

Accepted Manuscript

Lithium isotope behaviour during weathering in the Ganges alluvial plain

Philip A.E. Pogge von Strandmann, Patrick J. Frings, Melissa J. Murphy

PII: S0016-7037(16)30659-7

DOI: <http://dx.doi.org/10.1016/j.gca.2016.11.017>

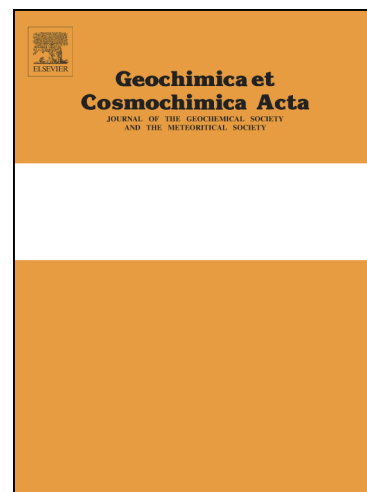
Reference: GCA 10025

To appear in: *Geochimica et Cosmochimica Acta*

Received Date: 17 May 2016

Revised Date: 21 September 2016

Accepted Date: 9 November 2016



Please cite this article as: A.E. Pogge von Strandmann, P., Frings, P.J., Murphy, M.J., Lithium isotope behaviour during weathering in the Ganges alluvial plain, *Geochimica et Cosmochimica Acta* (2016), doi: <http://dx.doi.org/10.1016/j.gca.2016.11.017>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Lithium isotope behaviour during weathering in the Ganges alluvial plain

Philip A.E. Pogge von Strandmann^{1*}, Patrick J. Frings^{2,3}, Melissa J. Murphy⁴

¹London Geochemistry and Isotope centre (LOGIC), Institute of Earth and Planetary Sciences, University College London and Birkbeck, University of London, Gower Street, London, WC1E 6BT, UK.

²Earth Surface Geochemistry, Helmholtz Centre Potsdam, GFZ German Research Centre for Geosciences, Telegraphenberg, 14473 Potsdam, Germany.

³Department of Geoscience, Swedish Museum of Natural History, 10405 Stockholm, Sweden.

⁴Department of Earth Sciences, Oxford University, South Parks Road, Oxford, OX1 3AN, UK.

*Corresponding author: p.strandmann@ucl.ac.uk

Abstract

The Ganges river system is responsible for the transportation of a large flux of dissolved materials derived from Himalayan weathering to the oceans. Silicate weathering-driven cooling resulting from uplift of the Himalayas has been proposed to be a key player in Cenozoic climate variation. This study has analysed Li isotope ($\delta^7\text{Li}$) ratios from over 50 Ganges river waters and sediments, in order to trace silicate weathering processes. Sediments have $\delta^7\text{Li}$ of $\sim 0\text{‰}$, identical to bulk continental crust, however suspended sediment depth profiles do not display variations associated with grain size that have been

observed in other large river systems. Dissolved $\delta^7\text{Li}$ are low ($\sim 11\text{‰}$) in the Ganges headwaters, but reach a constant value of $21 \pm 1.6\text{‰}$ within a relatively short distance downstream, which is then maintained for almost 2000 km to the Ganges mouth. Given that Li isotopes are controlled by the ratio of primary mineral dissolution to secondary mineral formation, this suggests that the Ganges floodplain is at steady-state in terms of these processes for most of its length. Low $\delta^7\text{Li}$ in the mountainous regions suggest silicate weathering is therefore at its most congruent where uplift and fresh silicate exposure rates are high. However, there is no correlation between $\delta^7\text{Li}$ and the silicate weathering rate in these rivers, suggesting that Li isotopes cannot be used as a weathering-rate tracer, although they do inform on weathering congruency and intensity. The close-to-constant $\delta^7\text{Li}$ values for the final 2000 km of Ganges flow also suggest that once the size of the alluvial plain reached more than ~ 500 km (the flow distance after which riverine $\delta^7\text{Li}$ stops varying), the Ganges exerted little influence on the changing Cenozoic seawater $\delta^7\text{Li}$, because riverine $\delta^7\text{Li}$ attained a near steady-state composition.

1.0 Introduction

Chemical weathering of silicate rocks is a significant long-term removal process of atmospheric CO_2 , both through supply of cations and alkalinity for marine carbonate precipitation, and through supply of nutrients for organic carbon burial (Berner, 2003; Berner et al., 1983; Walker et al., 1981; West et al., 2002; West et al., 2005). As such, it has long been postulated as a key long-term climate control and stabilisation mechanism. In the Cenozoic, in particular, it is

questioned whether the observed ~ 40 Myr cooling trend and CO_2 decline were caused by uplift of the Himalayas, which increased the supply of primary material for weathering, which in turn removed more atmospheric CO_2 (Raymo, 1994; Raymo and Ruddiman, 1992; Raymo et al., 1988). The question of whether tectonic processes can strongly affect CO_2 drawdown is critical for understanding the Earth's climate system, because it may suggest that a temperature-driven stabilising feedback on CO_2 via weathering (the Earth's "weathering thermostat") is at times a relatively weak control on climate compared to a supply-driven or organic carbon-driven control (Gíslason et al., 2006; Gíslason et al., 2009; Maher and Chamberlain, 2014; Oelkers et al., 2012; West, 2012).

Evidence for the controls on weathering initially focussed on marine Sr isotope ratios, which started to increase approximately 40 Ma ago (McArthur et al., 2001). This increase was interpreted as a greater input of radiogenic continental material, implying greater weathering and CO_2 drawdown, likely due to Himalayan uplift. However, it has since become clear that the interpretation of the $^{87}\text{Sr}/^{86}\text{Sr}$ curve is not straightforward, because of the effect of metamorphosed radiogenic Himalayan carbonates (Bickle et al., 2005; Galy et al., 1999; Oliver et al., 2003; Palmer and Edmond, 1992). It is therefore not clear how much of the increase in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ is due to weathering of continental silicates, and how much due to metamorphosed carbonates (Galy et al., 1999), the latter of which would not affect atmospheric CO_2 on timescales $> \sim 10,000$ years, and may even be a source of CO_2 , if the dominant source of acidity is sulphuric acid (Torres et al., 2014). Equally, seawater osmium isotopes show a punctuated increase from ~ 60 Ma (Peucker-Ehrenbrink and Ravizza,

2000; Peucker-Ehrenbrink et al., 1995), and here debate has focussed on the control radiogenic black shales in Himalayan lithologies may exert on seawater $^{187}\text{Os}/^{188}\text{Os}$ ratios (Pierson-Wickmann et al., 2002a, b). Hence, both of the above radiogenic isotope systems can at best only provide somewhat ambiguous interpretations as to whether weathering rates, or rock weatherability, increased due to the Himalayas, because of the effect of individual Sr- and Os-rich lithologies.

More recently, lithium isotopes have been used to try to answer this question. Seawater $\delta^7\text{Li}$ appears to have started increasing between 50 and 60 Ma, with behaviour more similar to Os than Sr isotope records (Hathorne and James, 2006; Misra and Froelich, 2012). As a stable isotope system, Li is virtually unaffected by the lithologies undergoing weathering, and is isotopically fractionated by the weathering process. Specifically, Li in rocks is overwhelmingly dominated by the silicate fraction, meaning that Li isotopes are probably the only proxy that solely traces silicate weathering (Kisakürek et al., 2005; Millot et al., 2010). The Li isotope ratio of silicate rocks describes a very narrow range ($\delta^7\text{Li}_{\text{continental crust}} \sim 0.6 \pm 0.6\text{‰}$ (Sauzeat et al., 2015; Teng et al., 2004); $\delta^7\text{Li}_{\text{basalt}} = \sim 3\text{--}5\text{‰}$ (Elliott et al., 2006; Tomascak et al., 2008)), relative to that reported in river waters ($\delta^7\text{Li} = 2\text{--}44\text{‰}$; global mean 23‰ (Bagard et al., 2015; Dellinger et al., 2014; Henchiri et al., 2016; Huh et al., 2001; Huh et al., 1998; Kisakürek et al., 2005; Liu et al., 2015; Millot et al., 2010; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006; Pogge von Strandmann and Henderson, 2015; Rad et al., 2013; Vigier et al., 2009; Wang et al., 2015; Wimpenny et al., 2010b; Witherow et al., 2010)). This high variability in rivers is caused by weathering processes: dissolution of silicates causes no

isotope fractionation, but secondary minerals formed during weathering preferentially take up ^6Li , driving residual waters isotopically heavy (Huh et al., 2001; Pistiner and Henderson, 2003; Pogge von Strandmann et al., 2010; Vigier et al., 2008; Wimpenny et al., 2010a). Therefore, surface water $\delta^7\text{Li}$ is controlled by the ratio of primary mineral dissolution (low $\delta^7\text{Li}$, high $[\text{Li}]$) relative to secondary mineral formation (driving waters to high $\delta^7\text{Li}$, and low $[\text{Li}]$). This ratio has also been described as the weathering congruency (Misra and Froelich, 2012; Pogge von Strandmann et al., 2013), weathering efficiency (Pogge von Strandmann and Henderson, 2015) or weathering intensity (Dellinger et al., 2015; Pogge von Strandmann et al., 2010). When riverine $\delta^7\text{Li} = \text{rock } \delta^7\text{Li}$, then weathering is congruent (water chemistry = rock chemistry), efficient (cations are not retained in clays, but are delivered to the oceans) and low intensity (little clay formation, and a low weathering to denudation ratio – bearing in mind that “weathering intensity” has been defined differently by different authors).

If, as seems likely, the $\sim 9\text{‰}$ increase from early Cenozoic seawater to the present day was controlled by changes in weathering rates or processes, it would imply an increasing relative proportion of secondary mineral formation (Bouchez et al., 2013; Li and West, 2014; Misra and Froelich, 2012; Vigier and Godderis, 2015; Wanner et al., 2014). Initially, this was interpreted as directly due to mountain uplift (Misra and Froelich, 2012). However, High Himalayan rivers tend to have low $\delta^7\text{Li}$ values suggesting little clay formation (Kisakürek et al., 2005), and in general uplifting and denuding terrains tend to have lower $\delta^7\text{Li}$ than flatter terrains, because of the continuous exposure of isotopically light primary rock, and lower rock-water interaction times in the former, and longer water-rock interaction times leading to greater precipitation of secondary

minerals in the low-lying areas (Dellinger et al., 2015; Pogge von Strandmann and Henderson, 2015). This has led to the proposal that the seawater $\delta^7\text{Li}$ curve is charting the evolution of the Himalayan floodplains (or others, such as those of the Andes), rather than the mountain uplift and exposure itself (Pogge von Strandmann and Henderson, 2015). This also agrees with the concept that more CO_2 is drawn down in these floodplains, rather than in the mountains (Lupker et al., 2012; West et al., 2002).

Therefore, studies have begun examining the Ganges-Brahmaputra floodplains to examine weathering and Li behaviour in low-lying floodplain settings. Sample sets taken ~ 10 years apart (in the late 1980s and late 1990s) from Rishikesh in the Ganges headwaters have lower $\delta^7\text{Li}$ than samples taken close to the river mouth (Bagard et al., 2015; Huh et al., 1998). To date, the highest sample resolution is from Bagard et al. (2015), which comprises four samples along the ~ 2500 km of the Ganges, with $\delta^7\text{Li}$ increasing from ~ 10 to 24‰ .

This study has increased this sample resolution by an order of magnitude, with an average sample spacing of ~ 50 km along the Ganges and its tributaries, using samples that have previously been analysed for silicon isotopes (Frings et al., 2015). We have also analysed the Li isotope composition of a series of sediments and suspended load material from various parts of the Ganges plain, which has not previously been attempted in this region. In combination with published data from the High Himalayas, and the above-mentioned low sample-resolution studies, we provide an insight into how the Ganges-Brahmaputra floodplain affects Li isotope signals discharging into the ocean, and

what this tells us about modern floodplain weathering and global weathering signals in the geological past.

2.0 Samples

The study area and samples are described by Frings et al. (2015), and focus on the Ganges Alluvial Plain. Briefly, the Ganges (Fig. 1) drains a basin of $\sim 0.98 \times 10^6 \text{ km}^2$ and has a mean annual discharge in Bangladesh of $\sim 490 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$. The drainage area covers the Himalayas to the north, the hills of the Indian peninsular to the south, and the Ganges Alluvial Plain between them (Fig. 1). 80% of water in the drainage area is provided during the summer monsoon. Sampling occurred at the end of the peak flood, in September 2013, and samples were taken from 51 locations from tributaries around Rishikesh in NW India, at the base of the Himalayas, along the Ganges and tributaries, to Farrakah, which is where the Ganges distributary system begins. A further sample was taken close to Calcutta, along the Hooghly River, which is one of these distributaries draining into the Bay of Bengal. Overall the Ganges Basin has been extensively studied for weathering processes, with a particular emphasis on the Himalayan portion of the system (Bickle et al., 2005; Dalai et al., 2002; Galy and France-Lanord, 1999; Galy et al., 1999; Rai et al., 2010).

3.0 Methods

Samples were collected in 2013 as detailed by Frings et al. (2015). At most locations, water depth was determined with a ballasted sounding line, and 5 litres of water collected at the surface, at maximum depth, and at the centre point using a horizontal van Dorn style water sampler. This was filtered at 0.4

μm within a few hours using a Teflon-coated pressure filtration system. The filters were retained, freeze-dried and the sediment gently removed from the filter.

Anion concentrations were measured by ion chromatography at the Department of Biology, Lund University, while major and minor cations, including Li, were measured by ICP-OES and ICP-MS, respectively, at University College London. The precision of these measurements is $<\pm 5\%$ (Frings et al., 2015). Sediments and rock standards were dissolved in steps of HF-HNO₃, followed by HNO₃ and HCl.

For Li isotope analysis, sufficient sample was dried down to attain $\sim 20\text{ng}$ of Li, and passed through a two-step cation exchange chromatography (AG50W X-12), using dilute HCl as an eluent. Isotopic analyses were conducted on a Nu Instruments HR multi-collector ICP-MS, relative to the standard L-SVEC (Flesch et al., 1973), at the Department of Earth Sciences, Oxford University. The exact methods for chemistry and analysis are detailed elsewhere (Pogge von Strandmann et al., 2011; Pogge von Strandmann and Henderson, 2015; Pogge von Strandmann et al., 2013). Seawater was run as an “unknown” standard, yielding $\delta^7\text{Li} = 31.3 \pm 0.6\text{‰}$ (2sd, $n=48$, column passes=48) over a three-year period. Two rock standards were also run, granite JG-2 ($\delta^7\text{Li} = 0.4 \pm 0.2\text{‰}$, $n=3$) and Wyoming oil shale SGR-1b ($\delta^7\text{Li} = 3.6 \pm 0.4\text{‰}$, $n=3$), where results are within uncertainty of other published values (Jeffcoate et al., 2004; Phan et al., 2016; Vigier et al., 2008; Wunder et al., 2006). The total procedural blank of this method was effectively undetectable ($<0.005\text{ng Li}$), which is insignificant relative to the 10–20 ng of Li analysed in each sample.

4.0 Results

Overall, the sampled rivers exhibit a standard positive trend between Ca/Na and Mg/Na (not shown), and exhibit a broadly similar range to that displayed by global rivers (Gaillardet et al., 1999b). Most samples are closer to the lower, silicate, end-member.

Lithium concentrations in the river waters vary between 0.4 and 11.7 ng/ml (Table 1). This is a similar range to other large multi-lithology rivers systems that have been studied, such as the Mackenzie River (Millot et al., 2010) and the Amazon (Dellinger et al., 2015). Highest [Li] in these river samples are in the Yamuna River, but concentrations decrease in the Yamuna before it joins the Ganges, and therefore at the confluence of the two rivers, [Li] in both is broadly similar. Lowest [Li] occurs in the Ganges at the base of the Himalayas, and also in all rivers within ~1000km of the river mouth, within the lower reaches of the alluvial plain (Fig. 2a).

Li isotope ratios range between 10.7 and 24.8‰, with the bulk of the data clustered in a relatively narrow band between 19 and 22‰. This is a narrower range than the Mackenzie and Amazon river systems overall (9–29‰ and 1.2–33‰, respectively), but greater than the Mackenzie lowland regions (10–17‰) (Dellinger et al., 2015; Millot et al., 2010). The Ganges itself has the lowest $\delta^7\text{Li}$ in the Himalayan foothills (10.7–12.9‰; Fig. 2b). At a similar distance upstream, the Yamuna has a much higher $\delta^7\text{Li}$ (18–22‰), highlighting the difference between alluvial plain and foothills weathering. From ~2000km upstream of the river mouth, $\delta^7\text{Li}$ values are fairly constant at $\delta^7\text{Li} = 21 \pm 1.6\text{‰}$. Thus, rivers wholly draining the alluvial plain have virtually identical $\delta^7\text{Li}$ to the downstream Ganges. Unlike data reported from the Congo (Henchiri et al., 2016), Li data from

the Ganges do not appear represent simple two-endmember mixing, but imply isotope fractionation processes occurring during weathering (Section 5.1).

River sediment Li isotope ratios range from -2.6 to 2.9‰, with an average $\delta^7\text{Li}$ of $-0.3 \pm 1.3\text{‰}$ (Table 2), which is within uncertainty of the value of the upper continental crust (Sauzeat et al., 2015; Teng et al., 2004), although they exhibit a larger range than values of -1.02 to +0.39‰ reported from a single location close to the mouth of the Ganges (Dellinger et al., 2014). Given that rivers such as the Amazon have displayed depth-trends in Li isotope composition, with decreasing $\delta^7\text{Li}$ values with increasing grain size (Dellinger et al., 2014), this study analysed $\delta^7\text{Li}$ values from sediments at different depths in several locations, as well as from a bank deposit. No trend with depth exists in these rivers, implying that the suspended load is better mixed, or has a more consistent mineralogy, than in the Amazon. Overall the 4.5‰ range in sediment isotope ratios over ~2000 km of river flow (Fig. 3) is similar to the 5‰ range in the Mackenzie River basin (Milot et al., 2010), but smaller than the 9‰ range reported from the Amazon (Dellinger et al., 2014).

5.0 Discussion

Lithium isotopes provide information on the balance of silicate rock dissolution to secondary mineral formation, described as the weathering congruency, or the weathering intensity. It is important to note that different studies define “weathering intensity” in different ways, such that high weathering intensity has been considered as high primary rock dissolution and low dissolved $\delta^7\text{Li}$ (Kisakürek et al., 2005; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2013), while in other studies it is considered as

high secondary mineral formation and high dissolved $\delta^7\text{Li}$ (Dellinger et al., 2015).

In this study we adopt the terminology of Dellinger et al., 2015, while noting that yet other definitions are also available (Millot et al., 2010). All of these studies however agree that high secondary mineral formation relative to primary mineral dissolution drives dissolved $\delta^7\text{Li}$ high.

5.1 Comparison of lithium isotopes to river chemistry

It has been demonstrated that Li isotopes are not affected by dissolution of carbonates, both in the High Himalayas (Kisakürek et al., 2005) and in the Mackenzie catchments (Millot et al., 2010), but are solely controlled by silicate weathering. Mixing relationships (e.g. between Ca/Na and Li/Ca) that were used in those studies to show this are not as apparent in the Ganges, possibly because secondary processes are affecting both [Ca] (e.g. plant growth/decay) and [Li] (e.g. secondary mineral destabilisation), as well as effects by the dissolution of evaporites on Na and possibly Li (Galy and France-Lanord, 1999; Rai et al., 2010). Nevertheless, it is clear that riverine $\delta^7\text{Li}$ values are not being controlled by carbonate weathering, because samples with highest Ca/Na have low $\delta^7\text{Li}$, while carbonates tend to have isotopically heavy, seawater-like, values (Lechler et al., 2015; Marriott et al., 2004; Pogge von Strandmann et al., 2013).

In a number of river studies, Li/Na ratios have been reported to have similar behaviour to Li isotope ratios, and the former has been inferred as a tracer of water-rock interaction time (Dellinger et al., 2015; Liu et al., 2015; Millot et al., 2010). This is because Na is thought to be significantly more mobile than Li during weathering, and, generally, little Na is incorporated into secondary minerals compared to Li. Waters with lowest $\delta^7\text{Li}$ have highest Li/Na,

defining a negative co-variation and thus agreeing with the trend shown in other studies (Bagard et al., 2015; Dellinger et al., 2015; Liu et al., 2015; Millot et al., 2010). However, in these Ganges waters, there is significant variation (over an order of magnitude) in Li/Na for a virtually constant $\delta^7\text{Li}$ (Fig. 4). This suggests a degree of decoupling between [Li] and $\delta^7\text{Li}$ in these waters, which is also observed in the lack of direct co-variation between these two parameters. Interestingly, data from the High Himalayas (Kisakürek et al., 2005) exhibit a similar pattern (Fig. 4), with relatively constant $\delta^7\text{Li}$ for a high variation in Li/Na (~ 0.0001 to 0.001). Although the data are sparser, the same could be argued for the Ganges-Brahmaputra study of Bagard et al. (2015).

Overall, some of the data from global rivers show a logarithmic relationship between $\delta^7\text{Li}$ and Li/Na, apparently consistent with kinetic fractionation, and possible to simulate with a Rayleigh equation. Given that much of river weathering is an open system, riverine behaviour should not be able to be attributed to closed-system Rayleigh behaviour, and we also examine equilibrium fractionation processes. To assess Rayleigh fractionation factors we use a standard approach used by a number of studies (Bagard et al., 2015; Dellinger et al., 2015; Pogge von Strandmann et al., 2012), but in this case we use an average continental crust $\delta^7\text{Li}$ of 0‰ as the initial composition, assuming entirely congruent weathering. There is significant scatter, most likely due to lithology effects on Li/Na ratios (for example, due to a range of initial Li/Na compositions or due to the formation of Na-bearing secondary minerals, such as zeolites (e.g. analcime, chabazite, phillipsite, etc.), or smectites such as Na-montmorillonite), and similar effects on $\delta^7\text{Li}$, because primary lithology will determine secondary mineralogy, which will affect Li isotope fractionation

factors (Millet and Girard, 2007; Pistiner and Henderson, 2003; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006; Vigier et al., 2008; Williams and Hervig, 2005). It is possible that in rivers draining multiple lithologies, though, less concentrated terrains (such as basaltic ones) do not contribute enough Li to affect fractionation. For example, the Chambal tributaries to the Yamuna have similar $\delta^7\text{Li}$ and [Li] values, despite also draining basalts (Lupker et al., 2012). However, a best-fit Li isotope Rayleigh fractionation factor for global data (Fig. 4) is $\alpha \sim 0.995$ ($\Delta^7\text{Li} = -5\text{‰}$), as also suggested for the Ganges-Brahmaputra (Bagard et al., 2015). Maximum and minimum fractionation factors, which incorporate the totality of the data (excluding Amazonian samples that are controlled by secondary mineral re-dissolution (Dellinger et al., 2015)) are $\alpha = 0.985$ ($\Delta^7\text{Li} = -15\text{‰}$) and $\alpha = 0.9975$ ($\Delta^7\text{Li} = -2.5\text{‰}$). As mentioned above, it is notable that almost all of the High Himalayan data (Kisakürek et al., 2005) and the Ganges data from this study plot above the median $\alpha = 0.995$ line. This study's Ganges samples are encompassed by fractionation factors of 0.9955 – 0.985, although when precipitation corrected Li/Na* ratios are used (using the correction detailed by Frings et al., 2015, using the methods of other Ganges studies (Bickle et al., 2005; Dalai et al., 2002; Galy and France-Lanord, 1999; Galy et al., 1999; Rai et al., 2010)), this changes slightly to 0.995–0.98, with a median fractionation factor of 0.988 ($\Delta^7\text{Li} = -13\text{‰}$). Other large rivers like the Amazon also plot above the 0.995 line, where their starting compositions are similar to those of the Ganges (Dellinger et al., 2014).

Generally, sediments from these rivers exhibit a similar range in Li/Na to each other and to global shales (Fig. 4). In contrast, rivers that drain basaltic terrains (Iceland, Azores, Columbia River Basalts (Liu et al., 2015; Pogge von Strandmann

et al., 2010; Pogge von Strandmann et al., 2006) do have a significantly different starting Li/Na (Fig. 4), although the effect of using a basaltic starting $\delta^7\text{Li}$ composition of 3–5‰ higher than the continental crust is relatively minor.

Whereas basaltic data follow a Rayleigh relationship (Fig. 4), this study's Ganges data appear to be closer to an equilibrium (batch) relationship (dashed lines in Fig. 4), mostly plotting between fractionation factors of 0.97–0.98. Such a relationship implies that the Ganges reaches a steady-state between primary rock dissolution and secondary mineral formation (this is discussed in more detail in Section 5.2), whereas the supply-rich (i.e. kinetically-limited) basaltic terrains and High Himalayas do not.

Generally, then, weathering of large continental crust floodplains such as that of the Ganges appears to cause an equilibrium-style relationship, requiring higher Li isotope fractionation factors than basaltic terrains. This is likely due to the different types of secondary mineral that form in different weathering environments. For example, kaolinites, which tend to be associated with weathering of intermediate to felsic continental crust rather than basalt, are thought to impart relatively high Li isotope fractionation factors (Millot and Girard, 2007; Pistiner and Henderson, 2003). There therefore appears to be some degree of lithological control over Li isotope ratios in rivers in general, because the primary lithology will control secondary mineralogy, and hence the fractionation factors it imposes (Pogge von Strandmann et al., 2010; Wang et al., 2015). This means, for example, that the interpretation of Li isotopes as a palaeo-weathering proxy (Hathorne and James, 2006; Lechler et al., 2015; Misra and Froelich, 2012; Pogge von Strandmann et al., 2013; Ullmann et al., 2013) requires

some knowledge of the weathered lithology to make quantitative interpretations about the weathering fluxes.

Using the median fractionation factors described above for the Ganges, the same distillation relationships can be used to describe the fraction of Li in solution, relative to that in the solid phase (Frings et al., 2015; Millot et al., 2010; Pogge von Strandmann et al., 2012; Vigier et al., 2009). Hence, if the $\delta^7\text{Li}$ of a river were 0‰, identical to the source rocks, 100% of Li would be in solution. For Rayleigh fractionation (median $\alpha = 0.988$), on average 19% of Li is in solution (2–37% for the full range of α), while this number is 20% for equilibrium fractionation (median $\alpha = 0.975$). Frings et al. (2015) determined catchment areas and estimated river fluxes to give the yield of major elements. For Si, they then divided this yield by the fraction of Si in solution, determined from Si isotope ratios using a Rayleigh relationship, to give the initial Si mobilisation rate, independent of secondary mineral formation. This determined that ~75% of Si mobilisation in the Ganges occurs outside the Himalayas, in the alluvial plain and peninsular rivers.

Here, we perform the same type of calculation for Li, which shows that around 63% of initial Li mobilisation (total ~12 Gmol/yr Li if Rayleigh, ~1.1 Gmol/yr if equilibrium) occurs outside the Himalayas. This percentage is highly insensitive to the fractionation factor used (the entire range in α for these Ganges samples changes this percentage by 0.6%). This therefore shows that greater silicate weathering occurs away from the mountain areas, which agrees with estimates based on bulk chemistry (West et al., 2002), and Li isotope studies from New Zealand (Pogge von Strandmann and Henderson, 2015), as well as reactive-flow modelling (Bouchez et al., 2013). However, there is a

difference in the estimates based on Si isotopes (~25% of initial Si is from the Himalayas (Frings et al., 2015)), with those based on Li isotopes (~38% of initial Li is from the Himalayas, where the isotopic analytical uncertainty does not resolvably affect the final calculations). No analyses are available of Li concentrations of a broad range of sediments of the Ganges floodplain, and therefore approximate Ca or Mg fluxes based on Li isotopes cannot be calculated. The difference between Li and Si isotopes as a tracer is discussed below, but it is probable that the difference in estimates is due to different mobilities in the weathering environment. While Li and Si are similarly mobile during basalt weathering (Pogge von Strandmann et al., 2016), the complex environment of floodplains such as that of the Ganges, and the general lack of Li concentration analyses, means that such estimates are not possible yet for these terrains. In addition, some degree of control by biology over Si isotopes and concentrations is likely - in particular, due to the intensive agriculture of the Ganges alluvial plain. In contrast, Li isotopes are unlikely to be directly affected by enhanced plant growth (Clergue et al., 2015; Lemarchand et al., 2010; Pogge von Strandmann et al., 2016), and fertilisers in the High Himalayan region are thought to have higher $\delta^7\text{Li}$ than any samples observed here (Kisakürek et al., 2005).

5.2 Comparison of lithium isotopes to physical parameters

The samples furthest up the Ganges and its catchment were taken above the town of Rishikesh, almost 2500 km from the river mouth, and located in the Himalayan foothills. Lithium concentrations are relatively low here (2–3 ng/ml), but increase sharply several hundred km downstream (Fig. 2a), apparently when

highly concentrated tributaries from the north (with up to ~ 12 ng/ml Li) merge with the Ganges. One of the largest tributaries, the Yamuna River, also has relatively high [Li], and this also appears to serve to keep the Ganges [Li] high. After the confluence of the Yamuna with the Ganges ~ 1500 km above the river mouth, Li concentrations start to decline, and after the Ganges enters the southern alluvial plain, [Li] is lower than in the Himalayan foothills. This decline in concentration again appears to be driven by the tributaries in the alluvial plain, which have low Li concentrations. Enhanced secondary mineral formation is unlikely to be causing this concentration decline, because Li isotope ratios are not being changed by whatever process is causing the concentration decrease. The change in [Li] is more likely a result of dilution by precipitation-sourced waters, as other elemental concentrations are also affected. However, dissolved [Li] does not directly co-vary with discharge values, although it must be noted that these are literature compilations rather than direct snapshot values (Frings et al., 2015; Jain et al., 2007). There is a co-variation between discharge and [Li] in the final ~ 400 km, but not before (Fig. 5), suggesting that dilution is not a big effect on Li concentrations aside from this final part of the Ganges (and that $\delta^7\text{Li}$ is not affected by this dilution). Such a relationship is opposite to that reported from the Congo (Henchiri et al., 2016).

In contrast, Li isotope ratios exhibit their largest variation in the headwaters of the Ganges. Including this study, the river at Rishikesh has been sampled for Li isotopes approximately every decade for the last 30 years (Bagard et al., 2015; Huh et al., 1998), and has had uniformly low $\delta^7\text{Li}$ values of ~ 10 – 13 ‰. In comparison, samples taken 1500–2000 km further downstream by all three studies are consistently isotopically heavier, with $\delta^7\text{Li} \sim 20$ – 23 ‰.

Figure 6a summarises all Li isotope studies of rivers associated with the Ganges as a function of distance from the Main Frontal Thrust (MFT), which delineates the uplifting areas from the floodplain (Huang et al., 2015). Data from the High Himalayas (Kisakurek et al., 2005), which eventually drain into the Ganges, generally have lower $\delta^7\text{Li}$ than the Ganges mainstream. In these data, rivers with lower [Li] have higher $\delta^7\text{Li}$, so that High Himalayan rivers with high $\delta^7\text{Li}$ have little overall influence on the composition of waters downstream. The general relationship with distance clearly shows that only relatively low $\delta^7\text{Li}$ values are from the Himalayan foothills or mountains. Interestingly, the three studies of the Ganges mainstream were sampled at different time periods, i.e. those of Bagard et al. (2015) represent a low flow period, while this study represents the end of peak flooding. Nevertheless, samples from the same location are similar, implying that hydrological regime does not resolvably affect Li behaviour.

After a distance of ~ 500 km of flow, $\delta^7\text{Li}$ values are relatively constant, and both the Ganges and its tributaries are close to the global riverine mean of $\sim 23\text{‰}$ (Huh et al., 1998). Such constant $\delta^7\text{Li}$ values for such a long distance imply a balance between mineral dissolution and precipitation, as would be thought to characterise a floodplain at steady-state, i.e. one that maintains an approximately constant level of weathering intensity. Our data suggest that the Ganges floodplain is broadly in steady-state for $\sim 80\%$ of its flow length, from the area of Kanpur to the river mouth (Fig. 1 & 2b), and that weathering is only out of balance in the foothills regions of the studied area.

Pogge von Strandmann and Henderson (2015) and Dellinger et al. (2015) have both showed that Li isotope ratios in rivers tend to be driven lower in regions of higher uplift and therefore higher denudation and exposure rates,

because more fresh primary rock is being made available for dissolution, relative to the formation of secondary minerals. In contrast, in flatter regions where uplift and exposure are low (i.e. floodplains), secondary mineral formation becomes relatively greater, and riverine $\delta^7\text{Li}$ values increase. These studies are also backed up by the observation that rivers in the High Himalayas generally have $\delta^7\text{Li}$ values lower than the global mean (Huh et al., 1998; Kisakürek et al., 2005), or indeed lower than values in rivers on the floodplain at the same distance from the river mouth, as shown by comparing the floodplain-based Yamuna and the foothills-sourced Ganges Rivers (Fig. 2b).

While uplift rates are not available for these samples, in the Himalayan region, altitude is an approximate facsimile to exposure. Figure 6b shows a literature compilation of Li isotopes in the Ganges-Brahmaputra catchment area, and there is a broad co-variation where lower altitude corresponds to higher dissolved $\delta^7\text{Li}$. There is considerable variation in the High Himalayas (Kisakürek et al., 2005), which may be because very small streams are also represented in that study, but as described above, rivers with lower $\delta^7\text{Li}$ will have the greater influence on riverine signals downstream. Overall, however, it is probable that the low $\delta^7\text{Li}$ values observed in the Ganges headwaters are due to relatively greater primary rock exposure and dissolution (more congruent silicate weathering), while the increase in $\delta^7\text{Li}$ further downstream is due to increasing secondary mineral formation (more incongruent silicate weathering), due to increased water-rock interaction times (reaction kinetics) driving a greater degree of secondary mineral oversaturation and precipitation (reaction thermodynamics).

5.3 Li isotopes as a proxy for silicate weathering rates

While Li isotopes are generally thought to be an excellent tracer of silicate weathering congruency or intensity, a number of studies have also found correlations between riverine $\delta^7\text{Li}$ and the silicate weathering rate. In particular, negative co-variations have been reported from Iceland (Vigier et al., 2009) and the Mackenzie River basin (Millot et al., 2010) (the Mackenzie River accounts for ~2% of global riverine discharge (Huh et al., 1998)). Some interpretations of palaeo $\delta^7\text{Li}$ data have been based on these two published negative relationships, and the assumption that clays and the dissolved load co-behave (Dosseto et al., 2015). Overall, however, it seems highly unlikely that $\delta^7\text{Li}$ can be used as a weathering rate tracer, unless the weathering system is extremely simple, and the secondary mineral formation rate and fractionation factor stays constant, while the primary mineral dissolution rate is then solely a function of the weathering rate.

In the case of these Ganges data, silicate weathering rates were calculated from the discharge rates, precipitation-corrected major element data and catchment areas calculated by Frings et al. (2015), using the methods demonstrated by numerous other studies, by correcting for silicate and evaporate components (Dalai et al., 2002; Gaillardet et al., 1999a; Galy and France-Lanord, 1999; Rai et al., 2010). As shown in Figure 7, there is no relationship between silicate weathering rate and $\delta^7\text{Li}$ for these samples ($r^2 = 0.01$). In other words, for one of the Earth's major rivers, that supplies ~3% of the global riverine Li flux (Huh et al., 1998), dissolved Li isotopes are not a tracer of the silicate weathering rate. Figure 7 also shows data from globally significant

rivers responsible for ~30% of the global riverine discharge (Huh et al., 1998), which similarly exhibit no relationship between $\delta^7\text{Li}$ and weathering rate.

Hence, while some river systems show co-variations between these two factors, overall it is clear that Li isotopes cannot be used as a weathering rate-tracer, and therefore modelling must be used to determine any useful weathering fluxes from riverine or seawater records (Bouchez et al., 2013; Lechler et al., 2015; Li and West, 2014; Pogge von Strandmann et al., 2013; Pogge von Strandmann et al., 2014; Vigier and Godderis, 2015; Wanner et al., 2014).

5.4 Comparison between Li and Si isotopes

Silicon isotope ratios have also been determined for these samples (Frings et al., 2015). In theory, $\delta^{30}\text{Si}$ behaves similarly to $\delta^7\text{Li}$, in that both systems are used as silicate weathering tracers, where secondary minerals preferentially take up light isotopes, driving river waters and seawater to isotopically heavy values (De la Rocha et al., 2000; Georg et al., 2006; Georg et al., 2007; Opfergelt et al., 2013; Opfergelt et al., 2009; Ziegler et al., 2005). In addition, for Si isotopes, primary productivity (e.g. diatoms) and plant growth exert an influence, and preferentially take up light isotopes (Opfergelt et al., 2006). The Ganges's $\delta^{30}\text{Si}$ values have been interpreted similarly to Li isotopes by Frings et al. (2015), i.e. controlled by silicate weathering congruency, with additional, indistinguishable, effects from plants or other biological processes, and have been used to determine silicate weathering fluxes (Frings et al., 2015). It therefore makes sense to compare these two tracers, given their behavioural similarity, but also their differences, as Si is a major structural element of both

primary silicate rocks and many secondary minerals, while Li is only a trace element.

Overall, then, there is a positive co-variation between $\delta^7\text{Li}$ and $\delta^{30}\text{Si}$ (Fig. 8). This trend is pinned by the Ganges mainstream, which exhibits a good correlation ($r^2 = 0.78$). Himalayan headwaters are isotopically light (congruent weathering) for both systems. However, the Ganges tributaries show much greater relative variability for Si isotopes than for Li isotopes. Thus, while the Ganges mainstream makes up 80% of the total $\delta^7\text{Li}$ variation observed, it only makes up 50% of the $\delta^{30}\text{Si}$ variability. This difference is likely due to differing fractionation caused to both systems by secondary minerals, because Si is a major structural component of many minerals, while Li is a trace element (Pogge von Strandmann et al., 2012). However, this does not necessarily explain relatively constant $\delta^7\text{Li}$ in samples with variable $\delta^{30}\text{Si}$, because a given secondary mineral should impose a set fractionation on both Li and Si isotopes. Differences in reaction kinetics may therefore be a primary control of the difference in isotope fractionation. Si may require more time to be incorporated into neoformed minerals, while Li is at least partially controlled by sorption (Millot and Girard, 2007; Pistiner and Henderson, 2003; Pogge von Strandmann et al., 2016; Pogge von Strandmann et al., 2012). Alternatively, Si isotopes are affected by plant and/or diatom growth, which may be imposing additional, and potentially quite spatially variable, fractionation (Opfergelt et al., 2006; Opfergelt et al., 2011), and therefore the $\delta^{30}\text{Si}$ variability beyond that which correlates with Li isotopes could be a biologically-induced effect. Hence, the Ganges system, with its longer water flow time in the alluvial plain compared to most rivers studied for Li isotopes, would be expected to approach a state where both Li and Si

isotopes reach a degree of steady-state. In addition, a co-variation has also been reported from plant- and organic-poor waters from Iceland (Fig. 8), suggesting that in systems where biological fractionation of Si isotopes is low, Li and Si isotopes will behave similarly (Opfergelt et al., 2013), because Li isotopes are unaffected by plants (Lemarchand et al., 2010; Pogge von Strandmann et al., 2016).

5.5 Global implications of the Ganges Li chemistry

It is clear from the comparison of Li and Si isotopes that silicate weathering is more congruent (less intense) in the Himalayan foothills of the Ganges than it is in the alluvial plain. It has equally been shown that on average High Himalayan catchments are even more congruent (Fontorbe et al., 2013; Kisakürek et al., 2005). This behaviour makes it abundantly clear that dominant secondary mineral formation, and hence isotope fractionation, occurs in the floodplains. This evidence is substantiated by both mineralogical analyses that suggest that authigenic clays only become dominant in alluvial plains (Chakrapani et al., 1995), and by other estimates of weathering by solute mass balance (Galy and France-Lanord, 1999; Lupker et al., 2012; West et al., 2002), which also suggest that the primary locus of CO₂ drawdown through silicate weathering is in floodplains rather than steep slopes.

Overall, an increase in Himalayan denudation, delivered to the oceans by the Ganges-Brahmaputra river system, has been argued to be the (or a) cause of increases in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{187}\text{Os}/^{188}\text{Os}$ (Bickle et al., 2005; Galy et al., 1999; Oliver et al., 2003; Pierson-Wickmann et al., 2002a, b; Sharma et al., 1999). The increase in Cenozoic seawater $\delta^7\text{Li}$ (Hathorne and James, 2006; Misra and

Froelich, 2012) has also been interpreted as due to increased Himalayan weathering (Froelich and Misra, 2014). More recently, data from other uplift and exposure sites have suggested that mountain regions themselves are only the drivers of physical erosion, and that the Li isotope fractionation occurs in the floodplains (Dellinger et al., 2015; Pogge von Strandmann and Henderson, 2015).

Interestingly, the Ganges controls the Li flux to the oceans to a similar extent as it does the Sr or Os fluxes, despite the latter two systems also having carbonate sources. The Ganges provides ~3% of the total riverine supply of Li to the oceans (compared to 2% of Os (Levasseur et al., 1999) and ~3% of Sr (Krishnaswami et al., 1992)), and the whole Ganges-Brahmaputra system ~7% (Huh et al., 1998), with another estimated 2% of the total flux provided by groundwater flow into the Bengal Basin (Bagard et al., 2015). Combined, the three main mountain-sourced river systems with floodplains that greatly increased in size during the Cenozoic (Ganges-Brahmaputra, Amazon and Orinoco) provide almost 16% of the modern global Li flux from rivers to the oceans, compared to an estimated ~20% for Sr (Raymo et al., 1988). The three rivers mentioned above would have to increase their mean $\delta^7\text{Li}$ by 30–40‰ to drive the observed seawater change at equilibrium, with no change in flux, which is extremely unlikely, given observations of modern rivers. Even the evolution of their floodplains (Pogge von Strandmann and Henderson, 2015) is unlikely to be responsible for the entire change in seawater $\delta^7\text{Li}$. Hence, the relationship between continental weathering changes and seawater $\delta^7\text{Li}$ is not straightforward, and other Cenozoic changes, such as a “sink-shift” (Li and West, 2014) or temperature-dependent changes in deep-ocean fractionation factors

(Coogan and Dosso, 2015), may have to be invoked in combination with a weathering change.

The other inference that can be made from these Ganges data for the Cenozoic evolution of seawater $\delta^7\text{Li}$ is that it appears that growth of the Ganges floodplain beyond $\sim 500\text{km}$ from the Himalayan foothills would no longer change seawater $\delta^7\text{Li}$, as evidenced by the near constant riverine $\delta^7\text{Li}$ values. Beyond this point, under present climatic conditions, the floodplain is in approximate steady-state for Li isotopes (and also for Si isotopes (Frings et al., 2015)). A similar observation can be made for the Amazon, where most fractionation occurs close to the foothills, and then remains constant across the floodplain (Dellinger et al., 2015). If present-day measurements can be used as an analogy for general Cenozoic behaviour (as used for Sr isotopes (Galy et al., 1999)), then the final 2000 km of Ganges flow creates no change in $\delta^7\text{Li}$, and the evolution of the floodplain beyond $\sim 500\text{km}$ will not create further change in seawater $\delta^7\text{Li}$ once this has reached equilibrium with regards to input.

6.0 Conclusions

This study has analysed Li isotopes from over 50 samples of the Ganges river and its tributaries, representing over an order of magnitude increase in sampling density compared to previous studies. Lithium isotope ratios are fairly constant for the lower $\sim 2000\text{ km}$ of flow of the Ganges, and $\delta^7\text{Li}$ only decreases at the head of the river in the Himalayan foothills. Silicate weathering is therefore at its most congruent in mountainous regions where uplift and fresh silicate exposure rates are high. These data were used to calculate a Li yield from primary rock, indicating that over 63% of Ganges Li stems from the floodplains,

rather than the mountainous regions. This observation agrees with those made from bulk river chemistry, as well as Si isotopes, although the precise fraction of Li and Si coming from the Himalayas appears to be different, based on their individual isotope systems, likely due to a combination of secondary mineral reaction kinetics, and the influence of biology over Si.

Overall, despite some publications using Li isotopes as a tracer for the silicate weathering rate, there is no correlation whatsoever between Ganges $\delta^7\text{Li}$ and silicate weathering rates. The lack of such a correlation in one of the Earth's major rivers strongly indicates that $\delta^7\text{Li}$ also cannot be used as a direct palaeo-weathering rate tracer.

Finally, the Li isotope data (which are controlled by the ratio of primary mineral dissolution relative to secondary mineral formation) suggest that the Ganges floodplains are broadly at steady-state, with dissolution and transport in equilibrium. The close-to-constant $\delta^7\text{Li}$ values for the final 2000km of Ganges flow also suggest that once the size of the alluvial plain reached more than ~500 km under present climatic conditions, the Ganges exerted little influence on the changing Cenozoic seawater $\delta^7\text{Li}$.

Acknowledgements

Analyses were supported by PPvS's NERC Advanced Research Fellowship NE/I020571/2. We thank Wim Clymans for help with fieldwork, Chakrapani Govind for logistical support and Will Gray for assistance with ICP-OES/MS analysis. We thank Paul Tomascak, Maarten Lupker and an anonymous reviewer for their insightful comments.

- Bagard, M.-L., West, A.J., Newman, K. and Basu, A.K. (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. (2003) The long-term carbon cycle, fossil fuels and atmospheric composition. *Nature* 426, 323–326,
- Berner, R.A., Lasaga, A.C. and Garrels, R.M. (1983) The Carbonate-Silicate Geochemical Cycle and Its Effect on Atmospheric Carbon-Dioxide over the Past 100 Million Years. *Am. J. Sci.* 283, 641–683,
- Bickle, M.J., Chapman, H.J., Bunbury, J., Harris, N.B.W., Fairchild, I.J., Ahman, T. and Pomies, C. (2005) Relative contributions of silicate and carbonate rocks to riverine Sr fluxes in the headwaters of the Ganges. *Geochim. Cosmochim. Acta* 69, 2221–2240,
- Bouchez, J., von Blanckenburg, F. and Schuessler, J.A. (2013) Modeling novel stable isotope ratios in the weathering zone. *Am. J. Sci.* 313, 10.2475/04.2013.001.
- Chakrapani, G.J., Subramanian, V., Gibbs, R.J. and Jha, P.K. (1995) Size characteristics and mineralogy of suspended sediments of the Ganges river, India. 25, 192–196,
- Clergue, C., Dellinger, M., Buss, H.L., Gaillardet, J., Benedetti, M.F. and Dessert, C. (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,
- Coogan, L.A. and Dosso, S.E. (2015) Alteration of ocean crust provides a strong temperature dependent feedback on the geological carbon cycle and is a primary driver of the Sr-isotopic composition of seawater. *Earth Planet. Sci. Lett.* 415, 38–46,
- Dalai, T.K., Krishnaswami, S. and Sarin, M.M. (2002) Major ion chemistry in the headwaters of the Yamuna river system: Chemical weathering, its temperature dependence and CO₂ consumption in the Himalaya. *Geochim. Cosmochim. Acta* 66, 3397–3416,
- De la Rocha, C.L., Brzezinski, M.A. and DeNiro, M.J. (2000) A first look at the distribution of the stable isotopes of silicon in natural waters. *Geochim. Cosmochim. Acta* 64, 2467–2477,
- Dellinger, M., Gaillardet, J., Bouchez, J., Calmels, D., Galy, V., Hilton, R.G., Louvat, P. and France-Lanord, C. (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., Gaillardet, J., Bouchez, J., Calmels, D., Louvat, P., Dosseto, A., Gorge, C., Alanoca, L. and Maurice, L. (2015) Riverine Li isotope fractionation in the Amazon River basin controlled by the weathering regimes. *Geochim. Cosmochim. Acta* 164, 71–93,
- Dosseto, A., Vigier, N., Joassnes-Boyau, R., Moffat, I., Singh, T. and Srivastava, P. (2015) Rapid response of silicate weathering rates to climate change in the Himalaya. *Geochemical Perspectives Letters* 1, 10–19,

- Elliott, T., Thomas, A., Jeffcoate, A. and Niu, Y.L. (2006) Lithium isotope evidence for subduction-enriched mantle in the source of mid-ocean-ridge basalts. *Nature* 443, 565–568,
- Flesch, G.D., Anderson, A.R. and Svec, H.J. (1973) A secondary isotopic standard for $6\text{Li}/7\text{Li}$ determinations. *Int. J. Mass Spectrom. Ion Process.* 12, 265–272,
- Fontorbe, G., De la Rocha, C.L., Chapman, H.J. and Bickle, M.J. (2013) The silicon isotopic composition of the Ganges and its tributaries. *Earth Planet. Sci. Lett.* 381, 21–30,
- Frings, P.J., Clymans, W., Fontorbe, G., Gray, W., Chakrapani, G.J., Conley, D.J. and De la Rocha, C.L. (2015) Silicate weathering in the Ganges alluvial plain. *Earth Planet. Sci. Lett.* 427, 136–148,
- Froelich, P.N. and Misra, S. (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, 36–49,
- Gaillardet, J., Dupré, B. and Allègre, C.J. (1999a) Geochemistry of large river suspended sediments: silicate weathering or recycling tracer? *Geochim. Cosmochim. Acta* 63, 4037–4051,
- Gaillardet, J., Dupre, B., Louvat, P. and Allegre, C.J. (1999b) Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* 159, 3–30,
- Galy, A. and France-Lanord, C. (1999) Weathering processes in the Ganges–Brahmaputra basin and the riverine alkalinity budget. *Chem. Geol.* 159, 31–60,
- Galy, A., France-Lanord, C. and Derry, L.A. (1999) The strontium isotopic budget of Himalayan Rivers in Nepal and Bangladesh. *Geochim. Cosmochim. Acta* 63, 1905–1925,
- Georg, R.B., Reynolds, B.C., Frank, M. and Halliday, A.N. (2006) Mechanisms controlling the silicon isotopic compositions of river waters. *Earth Planet. Sci. Lett.* 249, 290–306, 10.1016/j.epsl.2006.07.006I.
- Georg, R.B., Reynolds, B.C., West, A.J., Burton, K.W. and Halliday, A.N. (2007) Silicon isotope variations accompanying basalt weathering in Iceland. *Earth Planet. Sci. Lett.* 261, 476–490,
- Georg, R.B., West, A.J., Basu, A.R. and Halliday, A.N. (2009) Silicon fluxes and isotope composition of direct groundwater discharge into the Bay of Bengal and the effect on the global ocean silicon isotope budget. *Earth Planet. Sci. Lett.* 283, 67–74,
- Gislason, S.R., Oelkers, E. and Snorrason, A. (2006) Role of river-suspended material in the global carbon cycle. *Geology* 34, 49–52,
- Gislason, S.R., Oelkers, E.H., Eiriksdottir, E.S., Kardjilov, M.I., Gisladdottir, G., Sigfusson, B., Snorrason, A., Elefsen, S., Hardardottir, J., Torssander, P. and Oskarsson, N. (2009) Direct evidence of the feedback between climate and weathering. *Earth Planet. Sci. Lett.* 277, 213–222, 10.1016/j.epsl.2008.10.018I.
- Hathorne, E.C. and James, R.H. (2006) Temporal record of lithium in seawater: a tracer for silicate weathering? *Earth Planet. Sci. Lett.* 246, 393–406,
- Henchiri, S., Gaillardet, J., Dellinger, M., Bouchez, J. and Spencer, R.G.M. (2016) Riverine dissolved lithium isotopic signatures in low-relief central Africa and their link to weathering regimes. *Geophysical Research Letters* 43, 10.1002/2016GL067711.I.

- Huang, W., van Hinsbergen, D.J.J. and Kapp, P. (2015) Paleolatitudes of the Tibetan Himalaya from primary and secondary magnetizations of Jurassic to Lower Cretaceous sedimentary rocks. *Geochem. Geophys. Geosyst.*, 10.1002/2014GC005624.
- Huh, Y., Chan, L.H. and Edmond, J.M. (2001) Lithium isotopes as a probe of weathering processes: Orinoco River. *Earth Planet. Sci. Lett.* 194, 189–199,
- Huh, Y., Chan, L.H., Zhang, L. and Edmond, J.M. (1998) Lithium and its isotopes in major world rivers: Implications for weathering and the oceanic budget. *Geochim. Cosmochim. Acta* 62, 2039–2051,
- Jain, S.K., Agarwal, P.K. and Singh, V.P. (2007) *Hydrology and Water Resources of India*. Springer.
- Jeffcoate, A.B., Elliott, T., Thomas, A. and Bouman, C. (2004) Precise, small sample size determinations of lithium isotopic compositions of geological reference materials and modern seawater by MC-ICP-MS. *Geostandards and Geoanalytical Research* 28, 161–172,
- Kisakürek, B., James, R.H. and Harris, N.B.W. (2005) Li and $\delta^7\text{Li}$ in Himalayan rivers: Proxies for silicate weathering? *Earth Planet. Sci. Lett.* 237, 387–401,
- Krishnaswami, S., Trivedi, J.R., Sarin, M.M., Ramesh, R. and Sharma, K.K. (1992) Strontium isotopes and rubidium in the Ganga-Brahmaputra river system: Weathering in the Himalaya, fluxes to the Bay of Bengal and contributions to the evolution of oceanic $87\text{Sr}/86\text{Sr}$. *Earth Planet. Sci. Lett.* 109, 243–253,
- Lechler, M., Pogge von Strandmann, P.A.E., Jenkyns, H.C., Prosser, G. and Parente, M. (2015) Lithium-isotope evidence for enhanced silicate weathering during OAE 1a (Early Aptian Selli event). *Earth Planet. Sci. Lett.* 432, 210–222,
- Lemarchand, E., Chabaux, F., Vigier, N., Millot, R. and Pierret, M.C. (2010) Lithium isotope systematics in a forested granitic catchment (Strengbach, Vosges Mountains, France). *Geochim. Cosmochim. Acta* 74, 4612–4628,
- Levasseur, S., Birck, J.L. and Allègre, C.J. (1999) The osmium riverine flux and the oceanic mass balance of osmium. *Earth Planet. Sci. Lett.* 174, 7–23,
- Li, G. and West, A.J. (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., Wanner, C., Rudnick, R.L. and McDonough, W.F. (2015) Processes controlling $\delta^7\text{Li}$ in rivers illuminated by study of streams and groundwaters draining basalts. *Earth Planet. Sci. Lett.* 409, 212–224,
- Lupker, M., France-Lanord, C., Galy, V., Lave, J., Gaillardet, J., Gajurel, A.P., Guilmette, C., Rahman, M., Singh, S.K. and Sinha, R. (2012) Predominant floodplain over mountain weathering of Himalayan sediments (Ganga basin). *Geochim. Cosmochim. Acta* 84, 410–432,
- Maher, K. and Chamberlain, C.P. (2014) Hydrologic Regulation of Chemical Weathering and the Geologic Carbon Cycle. *Science* 343, 1502–1504,
- Marriott, C.S., Henderson, G.M., Crompton, R., Staubwasser, M. and Shaw, S. (2004) Effect of mineralogy, salinity, and temperature on Li/Ca and Li isotope composition of calcium carbonate. *Chem. Geol.* 212, 5–15,
- McArthur, J.M., Howarth, R.J. and Bailey, T.R. (2001) Strontium isotope stratigraphy: LOWESS version 3: Best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up table for deriving numerical age. *Journal of Geology* 109, 155–170,

- Millot, R. and Girard, J.P. (2007) Lithium Isotope Fractionation during adsorption onto mineral surfaces, Int. meet., Clays in natural & engineered barriers for radioactive waste confinement, Lille, France.
- Millot, R., Vigier, N. and Gaillardet, J. (2010) Behaviour of lithium and its isotopes during weathering in the Mackenzie Basin, Canada. *Geochim. Cosmochim. Acta* 74, 3897–3912,
- Misra, S. and Froelich, P.N. (2012) Lithium Isotope History of Cenozoic Seawater: Changes in Silicate Weathering and Reverse Weathering. *Science* 335, 818–823,
- Oelkers, E.H., Jones, M.T., Pearce, C.R., Jeandel, C., Eiriksdottir, E.S. and Gislason, S.R. (2012) Riverine particulate material dissolution in seawater and its implications for the global cycles of the elements. *C. R. Geosci.* 344, 646–651,
- Oliver, L., Harris, N., Bickle, M., Chapman, H., Dise, N. and Horstwood, M. (2003) Silicate weathering rates decoupled from the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the dissolved load during Himalayan erosion. *Chem. Geol.* 201, 119–139,
- Opfergelt, S., Burton, K.W., Pogge von Strandmann, P.A.E., Gislason, S.R. and Halliday, A.N. (2013) Riverine silicon isotope variations in glaciated basaltic terrains: Implications for the Si delivery to the ocean over glacial–interglacial intervals. *Earth Planet. Sci. Lett.* 369–370, 211–219,
- Opfergelt, S., Cardinal, D., Henriet, C., Drave, X., Andre, L. and Delvaux, B. (2006) Silicon Isotopic Fractionation by Banana (*Musa* spp.) Grown in a Continuous Nutrient Flow Device. *Plant Soil* 285, 333–345,
- Opfergelt, S., de Bournonville, G., Cardinal, D., Andre, L., Delstanche, S. and Delvaux, B. (2009) Impact of soil weathering degree on silicon isotopic fractionation during adsorption onto iron oxides in basaltic ash soils, Cameroon. *Geochim. Cosmochim. Acta* 73, 7226–7240,
- Opfergelt, S., Eiriksdottir, E.S., Burton, K.W., Einarsson, A., Siebert, C., Gislason, S.R. and Halliday, A.N. (2011) Quantifying the impact of freshwater diatom productivity on silicon isotopes and silicon fluxes: Lake Myvatn, Iceland. *Earth Planet. Sci. Lett.* 305, 73–82, 10.1016/j.epsl.2011.02.043I.
- Palmer, M.R. and Edmond, J.M. (1992) Controls over the strontium isotope composition of river water. *Geochim. Cosmochim. Acta* 56, 2099–2111,
- Peucker-Ehrenbrink, B. and Ravizza, G. (2000) The marine osmium isotope record. *Terra Nova* 12, 205–219,
- Peucker-Ehrenbrink, B., Ravizza, G. and Hofmann, A.W. (1995) The Marine Os-187/Os-186 Record of the Past 80-Million Years. *Earth Planet. Sci. Lett.* 130, 155–167,
- Phan, T.T., Capo, R.C., Stewart, B.W., Macpherson, G.L., Rowan, E.L. and Hammack, R.W. (2016) Factors controlling Li concentration and isotopic composition in formation waters and host rocks of Marcellus Shale, Appalachian Basin. *Chem. Geol.* 420, 162–179,
- Pierson-Wickmann, A.C., Reisberg, L. and France-Lanord, C. (2002a) Behavior of Re and Os during low-temperature alteration: Results from Himalayan soils and altered black shales. *Geochim. Cosmochim. Acta* 66, 1539–1548,
- Pierson-Wickmann, A.C., Reisberg, L. and France-Lanord, C. (2002b) Impure marbles of the Lesser Himalaya: another source of continental radiogenic osmium. *Earth Planet. Sci. Lett.* 204, 203–214,
- Pistiner, J.S. and Henderson, G.M. (2003) Lithium-isotope fractionation during continental weathering processes. *Earth Planet. Sci. Lett.* 214, 327–339,

- Pogge von Strandmann, P.A.E., Burton, K.W., James, R.H., van Calsteren, P. and Gislason, S.R. (2010) Assessing the role of climate on uranium and lithium isotope behaviour in rivers draining a basaltic terrain. *Chem. Geol.* 270, 227–239,
- Pogge von Strandmann, P.A.E., Burton, K.W., James, R.H., van Calsteren, P., Gislason, S.R. and Mokadem, F. (2006) Riverine behaviour of uranium and lithium isotopes in an actively glaciated basaltic terrain. *Earth Planet. Sci. Lett.* 251, 134–147,
- Pogge von Strandmann, P.A.E., Burton, K.W., Opfergelt, S., Eiríksdóttir, E.S., Murphy, M.J., Einarsson, A. and Gislason, S.R. (2016) The effect of hydrothermal spring weathering processes and primary productivity on lithium isotopes: Lake Myvatn, Iceland. *Chem. Geol.* in press, 10.1016/j.chemgeo.2016.02.026.
- Pogge von Strandmann, P.A.E., Elliott, T., Marschall, H.R., Coath, C., Lai, Y.J., Jeffcoate, A.B. and Ionov, D.A. (2011) Variations of Li and Mg isotope ratios in bulk chondrites and mantle xenoliths. *Geochim. Cosmochim. Acta* 75, 5247–5268,
- Pogge von Strandmann, P.A.E. and Henderson, G.M. (2015) The Li isotope response to mountain uplift. *Geology* 43, 67–70,
- Pogge von Strandmann, P.A.E., Jenkyns, H.C. and Woodfine, R.G. (2013) Lithium isotope evidence for enhanced weathering during Oceanic Anoxic Event 2. *Nature Geoscience* 6, 668–672,
- Pogge von Strandmann, P.A.E., Opfergelt, S., Lai, Y.J., Sigfusson, B., Gislason, S.R. and Burton, K.W. (2012) Lithium, magnesium and silicon isotope behaviour accompanying weathering in a basaltic soil and pore water profile in Iceland. *Earth Planet. Sci. Lett.* 339–340, 11–23,
- Pogge von Strandmann, P.A.E., Porcelli, D., James, R.H., van Calsteren, P., Schaefer, B.F., Cartwright, I., Reynolds, B.C. and Burton, K.W. (2014) Chemical weathering processes in the Great Artesian Basin: Evidence from lithium and silicon isotopes. *Earth Planet. Sci. Lett.* 406, 24–36,
- Rad, S., Rive, K., Vittecoq, B., Cerdan, O. and Allegre, C.J. (2013) Chemical weathering and erosion rates in the Lesser Antilles: An overview in Guadeloupe, Martinique and Dominica. *Journal of South American Earth Sciences* 45, 331–344, 10.1016/j.jsames.2013.03.004.
- Rai, S.K., Singh, S.K. and Krishnaswami, S. (2010) Chemical weathering in the plain and peninsular sub-basins of the Ganga: Impact on major ion chemistry and elemental fluxes. *Geochim. Cosmochim. Acta* 74, 2340–2355,
- Raymo, M.E. (1994) The Himalayas, organic carbon burial, and climate in the Miocene. *Paleoceanography* 9, 399–404,
- Raymo, M.E. and Ruddiman, W.F. (1992) Tectonic Forcing of Late Cenozoic Climate. *Nature* 359, 117–122,
- Raymo, M.E., Ruddiman, W.F. and Froelich, P.N. (1988) Influence of late Cenozoic mountain building on ocean geochemical cycles *Geology* 16, 649–653,
- Sauzeat, L., Rudnick, R.L., Chauvel, C., Garçon, M. and Tang, M. (2015) New perspectives on the Li isotopic composition of the upper continental crust and its weathering signature. *Earth Planet. Sci. Lett.* 428, 181–192,
- Savage, P.S., Georg, R.B., Armytage, R.M.G., Williams, H.M. and Halliday, A.N. (2010) Silicon isotope homogeneity in the mantle. *Earth Planet. Sci. Lett.* 295, 139–146,

- Sharma, M., Wasserburg, G.J., Hoffmann, A.W. and Chakrapani, G.J. (1999) Himalayan uplift and osmium isotopes in oceans and rivers. *Geochim. Cosmochim. Acta* 63, 4005-4012,
- Teng, F.Z., McDonough, W.F., Rudnick, R.L., Dalpe, C., Tomascak, P.B., Chappell, B.W. and Gao, S. (2004) Lithium isotopic composition and concentration of the upper continental crust. *Geochim. Cosmochim. Acta* 68, 4167-4178,
- Tomascak, P.B., Langmuir, C.H., Le Roux, P.J. and Shirey, S.B. (2008) Lithium isotopes in global mid-ocean ridge basalts. *Geochim. Cosmochim. Acta*, 1626-1637,
- Torres, M.A., West, A.J. and Li, G. (2014) Sulphide oxidation and carbonate dissolution as a source of CO₂ over geological timescales. *Nature* 507, 346-349,
- Ullmann, C.V., Campbell, H.J., Frei, R., Hesselbo, S.P., Pogge von Strandmann, P.A.E. and Korte, C. (2013) Partial diagenetic overprint of Late Jurassic belemnites from New Zealand: Implications for the preservation potential of $\delta^7\text{Li}$ values in calcite fossils. *Geochim. Cosmochim. Acta* 120, 80-96,
- Vigier, N., Decarreau, A., Millot, R., Carignan, J., Petit, S. and France-Lanord, C. (2008) Quantifying Li isotope fractionation during smectite formation and implications for the Li cycle. *Geochim. Cosmochim. Acta* 72, 780-792,
- Vigier, N., Gislason, S.R., Burton, K.W., Millot, R. and Mokadem, F. (2009) The relationship between riverine lithium isotope composition and silicate weathering rates in Iceland. *Earth Planet. Sci. Lett.* 287, 434-441,
- Vigier, N. and Godderis, Y. (2015) A new approach for modeling Cenozoic oceanic lithium isotope paleo-variations: the key role of climate. *Climate of the Past* 11, 635-645,
- Walker, J.C.G., Hays, P.B. and Kasting, J.F. (1981) A Negative Feedback Mechanism for the Long-Term Stabilization of Earth's Surface-Temperature. *Journal of Geophysical Research-Oceans and Atmospheres* 86, 9776-9782,
- Wang, Q.-L., Chetelat, B., Zhao, Z.-Q., Ding, H., Li, S.-L., Wang, B.-L., Li, J. and Liu, X.-L. (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., Sonnenthal, E.L. and Liu, X.-M. (2014) Seawater $\delta^7\text{Li}$: A direct proxy for global CO₂ consumption by continental silicate weathering? *Chem. Geol.* 381, 154-167,
- West, A.J. (2012) Thickness of the chemical weathering zone and implications for erosional and climatic drivers of weathering and for carbon-cycle feedbacks. *Geology*, 10.1130/G33041.1I.
- West, A.J., Bickle, M.J., Collins, R. and Brasington, J. (2002) Small-catchment perspective on Himalayan weathering fluxes. *Geology* 30, 355-358,
- West, A.J., Galy, A. and Bickle, M. (2005) Tectonic and climatic controls on silicate weathering. *Earth Planet. Sci. Lett.* 235, 211-228,
- Williams, L.B. and Hervig, R.L. (2005) Lithium and boron isotopes in illite-smectite: The importance of crystal size. *Geochim. Cosmochim. Acta* 69, 5705-5716,
- Wimpenny, J., Gislason, S.R., James, R.H., Gannoun, A., Pogge von Strandmann, P.A.E. and Burton, K.W. (2010a) The behaviour of Li and Mg isotopes during primary phase dissolution and secondary mineral formation in basalt. *Geochim. Cosmochim. Acta* 74, 5259-5279,

- Wimpenny, J., James, R.H., Burton, K.W., Gannoun, A., Mokadem, F. and Gislason, S.R. (2010b) Glacial effects on weathering processes: New insights from the elemental and lithium isotopic composition of West Greenland rivers *Earth Planet. Sci. Lett.* 290, 427-437,
- Witherow, R.A., Berry Lyons, W. and Henderson, G.M. (2010) Lithium isotopic composition of the McMurdo Dry Valleys aquatic systems. *Chem. Geol.* 275, 139-147,
- Wunder, B., Meixner, A., Romer, R.L. and Heinrich, W. (2006) Temperature-dependent isotopic fractionation of lithium between clinopyroxene and high-pressure hydrous fluids. *Contrib. Mineral. Petrol.* 151, 112-120,
- Ziegler, K., Chadwick, O.A., Brzezinski, M.A. and Kelly, E.F. (2005) Natural variations of $\delta\text{Si-30}$ ratios during progressive basalt weathering, Hawaiian Islands. *Geochim. Cosmochim. Acta* 69, 4597-4610,

Table 1. Dissolved load Li isotope ratios and silicate weathering rates. See Frings et al. (2015) for major and trace element concentrations. "2sd" refers to the 2 standard deviations of multiple analyses of the same solution (generally $n=3$).

Table 2. Sediment Li isotope ratios. Sample locations are the same as for Table 1.

Figure 1. Sample location map, modified from Frings et al. (2015). The dotted grey lines show the individual catchment areas. The sample location symbols are

the same as those used in Figures 2 and 8. The blue curved line shows the location below which the floodplain is at steady-state according to dissolved Li isotopes (see text for details).

Figure 2. Comparison of the Li concentration (A) and isotope ratio (B) to flow distance upstream from the river mouth for the Ganges and its tributaries.

Figure 3. Li isotope ratio of river sediments plotted as a function of flow distance above the river mouth. Open diamonds are shallow samples from the river flow, filled grey symbol is medium depth, and black symbols are deeper samples. The grey bar is the mean continental crust (Sauzeat et al., 2015).

Figure 4. Dissolved Li/Na mass ratios plotted against $\delta^7\text{Li}$ for this study, the High Himalayas (Kisakürek et al., 2005), the Ganges-Brahmaputra (Bagard et al., 2015), the Amazon (Dellinger et al., 2015) and basalts from Iceland, the Azores and the Columbia River Basalts (Liu et al., 2015; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006; Vigier et al., 2009). The solid lines are Rayleigh fractionation relationships (see text for details), the dashed lines are Batch fractionation relationships and the associated numbers the isotopic fractionation factors (black for Rayleigh, grey for Batch). The black box represents the range of Li/Na from river sediments from the Amazon and Ganges, as well as global shales (Dellinger et al., 2014). The grey line is a Rayleigh

relationship for basaltic terrains, using the grey box as a starting composition (Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006). Dissolved load values have been corrected for precipitation input when data have been provided, otherwise are uncorrected.

Figure 5. Li concentrations plotted against discharge rates. Samples are unaffected by dilution, except potentially those with highest discharge, which are those close to the Ganges mouth and have constant $\delta^7\text{Li}$.

Figure 6. A) Dissolved Li isotope ratios for all studies of the Ganges-Brahmaputra rivers system, plotted against distance from the Main Frontal Thrust (MFT) that delineates the edge of the high relief areas (Bagard et al., 2015; Huh et al., 1998; Kisakürek et al., 2005), showing the unchanging nature of $\delta^7\text{Li}$ in the Ganges over at least 3 decades. Only rivers that actually cross the MFT are plotted. Distances for the Kisakürek et al. (2005) rivers were measured using Google Maps. B) The same data plotted against altitude, as an approximation of uplift and exposure rates. Samples from south of the MFT are considered floodplain samples.

Figure 7. Riverine Li isotopes plotted as a function of the silicate weathering rate. While there are correlations between the two parameters for two relatively small river systems (Iceland and the Mackenzie River (Milot et al., 2010; Vigier

et al., 2009)), there is not correlation for large global rivers (triangles (Huh et al., 1998)), or for the Ganges (this study – black diamonds) which are responsible for >30% of the global riverine discharge into the oceans. Lithium isotopes are therefore clearly not a weathering-rate tracer, and cannot be used as such in the palaeo-record.

Figure 8. Li isotopes plotted against Si isotopes (Frings et al., 2015) for the Ganges river system. The Ganges mainstream exhibits a positive correlation, which most other samples do not. In comparison, a few points from a previous Ganges-Brahmaputra (G-Br) study are shown (Bagard et al., 2015; Georg et al., 2009). Some basaltic rivers also exhibit a Li-Si co-variation (Opfergelt et al., 2013), while neither some other Icelandic rivers (Georg et al., 2007; Vigier et al., 2009), nor Icelandic soil pore waters exhibit a co-variation (Pogge von Strandmann et al., 2012). Average upper continental crust values are from Sauzeat et al., 2015; Savage et al., 2010.

Sample	River	Degrees North	Degrees East	Altitude (m)	Li (ng/ml)	$\delta^7\text{Li}$	2sd	Sil w.r. (t/km ² /yr)
1	Bhagirathi	30.156	78.603	648	3.23	10.9	0.9	
2	Alaknanda	30.145	78.601	476	2.29	10.7	0.5	
4	Ganga	30.127	78.354	353	3.03	12.9	0.1	8.37
5	Yamuna	28.748	77.226	210	6.65	22.0	0.4	10.3
6	Ganga	28.827	78.154	205	7.10	17.5	0.3	
7	Ramganga	28.666	78.896	185	6.03	23.0	1.0	
8	Unnamed Trib to Ganga	28.031	78.780	170	11.7	23.5	0.8	
9	Ganga	27.930	78.858	165	7.03	16.4	0.2	
10	Yamuna	27.177	78.043	157	10.8	18.4	0.1	
11	Unnamed Trib to Yamuna	26.963	78.365	142	7.60	21.6	0.5	
12	Chambal	26.870	78.367	138	6.72	18.9	0.2	
13	Yamuna	26.602	79.119	113	9.51	19.9	0.2	
14	Chambal	26.549	79.088	125	6.50	19.3	0.8	4.89
	Unknown Trib to							
15	Chambal	26.435	79.209	105	9.29	20.3	0.1	
16	Yamuna	26.425	79.246	105	7.63	22.0	0.2	
17	Ganga	27.010	79.987	127	6.45	21.9	0.1	
18	Unnamed Trib to Ganga	27.271	79.949	133	6.58	16.8	0.3	
19	Ramganga	27.498	79.696	137	6.13	24.8	0.6	19.1
20	Ganga	27.399	79.628	138	6.95	20.6	0.1	
21	Ganga	26.438	80.412	116	5.95	19.4	0.7	
22	Yamuna	25.955	80.160	110	7.59	22.1	0.7	
23	Betwa	25.944	80.156	107	5.52	20.8	0.1	5.09
24	Unnamed Trib to Yamuna	25.654	80.148	111	7.60	19.4	0.9	
25	Ken	25.480	80.313	96	4.61	22.5	0.2	6.39

26	Yamuna (South)	25.708	80.604	87	6.55	21.0	0.8	
27	Yamuna (North Bank)	25.714	80.607	87	6.68	21.5	0.6	
28	Yamuna	25.425	81.882	87	6.14	21.3	0.1	6.87
29	Ganga	25.427	81.887	86	6.39	19.1	0.5	
30	Tons	25.243	82.041	72	5.20	20.3	0.5	3.56
31	Ganga	25.309	82.076	89	6.35	20.9	0.6	
33	Ganga	25.152	82.546	64	5.60	20.2	0.2	
34	Varuna	25.341	82.981	71	6.41	20.0	0.2	
35	Ganga	25.290	83.006	82	6.53	21.2	0.1	
36	Gomati	25.506	83.142	66	6.32	21.4	0.3	5.84
37	Ganga	25.501	83.168	75	6.72	20.9	0.5	
38	Ganga	25.535	83.215	61	2.96	20.6	0.3	
39	Ganga	25.679	84.719	60	6.25	21.2	0.3	
40	Son	25.564	84.790	65	0.43	21.9	0.5	5.17
41	Ghaghara	25.821	84.590	61	6.01	20.9	0.8	6.63
42	Ganga	25.730	84.829	62	2.39	20.7	0.5	
43	Gandak	25.702	85.198	57	3.42	16.7	0.4	9.85
44	Ganga	25.615	85.201	52	2.00	21.7	1.0	
45	Ganga	25.381	86.001	49	2.32	20.8	0.6	
46	Unknown Trib to Ganga	25.502	86.481	42	1.64	21.7	1.0	2.31
47	Inundated Area	25.406	86.779	36	1.09	20.2	0.6	
48	Kosi	25.424	87.235	31	1.58	24.6	0.4	9.34
49	Ganga	25.282	87.248	40	2.23	20.9	0.2	
50	Ganga	24.801	87.948	27	1.66	22.1	0.1	
51	Hooghly	22.651	88.351	7	1.66	20.6	0.3	

Table 1.

Sample	Position	Depth (m)	$\delta^7\text{Li}$	2sd
1	Surface	0	-1.6	0.1
2	Surface	0	0.1	0.1
14	Bank		0.2	0.1
28	Shallow	0	-0.6	0.6
28	Deep	-	-1.3	0.7
40	Shallow	0	-2.6	0.6
40	Deep	3	2.9	0.6
41	Shallow	0	-0.1	0.6
41	Medium	5	0.1	0.6
41	Deep	9	0.0	0.5
49	Shallow	0	-0.4	0.2
49	Deep	10	0.1	0.2

Table 2.

