogge von Strandmann, P. A., K. W. Burton, R. H. James, P. van Calsteren, S. R. Gislason, and F. Mokadem (2006), Riverine behaviour of uranium and lithium isotopes in an actively glaciated basaltic terrain, *Earth Planet. Sci. Lett.*, *251*(1), 134–147.
- Rad, S., K. Rivé, B. Vittecoq, O. Cerdan, and C. J. Allègre (2013), Chemical weathering and erosion rates in the Lesser Antilles: An overview in Guadeloupe, Martinique and Dominica, *J. South Am. Earth Sci.*, *45*, 331–344.
- Spencer, R. G. M., A. Stubbins, and J. Gaillardet (2014), Geochemistry of the Congo River, estuary and plume, in *Biogeochemical Dynamics at Large River-Coastal Interfaces: Linkages With Global Climate Change*, edited by T. S. Bianchi, M. A. Allison, and W.-J. Cai, pp. 554–584, Cambridge Univ. Press.
- Spencer, R. G., et al. (2012), An initial investigation into the organic matter biogeochemistry of the Congo River, *Geochim. Cosmochim. Acta*, *84*, 614–627.
- Stallard, R. F., and J. M. Edmond (1983), Geochemistry of the Amazon: 2. The influence of geology and weathering environment on the dissolved load, *J. Geophys. Res.*, *88*(C14), 9671–9688, doi:10.1029/JC088iC14p09671.
- Torres, M. A., A. J. West, and K. E. Clark (2015), Geomorphic regime modulates hydrologic control of chemical weathering in the Andes–Amazon, *Geochim. Cosmochim. Acta*, *166*, 105–128.
- Viers, J., B. Dupré, M. Polvé, J. Schott, J. L. Dandurand, and J. J. Braun (1997), Chemical weathering in the drainage basin of a tropical watershed (Nsimi-Zoetele site, Cameroon): Comparison between organic-poor and organic-rich waters, *Chem. Geol.*, *140*(3), 181–206.
- Vigier, N., and Y. Godderis (2014), A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations: The key role of climate, *Clim. Past Discuss.*, *10*(4), 3027–3051.
- Vigier, N., S. R. Gislason, K. W. Burton, R. Millot, and F. Mokadem (2009), The relationship between riverine lithium isotope composition and silicate weathering rates in Iceland, *Earth Planet. Sci. Lett.*, *287*(3), 434–441.
- Wang, Q. L., B. Chetelat, Z. Q. Zhao, H. Ding, S. L. Li, B. L. Wang, J. Li, and X. L. Liu (2015), Behavior of lithium isotopes in the Changjiang River system: Sources effects and response to weathering and erosion, *Geochim. Cosmochim. Acta*, *151*, 117–132.
- Wanner, C., E. L. Sonenthal, and X. M. Liu (2014), Seawater  $\delta^7\text{Li}$ : A direct proxy for global  $\text{CO}_2$  consumption by continental silicate weathering?, *Chem. Geol.*, *381*, 154–167.
- West, A. J., A. Galy, and M. Bickle (2005), Tectonic and climatic controls on silicate weathering, *Earth Planet. Sci. Lett.*, *235*(1), 211–228.
- Wimpenny, J., R. H. James, K. W. Burton, A. Gannoun, F. Mokadem, and S. R. Gislason (2010), Glacial effects on weathering processes: New insights from the elemental and lithium isotopic composition of west Greenland rivers, *Earth Planet. Sci. Lett.*, *290*(3), 427–437.