

Tracing silicate weathering processes in the permafrost-dominated Lena River watershed using lithium isotopes

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Abstract

Increasing global temperatures are causing widespread changes in the Arctic, including permafrost thawing and altered freshwater inputs and trace metal and carbon fluxes into the ocean and atmosphere. Changes in the permafrost active layer thickness can affect subsurface water flow-paths and water-rock interaction times, and hence weathering processes. Riverine lithium isotope ratios (reported as $\delta^7\text{Li}$) are tracers of silicate weathering that are unaffected by biological uptake, redox, carbonate weathering and primary lithology. Here we use Li isotopes to examine silicate weathering processes in one of the largest Russian Arctic rivers: the Lena River in eastern Siberia. The Lena River watershed is a large multi-lithological catchment, underlain by continuous permafrost. An extensive dataset of dissolved Li isotopic compositions of waters from the Lena River main channel, two main tributaries (the Aldan and Viliui Rivers) and a range of smaller sub-tributaries are presented from the post-spring flood/early-summer period at the onset of active layer development and enhanced water-rock interactions. The Lena River main channel (average $\delta^7\text{Li}_{\text{diss}} \sim 19\text{‰}$) has a slightly lower isotopic composition than the mean global average of 23‰ (Huh et al., 1998a). The greatest range of [Li] and $\delta^7\text{Li}_{\text{diss}}$ are observed in catchments draining the south-facing slopes of the Verkhoyansk Mountain Range. South-facing slopes in high-latitude, permafrost-dominated regions are typically characterised by increased summer insolation and higher daytime temperatures relative to other slope aspects. The increased solar radiation on south-facing catchments promotes repeated freeze-thaw cycles, and contributes to more rapid melting of snow cover, warmer soils, and increased active layer thaw depths. The greater variability in $\delta^7\text{Li}$ and [Li] in the south-facing rivers likely reflect the greater infiltration of melt water and enhanced water-rock interactions within the active layer.

A similar magnitude of isotopic fractionation is observed between the low-lying regions of the Central Siberian Plateau (and catchments draining into the Viliui River), and catchments draining the Verkhoyansk Mountain Range into the Aldan River. This is in contrast to global rivers in non-permafrost terrains that drain high elevations or areas of rapid uplift, where

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high degrees of physical erosion promote dissolution of freshly exposed primary rock typically yielding low $\delta^7\text{Li}_{\text{diss}}$, and low-lying regions exhibit high riverine $\delta^7\text{Li}$ values resulting from greater water-rock interaction and formation of secondary mineral that fractionates Li isotopes. Overall, the range of Li concentrations and $\delta^7\text{Li}_{\text{diss}}$ observed within the Lena River catchment are comparable to global rivers located in temperate and tropical regions. This suggests that cryogenic weathering features specific to permafrost regions (such as the continual exposure of fresh primary minerals due to seasonal freeze-thaw cycles, frost shattering and salt weathering), and climate (temperature and runoff), are not a dominant control on $\delta^7\text{Li}$ variations. Despite vastly different climatic and weathering regimes, the same range of riverine $\delta^7\text{Li}$ values globally suggests that the same processes govern Li geochemistry – that is, the balance between primary silicate mineral dissolution and the formation (or exchange with) secondary minerals. This has implications for the use of $\delta^7\text{Li}$ as a palaeo-weathering tracer for interpreting changes in past weathering regimes.

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1. INTRODUCTION

Permafrost thawing in high-latitude polar regions induced by climate warming influences mineral, elemental, nutrient and carbon fluxes (dissolved and particulate) into the ocean and atmosphere. Changes in the permafrost active layer thickness dictate subsurface water flowpaths, as well as water-rock interaction times and hence weathering processes, and this may impact future terrestrial biogeochemical cycles (Frey and McClelland, 2009). The evolution of long-term climate is influenced by the supply of cations from silicate weathering (providing alkalinity, which sequesters CO_2 by carbonate precipitation in the oceans), as well as by delivering nutrients that facilitate organic carbon burial (Walker et al., 1981; Berner et al., 1983). To date, however, understanding the influence of climatic (e.g., temperature and runoff) and physical rock supply (e.g., sediment supply, physical erosion) controls on weathering are uncertain and highly debated (e.g., Raymo and Ruddiman, 1992; West et al., 2005; Hilley et al., 2010; Eiriksdottir et al., 2013). Changes in silicate weathering are in turn predicted to have significantly affected long- and short-term climate perturbations in the past (Raymo et al., 1988; Raymo and Ruddiman, 1992; Pogge von Strandmann et al., 2013).

Water-rock interactions, and hence silicate weathering, in cold-climate regions differ from those of warm and wet watersheds in temperate and tropical regions. The latter tend to be characterised by transport- or supply-limited regimes, where weathering rates are limited by the supply of fresh primary minerals. At low erosion rates, primary minerals are nearly completely altered, and the rate of secondary mineral formation exceeds that of primary mineral dissolution. This allows for the accumulation of thick soil profiles and long water-rock interaction times. In high erosion kinetically-limited weathering environments, the rate of chemical weathering is limited relative to physical erosion. Soil production is limited because physical erosion removes weathered material rapidly preventing significant accumulation of secondary minerals, resulting in shorter water-rock interaction times (Stallard and Edmond, 1983; West et al., 2005).

In high-latitude or alpine regions, low mean annual temperatures are expected to inhibit mineral reaction rates,

resulting in incomplete weathering of silicate material (West et al., 2005). Nonetheless, it has been proposed that high rates of physical erosion from frost action and salt weathering, and enhanced primary rock dissolution by organic acids, can promote greater chemical weathering than might otherwise be expected in high-latitude regions dominated by temperature-controlled slow reaction rates (Gislason et al., 1996; Nezat et al., 2001; Huh, 2003).

Most weathering processes observed in weathering regimes in tropical and temperate climates are also prevalent in regions underlain by permafrost. However, the presence of permafrost further complicates water-rock interactions at high altitude and polar regions. Permafrost underlies nearly a quarter of the northern hemisphere, and underlies approximately 90% of the Lena River catchment, NE Siberia (Brown et al., 1997). Rivers in permafrost-dominated regions have very different hydrologic regimes to rivers in non-permafrost areas. In continuous permafrost-dominated catchments, perennially frozen soil/bed rock inhibits infiltration of surface water, thereby restricting subsurface water storage and limiting water-rock interactions. Rapid melting of winter precipitation (snow) accumulated within the catchment over ~8 to 9 months results in the high runoff spring freshet, which flows over the still frozen permafrost. In early spring, increasing air temperatures promote thawing of the near-surface soils, and development of the ‘active layer’. This enables water infiltration into the uppermost shallow (often organic-rich) thawed soil, and water is temporarily stored as ponded surface waters perched above the permafrost in low-lying wetlands and fens. Throughout the summer and early autumn before refreezing occurs, the active layer thaws to its maximum depth, potentially promoting exposure of more readily weathered rocks, deepening of flow paths and allowing greater water interaction with mineral-rich soil horizons (Woo, 2012). Unlike in tropical and temperate regions, the majority of hydrological processes (and hence silicate weathering) in permafrost-dominated terrains occurs within the seasonally thawed active layer (and regions of unfrozen talik) over the short thaw period. Rivers in watersheds with higher permafrost coverage tend to have lower subsurface storage capacity and thus a lower winter base flow and a higher summer peak flow compared to non-permafrost rivers (Ye et al., 2009; Woo, 2012).

In principle, climate warming could drive large annual changes in both the rate of silicate weathering and the weathering regime by contraction of the area underlain by continuous permafrost, increasing active layer thickness, and allowing greater suprapermafrost and talik groundwater flow (Frey and McClelland, 2009). This could affect the biogeochemical cycles of many elements and the supply of micronutrients to northern oceans. It could also impact the Earth's climate feedback cycles through the release of carbon trapped within permafrost into the atmosphere and oceans. Since the response of weathering processes to permafrost thawing is not well understood (Pokrovsky et al., 2005; Frey et al., 2007; Frey and McClelland, 2009; Keller et al., 2010), it is unknown whether carbon removal via silicate weathering or carbon release from permafrost thawing will have the greatest effect on the carbon budget. Constraining the processes that govern silicate weathering in high-latitude, permafrost dominated regions is therefore critical for quantifying the global carbon cycle over modern and geological timescales.

To date, it has proven difficult to constrain weathering processes at any scale, particularly in permafrost-dominated regions, because most tracers that are used are affected by multiple processes (e.g. biology, lithology, redox, etc.). Riverine lithium isotope ratios ($^7\text{Li}/^6\text{Li}$, reported as $\delta^7\text{Li}$, that is, the permil deviation from the $^7\text{Li}/^6\text{Li}$ ratio of the L-SVEC standard) trace silicate weathering processes at scales ranging from soils and small monolithological catchments to significant global river watersheds that integrate large areas of variable lithology and often several climatic regions. Lithium isotopes are not fractionated in the environment by biological processes (Lemarchand et al., 2007; Pogge von Strandmann et al., 2016). Also, Li is orders of magnitude more concentrated in silicates over carbonates, so that even in carbonate catchments, Li isotopes are dominated by silicate weathering (Kısakürek et al., 2005; Millot et al., 2010). River $\delta^7\text{Li}$ values are controlled by what has been described as “silicate weathering congruency” (Misra and Froelich, 2012; Pogge von Strandmann and Henderson, 2015; Vigier and Godd  ris, 2015; Pogge von Strandmann et al., 2016, 2017). This is defined as the ratio of primary mineral dissolution (releasing largely unfractionated Li with crustal $\delta^7\text{Li} \sim 0$ to 5‰) to secondary mineral formation (which preferentially incorporate ^6Li , increasing the $\delta^7\text{Li}$ composition of Li remaining in solution; (Pistiner and Henderson, 2003; Vigier et al., 2008; Wimpenny et al., 2010a). High riverine $\delta^7\text{Li}$ values have been interpreted as reflecting less complete weathering, greater secondary mineral formation and thus greater ‘weathering intensity’ (i.e., the ratio of chemical to physical denudation; Bouchez et al., 2013; Dellinger et al., 2015). There have been a number of large global rivers in tropical and temperate environments where the behaviour of Li isotopes has been studied: e.g., the Amazon River (Chan et al., 1992; Huh et al., 1998a; Dellinger et al., 2015, 2015); the Orinoco River (Huh et al., 1998a; Huh et al., 2001); rivers in the High Himalayas and the Ganges-Brahmaputra (Huh et al., 1998a; Kısak  rek et al., 2005; Bagard et al., 2015; Manaka et al., 2017; Pogge von Strandmann et al., 2017) the Changjiang (Yangtze) River

(Huh et al., 1998a; Liu et al., 2011; Wang et al., 2015); the Mississippi River (Chan et al., 1992; Huh et al., 1998a) and the Congo River (Henchiri et al., 2016). However, there are fewer studies of rivers draining cold climate regions. Whilst some data from Siberia exist, the sampling sites are limited to a handful of locations from the major tributaries and river mouths (Huh et al., 1998a). The only comparable studies of high-latitude polar regions are the Mackenzie River basin (Millot et al., 2010) and the comparatively short rivers of Iceland (Pogge von Strandmann et al., 2006; Vigier et al., 2009; Pogge von Strandmann et al., 2016), Greenland (Wimpenny et al., 2010b), the McMurdo Dry Valleys in Antarctica (Witherow et al., 2010), and Svalbard (Hindshaw et al., 2018).

In this study, Li isotopic compositions were measured in over 70 river samples and 11 suspended sediments across the catchment of the vast and relatively unstudied Lena River in eastern Siberia. The multi-lithological catchment spans a latitudinal and climate gradient from 60   to 68   N and is largely underlain by continuous permafrost. The effects of secondary mineralogy, climate, topography and presence of permafrost on silicate weathering are investigated. This study vastly increases the amount of Li isotope data from high latitudes, which has been limited partly due to difficulties in logistics and gaining access.

2. BACKGROUND

2.1. Study Area

The Lena River basin is located in Yakutia in eastern Siberia (Fig. 1). The Lena River is one of the largest Russian Arctic rivers, draining a watershed area of $2.46 \times 10^6 \text{ km}^2$. The river flows northwards from 53  N near Lake Baikal to 71  N and enters the Arctic Ocean in the Laptev Sea. The headwaters originate in the discontinuous and patchy mountain permafrost of the Baikal, Stanovoi and Dzhugdzhur mountains. Northward from 60  N latitude, the Lena River watershed is underlain by variable thicknesses of continuous permafrost ranging from 50 meters to over 1500 m (Brown et al., 1997; Chevychev and Bosikov, 2010). The seasonally thawed active layer varies in thickness throughout the catchment from a few centimetres to several meters (Huh et al., 1998c). The Lena River contributes approximately 15% of the total freshwater input into the Arctic Ocean, of which ~85% is provided during the spring flood and summer months (May – September; Ye et al., 2003). The geology of eastern Siberia has been described in detail by Gordeev and Sidorov, (1993), Huh et al. (1998b, 1998c), and Huh and Edmond, (1999). Briefly, the Central Siberian Plateau (CSP; see Fig. 1) is underlain by Proterozoic crystalline and metamorphic basement of the stable Siberian Platform, which outcrop to the south in the mountainous Trans-Baikal region where the headwaters of the Lena River form, and to the east in the Archean Aldan-Stanovoy shield mountains which are drained by rivers in the Lena-Anginsky inter-river area (LAIRA). The CSP is typified by gentle topography and extensive flood plains, with thick sedimentary cover composed of Precambrian to Quaternary marine carbonates and evaporites, along

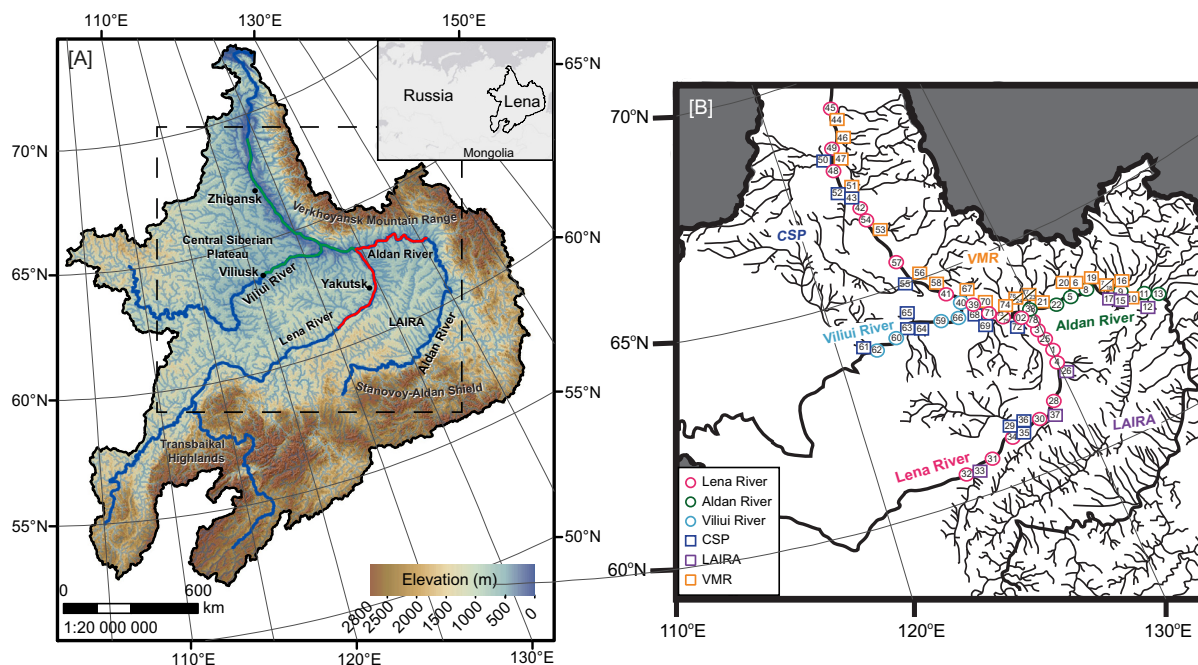


Fig. 1. Map showing [A] the Lena River catchment and its sub-catchment regions with the July 2012 sampling route shown in red and June 2013 in green. Sampling locations are shown [B] with samples within the Lena River main channel or the Viliui and Aldan Rivers, which are major tributaries, denoted by circles. Smaller tributaries of the Central Siberian Plateau (CSP), Lena-Amginsky inter-river area (LAIRA) and Verkhoyansk Mountain Range (VMR) are denoted by squares (maps modified after [Hirst et al. 2017](#)).

with terrigenous sandstone, shale, red beds, and coal beds. The Verkhoyansk Mountain Range forms a topographic high to the east and is composed of folded and metamorphosed rocks and uplifted detrital sediments. It is not actively undergoing tectonic uplift.

The climate of the watershed is continental, characterised by long cold winters and short, hot summers, with temperatures ranging from $-50\text{ }^{\circ}\text{C}$ to $+35\text{ }^{\circ}\text{C}$. The mean annual air temperature (MAAT) ranges from -6 to $-15\text{ }^{\circ}\text{C}$ across the region and decreases with increasing latitude ([Fedorov et al., 2014](#)). The mean annual precipitation (MAP) is typically low, ranging from 200 to 500 mm/yr ([Chevychev and Bosikov, 2010](#)). The drainage area is mainly composed of boreal taiga forest of larch and salix in the southern parts of the basin, with exposed rock outcrops, small shrubs, moss and lichen in the tundra regions of the northern part of the basin ([Gordeev and Sidorov, 1993](#)).

3. ANALYTICAL METHODS

3.1. Field sampling

The samples and methods are described in detail by [Hirst et al. \(2017\)](#) and [Kutscher et al. \(2017\)](#). Briefly, sampling occurred over two field campaigns (summer of July 2012 and late spring/early summer of June 2013) when the active layer is thickest and so suprapermafrost groundwater flow is deepest. Sampling dates, locations and descriptions are given in [Fig. 1](#) and Table S1. In the field, surface water samples were collected in acid-washed 10 L

low density polyethylene (LDPE) bottles by grab sampling from the upstream side of the ship or small motorised boat, or by wading out into river channels. Samples were filtered within a few hours using a polycarbonate Geotech[®] filter holder and $0.22\text{ }\mu\text{m}$ nitrocellulose filters (Millipore[®]) pre-washed with 5% acetic acid and ultrapure Milli-Q water. At each sampling locality, pH, temperature and electrical conductivity were measured *in-situ* using a multi-meter (YSI 556 multiprobe system) with analytical accuracies of ± 0.03 pH units, $\pm 0.1\text{ }^{\circ}\text{C}$, and $\pm 1\text{ }\mu\text{S/cm}$.

The rivers for this study have been geographically grouped according to [Kutscher et al. \(2017\)](#): (i) the Lena River main channel; (ii) the low-lying Central Siberian Plateau (CSP) tributaries; (iii) the main channel of the major Viliui River tributary that is sourced from that region; (iv) the mountainous tributaries draining the Verkhoyansk Mountain Range (VMR); (v) the main channel of the major Aldan River tributary; and (vi) tributaries draining the Lena-Amginsky inter-river area (LAIRA).

3.2. Major cation and trace element analyses

Major cations were measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES Thermo Icap 6500 Duo) at the Department of Geological Sciences, Stockholm University. For details, see [Sun et al. \(2018\)](#). For the majority of samples, Li concentrations were analysed using an Element 2 sector-field Inductively-Coupled-Plasma Mass Spectrometer (ICP-MS) at the University of Oxford. For Li analyses, standard addition calibration curves were prepared by doping a given sample with a

multi-elemental standard solution (Alfa Aesar®) to account for matrix effects. Both standard and water samples were doped with 1 ng/g of rhenium internal standard to correct for instrumental drift. Accuracy was assessed by analysing IAPSO seawater and the international river reference standard SLRS-5, and by measuring samples in duplicate, and external analytical uncertainties were better than 5%. For a handful of samples with Li concentrations below the limit of detection on the Element 2 (<60 nM Li, see Table 1), concentrations were estimated by intensity matching against a known concentration of L-SVEC on the MC-ICP-MS (see below), with uncertainties estimated to be $\pm 10\%$.

3.3. Li isotope measurements

For Li isotope analysis of the waters, a sufficient volume of each sample was evaporated to yield 10–20 ng Li, and refluxed 1–2 times with concentrated HNO_3 to break down organics prior to separation. This stage is necessary in these organic-rich samples, and resulted in an improvement of internal precision on the measurements by *ca.* 50%. For the suspended sediments, filters were digested using protocols outlined by (Hirst et al., 2017). Evaporated water samples and aliquots of the filter digests were dissolved in 0.2 M HCl and passed through a two-stage cation exchange chromatography procedure (BioRad® AG50W-X12), using dilute HCl as an eluent (Pogge von Strandmann et al., 2011; Pogge von Strandmann and Henderson, 2015). In order to confirm that quantitative Li yields on the column were achieved and no significant fractionation occurred on the column, aliquots before and after the main elution were analysed. Blanks for the total chemical procedure were less than 5 pg Li, which is negligible relative to the 10–20 ng of Li analysed in each sample.

Lithium isotope compositions were determined on a Nu Plasma HR-MC-ICP-MS at the Department of Earth Sciences, University of Oxford, in dry plasma mode using a Cetac Aridus-II desolvating system. Corrections for instrumental mass bias were made using sample-standard bracketing. Data are reported in $\delta^7\text{Li}$ notation, the permil deviation of the measured $^7\text{Li}/^6\text{Li}$ ratio from the L-SVEC standard (NIST SRM 8545; Flesch et al., 1973), where $\delta^7\text{Li} = [(^7\text{Li}/^6\text{Li}_{\text{sample}}) / (^7\text{Li}/^6\text{Li}_{\text{L-SVEC}}) - 1] \times 1000$. Each sample was analysed in triplicate during the course of each run. Individual errors are the two standard deviation around the mean of at least two, but typically three, replicate measurements. The external reproducibility was determined by repeat measurements of an internal seawater standard processed through the full chemical procedure, which yielded $\delta^7\text{Li} = 31.3 \pm 0.7\text{‰}$ (2sd; $n = 20$). 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 ($\delta^7\text{Li} = 3.6 \pm 0.4\text{‰}$, $n = 3$), and the results are within uncertainty of other published values (Pogge von Strandmann et al., 2017 and references therein). Replicates of samples processed in duplicate ($n = 9$ waters, 3 sediments) in different analytical sessions are indistinguishable from one another within analytical error, with the exception of LR2012-37, which shows slightly greater variability (1.5‰; Table 1).

Duplicates are plotted as the average of the two measurements.

4. RESULTS

Sample location and field parameter data (from Hirst et al. 2017; Kutscher et al. 2017), dissolved [Na] and [Li] (where square brackets denote concentrations), $\delta^7\text{Li}_{\text{diss}}$ and suspended sediment $\delta^7\text{Li}_{\text{susp}}$ are given in Table 1. Other major elemental data are presented in Sun et al. (2018). Lithium concentrations range from 12 to 1520 nM. This range is similar to that observed from long-term seasonal monitoring of the Lena River at Zhigansk (Fig. 1, [Li] = 115 to 628 nM; Holmes et al., 2018). Dissolved $\delta^7\text{Li}$ values range between +7.1 and +41.9‰ (Fig. 2). Despite the large range of values, the average $\delta^7\text{Li}_{\text{diss}}$ for the geographical regions vary within only a few permil. Average [Li] and $\delta^7\text{Li}_{\text{diss}}$ compositions are presented as box-and whisker plots in Supplementary Fig. 1 to show the distribution of data. Lithium concentrations within the Lena River main channel (average ~ 134 nM) are lower than the global mean of 215 nM, and are similar to shield-draining rivers elsewhere (Huh et al., 1998a). The Viliui River as well as the tributaries of the CSP, LAIRA and VMR have higher average [Li] (232–338 nM) when compared to the Lena River main channel and Aldan River. The greatest ranges in both [Li] and $\delta^7\text{Li}$ are observed in rivers draining the Verkhoyansk Mountain Range (VMR), and especially in catchments that predominantly have a south-facing aspect (See Fig. 1 and Table 1). Overall, the data presented here are comparable with the more limited previously published data in the Lena River catchment ([Li] = 40 to 3350 nM; $\delta^7\text{Li} = 19.0$ to 29.9‰ ; Huh et al., 1998a). The furthest downstream sample from this study (LR2013-45, [Li] = 192 nM, $\delta^7\text{Li} = 21.3\text{‰}$) is indistinguishable to sample UL607 from the Lena River outflow ~ 500 km at Kusr measured previously ([Li] = 220 nM, $\delta^7\text{Li} = 21.5\text{‰}$; Huh et al., 1998a). Both samples LR2013-45 and UL607 were collected during the early summer months (in June 2013 and July 1995, respectively).

Using published monthly discharge and [Li] data from R-ArcticNet (<http://www.r-arcticnet.sr.unh.edu/v4.0/index.html>), ArcticRIMS (<http://rims.unh.edu/data.shtml>) and the Arctic Great Rivers Observatory (<http://arcticgreaterivers.org/data.html>), an annual discharge-weighted Li flux into the Arctic Ocean of 1.29×10^8 mol/yr can be calculated. Using a [Li] = 192 nM of our northernmost sample (LR2013-45) and the average annual discharge, we obtain an annual flux of 1.03×10^8 mol/yr, which is comparable to the estimate of 1.18×10^8 mol/yr by Huh et al. (1998a). This accounts for approximately 1% of the global riverine Li flux into the ocean.

The Li isotopic composition of the Lena River main channel is relatively uniform throughout the catchment ($\sim 19 \pm 2\text{‰}$; 1σ), and is several permil lower than the global riverine mean of $\sim 23\text{‰}$ (Huh et al., 1998a), with the exception of one atypical sample with high [Li] and $\delta^7\text{Li}$ (LR2013-41; $\delta^7\text{Li} = 29.0\text{‰}$, 396 nM). The ranges of $\delta^7\text{Li}$ and [Li] measured in this study are similar to those of data from other large global rivers systems elsewhere (e.g., the

Table 1

Field parameters and dissolved Li concentrations and dissolved and suspended particulate isotopic compositions of Lena River samples.

Sample	Sampling date	Latitude	Longitude 'E	Mean slope (degree)	pH	Conductivity (us/cm ^C)	Na (μmol/L)	Li (nmol/L)	δ ⁷ Li _{diss} (‰)	2sd	δ ⁷ Li _{susp} (‰)	2sd
<i>Aldan (Алдан) River</i>												
LR2012-13 [†]	19-07-2012	62°38.296	134°55.313	3.44	7.7	86	56	61	21.2	0.7	2.2	0.7
LR2012-13 dup									20.9	0.7	2.8	0.7
LR2012-11	18-07-2012	62°42.635	134°41.712		7.3	99	52	63	23.1	0.7		
LR2012-09	18-07-2012	62°55.373	134°10.366		7.5	94	55	16	21.0	0.7		
LR2012-22	21-07-2012	63°26.290	129°40.001		6.8	105	55	76	22.5	0.7		
LR2013-38 [†]	12-06-2013	63°26.031	129° 38.390		7.4	86	39	112	18.7	0.7		
<i>Central Siberian Plateau</i>												
LR2012-29	25-07-2012	61°08.768	126°51.722	0.67	8.6	163	151	644	10.6	0.7		
LR2012-36	28-07-2012	61°10.079	126°52.061	0.67	9.4	171	162	732	13.4	0.7		
LR2012-35	28-07-2012	61°09.905	126°54.657	0.67	9.0	170	156	752	11.4	0.7		
LR2013-72	27-06-2013	63°28.065	128°47.392	0.42	7.4	201	653	225	20.8	0.7	5.1	0.7
LR2013-69	26-06-2013	63°58.454	127°01.742	0.47	7.5	346	1245	245	24.0	0.7	3.0	0.7
LR2013-68	26-06-2013	64°06.517	126°44.435	0.47	7.5	288	1007	217	25.0	0.7		
LR2013-61	23-06-2013	63°46.822	121°31.376	0.45	7.6	118	59	70	18.1	0.7	1.9	0.7
LR2013-63	24-06-2013	64°01.494	123°53.111	0.35	7.0	50	92	145	16.0	0.7		
LR2013-64	24-06-2013	64°01.658	124°05.540	0.3	8.4	159	270	334	24.5	0.7		
LR2013-65	24-06-2013	64°01.610	124°23.933	0.24	7.2	70	91	61	19.0	0.7		
LR2013-55	21-06-2013	64°57.121	124°35.775	0.43	6.7	58	102	54	16.6	0.7		
LR2013-43	14-06-2013	66°46.268	123°21.607	0.37	6.9	52	153	199	17.3	0.7		
LR2013-50	16-06-2013	67°52.577	123°02.186	1.04	7.1	134	333	139	23.5	0.7		
<i>Lena-Amginsky inter-river area (LAIRA)</i>												
LR2012-33	27-07-2012	60°35.619	124°16.356	1.65	8.2	305	61	725	15.5	0.7		
LR2012-37 [†]	29-07-2012	61°11.678	128 17.041		7.3	336	250	53	25.2	0.7	2.6	0.7
LR2012-37 dup									23.7	0.7		
LR2012-27	24-07-2012	61°15.061	128°46.172	1.37	8.0	310	53	320	18.3	0.7		
LR2012-27 dup									18.5	0.7		
LR2012-26 [†]	24-07-2012	61°54.233	129°50.831	0.52	7.2	106	166	93	19.9	0.7	4.6	0.8
LR2012-26 dup									19.5	0.7		
LR2012-12	19-07-2012	62°36.881	134°55.373	1.43	8.2	299	77	1061	16.4	0.7	4.0	0.7
LR2012-15	19-07-2012	62°56.787	134°00.503		6.5	145	87	30	30.5	0.9		
LR2012-17	20-07-2012	63°01.219	133 24.489	0.43	7.4	133	101	81	24.3	0.7		
<i>Lena (Лена) River Main Channel</i>												
LR2012-31	26-07-2012	60°52.334	125°38.010		7.22	-	481	101	17.4	0.7		
LR2012-31 dup									17.5	0.8		
LR2012-30	25-07-2012	61°06.475	126°53.429		7.7	125	368	106	16.4	0.7		
LR2012-28	24-07-2012	61°15.823	128°44.383		7.47	80	154	73	17.7	0.7		
LR2012-28 dup									18.2	0.7		
LR2012-04 [†]	14-07-2012	62°09.462	129° 54.481		6.63	81	191	77	17.8	0.7	1.6	0.7
LR2012-04 dup									17.2	0.7	1.4	0.7

LR2012-01	12-07-2012	62°15.758	130° 01.031		6.82	90	281	103	16.8	0.7		
LR2012-25	22-07-2012	62°38.949	129°54.446		6.86	90	192	106	18.9	0.7		
LR2012-03	13-07-2012	63°01.161	129° 41.079		6.52	84	237	85	17.0	0.7		
LR2013-78	28-06-2013	63°07.960	129°37.392		7.58	139	375	165	17.9	0.7		
LR2013-78 dup									18.4	0.7		
LR2012-02 [†]	12-07-2012	63°23.275	129° 32.356		6.57	69	146	73	18.2	0.7	2.6	0.7
LR2012-02 dup											2.5	0.7
LR2013-75 [†]	27-06-2013	63°31.690	128°51.598		7.56	92	56	12	21.8	0.7		
LR2013-73 [†]	27-06-2013	63°29.425	128°48.183		7.3	142	420	197	18.3	0.7		
LR2013-39 [†]	12-06-2013	64°13.095	126°51.861		7.57	101	45	94	14.5	0.7		
LR2013-41	13-06-2013	64°23.668	126°21.951		7.03	140	277	396	29.0	0.7		
LR2013-57 [†]	21-06-2013	65°03.067	124°48.330		6.99	83	48	14	21.3	0.7		
LR2013-54	19-06-2013	65°56.914	123°54.840		7.06	128	315	268	19.5	0.7		
LR2013-42	14-06-2013	66°20.636	123°40.556		7.29	139	356	322	23.1	0.7		
LR2013-48	16-06-2013	67°52.424	123°05.536		7.11	121	340	82	21.1	0.7		
LR2013-48 dup									20.5	0.7		
LR2013-49	16-06-2013	67°55.744	123°00.123		7.02	130	344	75	21.7	0.7		
LR2013-45	15-06-2013	68°44.599	123°59.794		7.09	91	79	192	21.3	0.7		
<i>Viliui (Вилуи)</i>												
LR2013-62	23-06-2013	63°45.493	121°35.897	0.96	7.4	111	254	261	23.5	0.7		
LR2013-60	23-06-2013	63°54.536	123°08.739		7.2	110	215	241	26.1	0.7	3.6	0.7
LR2013-59 [†]	22-06-2013	63°52.202	125°10.004		7.2	110	232	230	15.3	0.7		
LR2013-66	24-06-2013	64°03.180	126°04.148		7.4	112	238	220	23.1	0.7		
LR2013-40	13-06-2013	64°19.678	126°22.321		7.2	140	285	409	22.0	0.7		
<i>Verkhoyansk Mountain Range</i>												
LR2012-10 [†]	18-07-2012	62°38.249	134°54.869	3.82	7.0	148	67	57	28.6	0.7		
LR2012-16 [†]	20-07-2012	63°06.195	134 02.301	2.32	6.3	103	63	29	34.7	0.9	0.4	0.7
LR2012-07 [†]	17-07-2012	63°12.264	133°14.042	4.73	7.0	168	73	42	34.3	1.2		
LR2012-18	20-07-2012	63°022.064	133 016.417		6.6	118	41	24	24.9	0.7		
LR2012-19 [†]	20-07-2012	63°23.152	133°08.212	2.38	6.6	50	68	27	33.2	0.7		
LR2012-06 [†]	16-07-2012	63°19.254	131°55.854	6.34	7.4	206	77	62	30.0	0.8		
LR2012-20 [†]	20-07-2012	63°21.350	131°45.191	2.24	6.8	60	91	45	33.3	0.7		
LR2012-21	21-07-2012	63°20.639	130°22.743	4.13	7.0	244	119	216	22.0	0.7		
LR2012-23	21-07-2012	63°27.689	129°34.158	4.81	7.1	170	106	322	20.3	0.7		
LR2013-77	28-06-2013	63°28.084	129°35.651	4.81	7.6	206	158	668	21.2	0.7		
LR2012-24 [†]	21-07-2012	63°31.213	129°23.987	2.88	6.8	50	102	29	39.8	0.7		
LR2013-76 [†]	28-06-2013	63°31.325	129°23.775	2.88	7.5	49	92	28	41.9	0.7		
LR2013-74 [†]	27-06-2013	63°31.216	128°49.910	4.98	7.8	93	129	69	31.2	1.0		
LR2013-70	26-06-2013	64°01.146	127°21.009	2.08	7.4	88	168	97	35.4	0.7		
LR2013-70 dup									35.2	0.7		
LR2013-67 [†]	26-06-2013	64°09.811	126°57.998	2.82	7.2	73	156	1524	7.1	0.7		
LR2013-58 [†]	22-06-2013	64°36.009	125°43.076	4.64	7.1	89	47	16	22.8	0.7		
LR2013-56	21-06-2013	65°00.332	124°56.650	5.17	7.3	178	195	917	15.4	0.7		
LR2013-53	18-06-2013	66°13.971	124°09.683	4.01	7.2	159	134	178	14.5	0.7		
LR2013-51	17-06-2013	67°15.126	123°24.505	5.5	7.4	140	79	57	21.2	0.7		

(continued on next page)

Table 1 (continued)

Sample	Sampling date	Latitude	Longitude 'E	Mean slope (degree)	pH	Conductivity (us/cm ^C)	Na (μmol/L)	Li (nmol/L)	$\delta^7\text{Li}_{\text{diss}}$ (‰)	2sd	$\delta^7\text{Li}_{\text{susp}}$ (‰)	2sd
LR2013-47	16-06-2013	68°01.293	123°24.905	4.57	7.1	104	39	281	17.4	0.7		
LR2013-46	15-06-2013	68°23.313	123°58.426	0.94	7.1	64	77	151	24.8	0.7		
LR2013-44	15-06-2013	68°43.951	124°03.581	3.94	7.2	182	136	267	23.2	0.7		

** Sampling stations are listed from upstream to downstream

Mean slope angle for upstream Lena River main channel sample LR2012-32 (not measured for [Li] or $\delta^7\text{Li}_{\text{diss}}$) is 3.2°. See Kutscher et al. (2017).

VMR samples LR2012-10 to LR2012-23 and LR2012-77 to LR2012-78 are rivers draining south-facing catchments. See main text.

† Samples had [Li] below detection on the element 2, so [Li] were estimated by intensity matching against a known concentration of L-SVEC on the MC-ICP-MS, with uncertainties estimated at $\pm 10\%$.

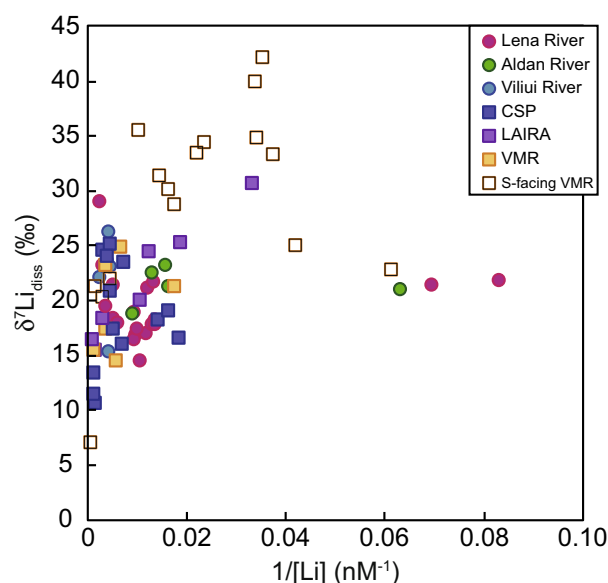


Fig. 2. $\delta^7\text{Li}_{\text{diss}}$ compositions versus the inverse of dissolved Li concentrations for rivers in the Lena River watershed. Previous values from the Lena River watershed are shown for comparison (not shown is one anomalous sample UL436 that drains the evaporitic marine carbonates within the Siberian Platform with high [Li] of 3350 nM and $\delta^7\text{Li}_{\text{diss}} = 21.2\text{‰}$ (Huh et al., 1998a)). The range of values do not define clear, straight line mixing trajectories, thus are unlikely to be explained by simple mixing between two riverine end-members, and reflect the complex behaviour of Li in this watershed. Uncertainties on $\delta^7\text{Li}$ smaller than the symbols. CSP = Central Siberian Plateau; LAIRA = Lena-Anginsky inter-river area; VMR = Verkhoyansk Mountain Range. Open symbols represent VMR rivers draining south-facing catchments, which show the greatest variation in both [Li] and $\delta^7\text{Li}_{\text{diss}}$.

Mackenzie River, Millot et al., 2010; the Ganges-Brahmaputra, Kısakürek et al., 2005, Bagard et al., 2015, Pogge von Strandmann et al., 2017; and the Amazon, Dellinger et al., 2015).

The rivers in the Lena catchment show a broad positive trend between $\delta^7\text{Li}_{\text{diss}}$ and $1/[\text{Li}]$, although the lack of a simple relationship between $\delta^7\text{Li}$ and Li concentration for the Lena River main channel and the main catchment regions (Fig. 2) indicates that there are a range of processes controlling the Li concentrations and isotope variations. In particular, the data cannot be adequately explained by simple mixing between two endmembers with different isotopic compositions and weathering regimes, as has been inferred for the Mackenzie River Basin (Millot et al., 2010) and the Congo River (Henchiri et al., 2016). This is not unexpected in such a large complex, multi-lithological drainage region.

Four sets of samples were collected from the same locations in both the July 2012 and June 2013 field campaigns (Table 1; LR2012-23/LR2013-77 and LR2012-24/LR2013-76 from a tributary draining the VMR; LR2012-03/LR2013-78 from the main channel of the Lena River; and LR2012-22/LR2013-38 from the Aldan River). With the exception of the LR2012-24/LR2013-76 pair of samples, which had similar [Li], the concentrations of samples collected in 2013 were almost double those of their 2012

counterparts. In all instances, however, the $\delta^7\text{Li}$ values of the samples from the same locations sampled during both campaigns were within 1–2‰ of one another. This might suggest that despite presumed increases in the thickness of the active layer during the warmer months, there is only limited $\delta^7\text{Li}$ variation.

The suspended sediments have a narrow $\delta^7\text{Li}_{\text{susp}}$ range from +0.4 to +5.1‰ (Supplementary Fig. 2), which broadly overlaps with average continental silicate rock values (UCC, $\sim 0.6 \pm 0.6\text{‰}$, Teng et al., 2004; Sauzéat et al., 2015; and basalts ~ 3 to 5‰ , Elliott et al., 2006, Tomascak et al., 2008). The suspended sediments are isotopically heavier than the global mean suspended sediment Li isotopic composition for large global rivers of $-1.5 \pm 1\text{‰}$ (1 σ ; Dellinger et al., 2014) but comparable to $\delta^7\text{Li}_{\text{susp}}$ values for other rivers (e.g., the Mackenzie River, Millot et al. 2010; the Ganges-Brahmaputra; Kısakürek et al. 2005, Bagard et al. 2015, Pogge von Strandmann et al. 2017; the Dongqu, Weynell et al., 2017); and the Amazon, Dellinger et al., 2014). Variations in $\delta^7\text{Li}$ have been reported for suspended sediments related to variations in Si/Al (a proxy for grain size) in depth profiles in the Amazon, Mackenzie and Ganges-Brahmaputra Rivers that are the result mineral sorting within the water column (Bouchez et al. 2013; Dellinger et al. 2014). However, only suspended sediments from near-surface waters have been collected in this study, and the use of HF in the filter dissolution protocol in these samples precludes the use of Si/Al as a proxy for grain size.

The isotopic offset between $\delta^7\text{Li}_{\text{susp}}$ and $\delta^7\text{Li}_{\text{diss}}$ ($\Delta^7\text{Li}_{\text{susp-diss}} = \delta^7\text{Li}_{\text{susp}} - \delta^7\text{Li}_{\text{diss}}$) for the different geographical regions within the Lena River watershed generally varies between 12.5 and -22.6‰ (shown in Supplementary Fig. 3). With the exception of the south-facing VMR sample with $\Delta^7\text{Li}_{\text{susp-diss}} = -34.3\text{‰}$, the narrow range of values do not allow for discrimination between the geographical regions. The magnitude of $\Delta^7\text{Li}_{\text{susp-diss}}$ observed within the Lena River is comparable to values observed in rivers elsewhere ($\Delta^7\text{Li}_{\text{susp-diss}} = -6$ to -36‰ ; Huh et al., 2001; Kısakürek et al., 2005; Pogge von Strandmann et al., 2006; Pogge von Strandmann et al., 2010).

5. DISCUSSION

The fractionation of Li isotopes is controlled by water-rock interactions during weathering processes, specifically the balance between release of Li during primary silicate rock dissolution, and the preferential incorporation or adsorption of ^6Li during formation of secondary minerals (Pistiner and Henderson, 2003; Vigier et al., 2008; Wimpenny et al., 2010a). The variations in $\delta^7\text{Li}_{\text{diss}}$ across the Lena River catchment reflect numerous complex processes occurring over the watershed. The lack of detailed observational data on the thermal regime for the individual catchment regions (e.g., active layer thaw depths, local microclimate, snow conditions, vegetation, soil properties, moisture content, lateral drainage, ground ice, etc.; Woo, 2012) complicates the interpretation of these isotopic variations to specific permafrost conditions. Here, we attempt to distinguish the dominant processes controlling Li isotope

fractionation over such a large, complex, permafrost-dominated watershed.

5.1. Sources of dissolved lithium

Although carbonate weathering is the dominant contributor to total dissolved solids (TDS) in the Lena River catchment (Huh et al., 1998b,c; Huh and Edmond, 1999), it contributes only a small fraction of the dissolved Li due to the low [Li] in carbonates. The possibility of inputs of Li from rainwater, ultimately derived from sea spray and so accompanied by other elements in the same proportions as in seawater, was investigated using the methods of Millot et al. (2010) and Dellinger et al. (2014) and a rainwater [Cl] after Gordeev et al. (1996). The range of measured Li/Cl ratios (1.6×10^{-4} to 7.9×10^{-2}) is much higher than the seawater ratio of 5×10^{-5} , and so a negligible ($<5\%$) proportion of riverine Li originates from precipitation. Thus, the $\delta^7\text{Li}$ data have not been corrected for these inputs, consistent with the approaches of other riverine studies (e.g. Millot et al., 2010; Bagard et al., 2015; Liu et al., 2015; Pogge von Strandmann et al., 2017).

Some of the rivers draining the CSP have elevated [Cl] and $[\text{SO}_4^-]$, which might be derived from weathering of evaporites that are abundant within the catchment region (Gordeev and Sidorov, 1993; Huh et al., 1998c; Yoon, 2010). However, as noted by Yoon, (2010), this may also reflect a contribution from high [Cl] and $[\text{SO}_4^-]$ groundwaters. Using the same approach as Dellinger et al. (2014), and assuming evaporites have $\text{Li}/\text{Na} = 3 \times 10^{-5}$, a low evaporite contribution has only been identified for a number of CSP (LR2013-50 (3%), LR2013-68 (8%), LR2013-79 (9%), LR2013-72 (5%)); and Lena River main channel samples (LR2012-30, LR2012-32 and LR2013-48 ($\sim 5\%$); LR2012-31, LR2012-34 and LR2013-49 ($\sim 6\%$)). Overall, the calculations show that dissolved Li is dominantly derived from the weathering of silicate material.

5.2. Secondary mineralogical controls on Li isotope fractionation - Mineral saturation states

The large range of Li isotope ratios observed in rivers has been proposed to reflect mineral-specific isotope fractionation factors controlled by the precipitation of (or interaction with) different secondary mineral assemblages. This has been attributed to differences in bedrock lithology as well as weathering regime and hence weathering intensity, which control the water chemistry by removing major and trace elements from solution as the various secondary mineral phases precipitate (e.g., Millot et al., 2010; Wimpenny et al., 2010b; Pogge von Strandmann et al., 2006, 2010).

In order to assess the likelihood and mineralogy of secondary mineral formation in the studied rivers, mineral saturation states were calculated with PHREEQC (Parkhurst and Appelo, 1999), using the measured dissolved major cation and anion, Al and Fe concentrations, and *in-situ* pH, alkalinity and temperature data (after Hirst et al. 2017; Sun et al. 2018). The PHREEQC calculations indicate that in river samples from all of the geographical regions

within the Lena River watershed, primary minerals such as quartz, olivine, pyroxene and feldspar are undersaturated and so are likely to be dissolving. In contrast, secondary minerals that are oversaturated ($SI > 0$) in all rivers (and hence are likely to be precipitating) include amorphous and crystalline Fe oxyhydroxides (e.g., goethite, hematite, magnetite), Al oxides (e.g., gibbsite), Mn oxides (e.g., birnessite) and phyllosilicate minerals (e.g., K-mica, kaolinite, pyrophyllite). Smectite clay minerals (Ca- and Na-montmorillonite) and illite are only oversaturated within the Aldan and Lena Rivers (Supplementary Fig. 4). These waters were filtered using a $0.22\ \mu\text{m}$ cutoff, and so the oversaturation of amorphous Fe, Al and Mn oxides might reflect colloidal particles that have passed through the filter. These results are consistent with mineralogical assemblages determined by transmission electron microscopy (TEM) and synchrotron-based scanning transmission X-ray microscopy (STXM) identification of colloidal and suspended particulates for the same samples, which show abundant amorphous Fe(III) ferrihydrite on the sample filters (Hirst et al., 2017), and lesser crystalline goethite and hematite, along with clay minerals. There may also be secondary minerals, such as clays, that are inherited from weathering within the soil profile (Dellinger et al., 2014).

Links between Li isotope fractionation and specific secondary mineral saturation indices have been reported in basaltic terrains (Pogge von Strandmann et al., 2006, 2010), and in glacial rivers draining permafrost in west Greenland (Wimpenny et al., 2010b). In the present study, however, there is no correlation between dissolved $\delta^7\text{Li}$ and any PHREEQC calculated mineral saturation states (Supplementary Fig. 3.). This is not unexpected for rivers draining large, multi-lithology catchments, where secondary mineralogy will also vary. Whilst an abundance of amorphous and crystalline Fe oxides were observed in the secondary mineral phases on the filters for the samples in this study (Hirst et al., 2017), the presence of other secondary minerals (particularly clay minerals) are also likely to have contributed to the $\delta^7\text{Li}_{\text{susp}}$ due to the incorporation or sorption of ^6Li .

5.3. Topographical and catchment area controls on Li isotope fractionation

Topography and relief can exert a strong influence on weathering. In regions unaffected by permafrost, topographically high regions are typically dominated by relatively high physical erosion with high denudation rates (often related to high uplift rates), and so high rates of exposure of fresh mineral surfaces and minimal water–rock interaction times (e.g., Montgomery and Brandon, 2002). This promotes the weathering of primary rock material and limits secondary mineral precipitation (low weathering intensity), and is expected to result in $\delta^7\text{Li}$ compositions that approach those of the primary weathering rocks. In contrast, non-permafrost rivers in low-lying regions are expected to have higher $\delta^7\text{Li}$ values, where greater water–rock interaction times promote the formation of secondary minerals and greater adsorption of Li, driving the riverine

$\delta^7\text{Li}$ towards higher values. This relationship has been suggested from a broad negative correlation between $\delta^7\text{Li}$ and uplift rate in rivers from New Zealand (Pogge von Strandmann and Henderson, 2015) and in rivers draining higher elevations in the Ganges (Pogge von Strandmann et al., 2017) and the Amazon (Dellinger et al., 2015). This is also supported by generally low $\delta^7\text{Li}$ observed in rivers in the High Himalayas (Huh et al., 1998a; Kısakürek et al., 2005).

In order to assess the effect of topography, the mean gradient of the watershed can be used as a general measure of the overall relief. At low slope angles ($<15^\circ$), a broad positive linear correlation has been shown between catchment slope angle and long-term erosion rate (Montgomery and Brandon, 2002). For catchments in the CSP, LAIRA and the VMR, the mean watershed gradient was calculated using a GIS-based approach as outlined in Kutscher et al. (2017), dividing the watershed length by its maximum elevation. While a meaningful watershed gradient cannot be estimated for the overall Lena, Aldan and Viliui River catchments, a watershed gradient has been estimated for the upper catchment regions draining in to the Viliui River (LR2013-62; 0.96°) and Aldan River (LR2012-13; 3.44°). Catchments of the low-lying CSP have catchment slope angles ranging from 0.24 to 1.04° . The LAIRA has catchment slope angles ranging from 0.43 to 1.65° , and rivers draining the VMR range from 0.94 to 6.34° . Both $[\text{Li}]$ and $\delta^7\text{Li}_{\text{diss}}$ show little relationship with mean watershed gradient (Fig. 3). Despite the *ca.* five degree difference in slope angles between rivers draining the low-lying LAIRA and CSP, and the VMR, there is no clear distinction between rivers draining the mountainous and the low-lying regions, with the entire range of $[\text{Li}]$ and $\delta^7\text{Li}_{\text{diss}}$ values spanning the full range of catchment slope angles. In fact, the highest $\delta^7\text{Li}_{\text{diss}}$ values observed in the Lena River watershed are from tributaries with the greatest slope angles draining the Verkhoyansk Mountain Ranges.

The lack of a trend between $\delta^7\text{Li}$ and relief in the Lena River catchment may be due to cryogenic weathering processes prevalent in regions of continuous permafrost e.g., the continual supply of fresh primary minerals due to seasonal freeze-thaw cycles, frost shattering and salt weathering (Woo, 2012), none of which are directly related to relief. The high degree of physical erosion in permafrost-dominated catchments is widespread, and not predominantly in regions of high topography as with rivers draining non-permafrost terrains (Goodfellow and Boelhouwers, 2013). Weathering rates can also be enhanced over predicted ‘inorganic’ weathering rates by organic acid weathering (Huh, 2003), and could also be a factor here.

The $[\text{Li}]$ and $\delta^7\text{Li}$ data are plotted against catchment area in Fig. 3. In general, discharge is expected to scale with increasing catchment area (Burgers et al., 2014). Whilst no trends can be seen between $[\text{Li}]$ and catchment area (except in south-facing VMR rivers, as discussed below), a broad negative trend can be seen with Li isotope composition, with greater variability observed in smaller catchments, and isotopic compositions that approach the global mean value of $\sim 23\text{‰}$ with larger catchment areas. This pattern

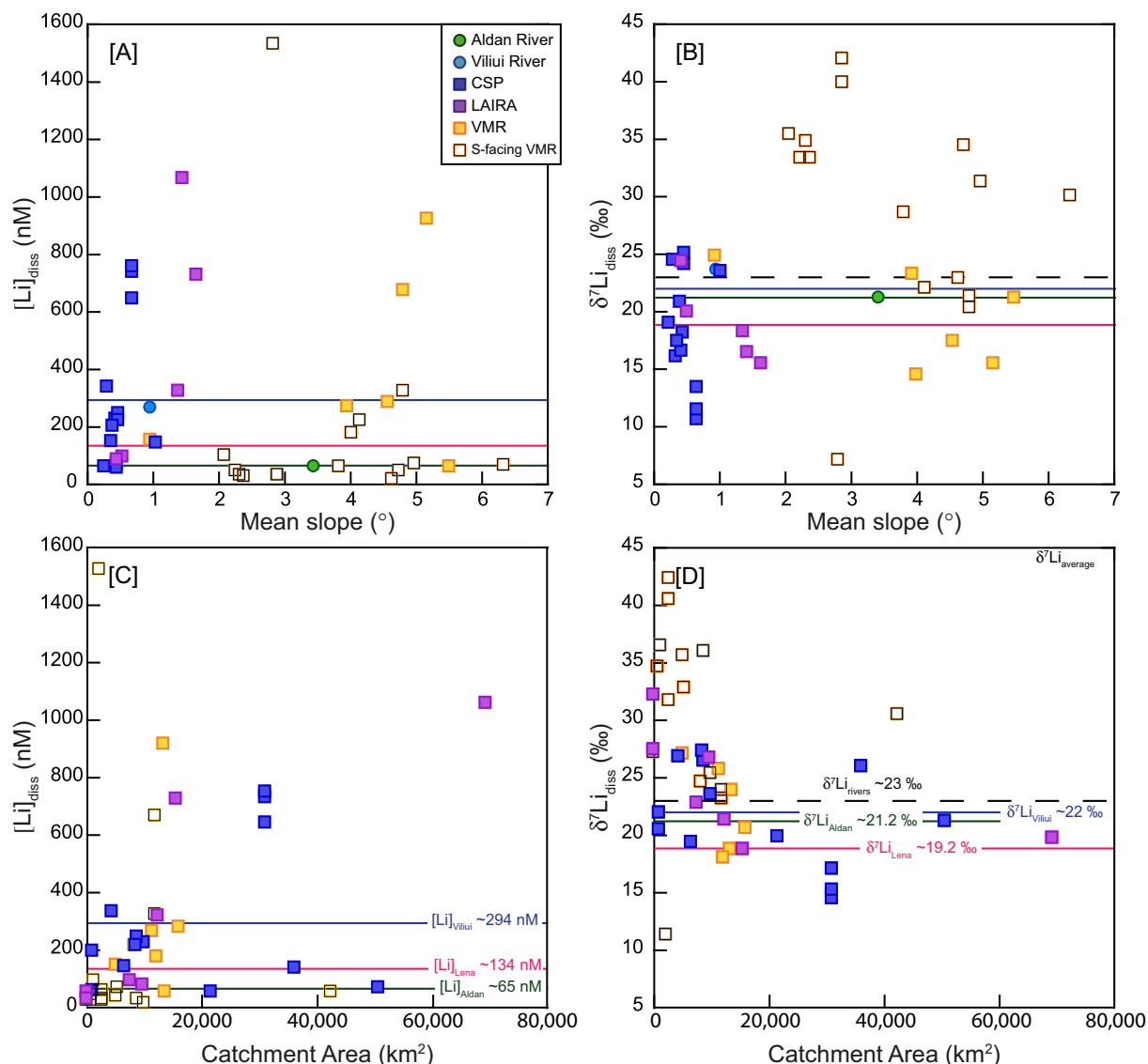


Fig. 3. Dissolved Li concentrations and $\delta^7\text{Li}$ compositions compared with watershed gradient [A, B] and catchment area [C, D] for tributaries draining the Central Siberian Plateau (CSP), Lena-Amginsky inter-river area (LAIRA) and Verkhoyansk Mountain Range (VMR) regions. The lack of trends with watershed gradient may in part be a result of the unique cryogenic physical erosion processes associated with the presence of continuous permafrost, which obscure relationships observed in rivers draining high topography in non-permafrost rivers. The greatest variation in $\delta^7\text{Li}_{\text{diss}}$ compositions is seen in smaller ($<10,000 \text{ km}^2$) catchment areas, particularly in rivers draining the south-facing catchments of the VMR (open symbols). Tributaries draining larger catchment areas tend to have $\delta^7\text{Li}_{\text{diss}}$ values closer to the global mean riverine value of 23‰ (shown as dashed line, after Huh et al. 1998a) as well as the average $\delta^7\text{Li}_{\text{diss}}$ compositions of the Lena, Aldan and Viliui Rivers (shown as solid lines in pink, green and blue respectively).

likely reflects the dominance of local processes in smaller catchments, which are homogenised and integrated in rivers draining larger catchments.

5.4. Permafrost and climatic controls on Li isotope variations

Since the Lena River watershed covers a vast area, the effects of climate on the distribution of Li isotopes can be considered. For this study, samples have been collected from a latitudinal and climate gradient from 60° to 68°N , corresponding to mean annual air temperatures (MAAT) of -6 to -15°C (Gordeev and Sidorov, 1993).

This corresponds to a range of maximum active layer temperatures, and so reaction rates for both dissolution and secondary mineral formation, as well as of depths and lengths of time of active layer thawing. To test the effects of temperature, and hence climate, $[\text{Li}]$ and $\delta^7\text{Li}_{\text{diss}}$ are shown plotted against latitude, used as a proxy for MAAT (Supplementary Fig. 5). The Lena River main channel $\delta^7\text{Li}_{\text{diss}}$ values show a weak 5‰ increase from the upper to the lower reaches ($R^2 = 0.47$) along the climate gradient. This progressive downstream increase in $\delta^7\text{Li}_{\text{diss}}$ values observed in the Lena River main channel (Fig. 4a) is also observed in the Ganges (Bagard et al., 2015) and the

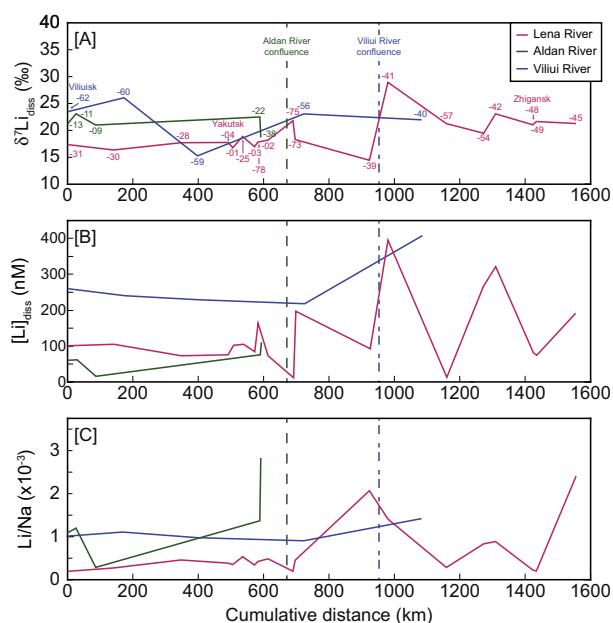


Fig. 4. Downstream variations in $\delta^7\text{Li}_{\text{diss}}$, $[\text{Li}]$ and Li/Na in the Lena River main channel, and major tributaries of the Aldan and Viliui Rivers that converge into the main channel. River sample numbers are shown adjacent to curves, and arrows indicate the downstream river location of major towns. Confluences of the Aldan and Viliui Rivers into the Lena River main channel are shown as dashed lines. See Fig. 1 for more information. No systematic trends can be observed in $[\text{Li}]$, or Li/Na . A gradual $\sim 5\%$ increase can be seen along the Lena River main channel, see text for further details.

Changjiang Rivers (Wang et al., 2015). After the confluence of the Viliui River, both Li concentrations and $\delta^7\text{Li}_{\text{diss}}$ in the Lena River main channel increase (Fig. 4). This is unlikely to be simple mixing between the two rivers, because there are no trends between $\delta^7\text{Li}_{\text{diss}}$ and $1/[\text{Li}]$ (Fig. 2). Equally, anthropogenic influences from cities such as Yakutsk and Zhigansk do not appear to influence $[\text{Li}]$ or $\delta^7\text{Li}_{\text{diss}}$. Thus, the evolution of the Lena River $\delta^7\text{Li}_{\text{diss}}$ value likely reflects Li isotope fractionation due to precipitation or interaction with secondary minerals within the river bed-load or inputs from deep groundwater into the Lena River.

Overall, there are also no clear trends in $[\text{Li}]$ and $\delta^7\text{Li}_{\text{diss}}$ values over a *ca.* nine degree latitude gradient, suggesting that variations in the MAAT, and thus climatic conditions, do not have a dominant influence on variations in $\delta^7\text{Li}$ in the Lena River catchment. This is consistent with the results for rivers in Iceland (Pogge von Strandmann et al., 2010), rivers from different climatic zones of the Cascade Mountains (Colombia River Basalts; Liu et al., 2015) and the Mackenzie River basin (Millot et al., 2010). Interestingly, the greatest variation in both $[\text{Li}]$ and $\delta^7\text{Li}_{\text{diss}}$ are observed in the south-facing slopes draining the VMR. South-facing slopes in permafrost regions are typically characterised by increased summer insolation and higher daily temperatures which contribute to more rapid thawing of snow cover, warmer soils, greater active layer depth and hence greater infiltration of melt water (Woo, 2012;

Hindshaw et al., 2018). Repeated freezing and thawing due to earlier snow melt can destabilise the soil cover, such that south-facing slopes are typically prone to greater hill-slope instability (Vasiliev, 2009; Goodfellow and Boelhouwers, 2013). This may contribute towards local variations in water flow and hence different water-rock interaction times. The lower $\delta^7\text{Li}_{\text{diss}}$ values observed in the VMR therefore likely reflect catchments dominated by lower intensity of weathering, enhanced dissolution of freshly exposed primary rock due to freeze-thaw processes and little fractionation of Li isotopes due to reduced secondary mineral precipitation or interaction with secondary minerals within the seasonally thawed active layer (i.e., a weathering-limited regime). In contrast, the much higher $\delta^7\text{Li}_{\text{diss}}$ values might reflect increased adsorption on secondary minerals, or dissolution/reprecipitation cycles due to repeated freeze-thaw cycles that promote greater water-rock interaction, significant secondary mineral formation and therefore greater Li isotope fractionation (i.e., high weathering intensity in a transport-limited regime). However, without detailed knowledge of the thermal regime in the individual catchments, it is difficult to speculate further on these processes. A detailed study of the cryogenic weathering processes occurring within a small, well-constrained river catchment draining continuous permafrost would shed some light on the relative importance of these contrasting processes.

5.5. Modelled Rayleigh fractionation factors and water residence time – Li/Na

Li and Na are both monovalent alkali metals that reside in primary silicate minerals, and are readily mobilised into solution during weathering processes. During weathering, it is assumed that Li and Na are released congruently, and the Li/Na ratio is progressively diminished by the incremental removal of Li through interaction with secondary minerals that preferentially remove ^6Li , either by adsorption onto the surface, by trapping within the interlayer (in the case of 2:1 clays), or by incorporation into the mineral structure. This in turn increases $\delta^7\text{Li}$ values and decreases Li/Na values in waters. Values for $\delta^7\text{Li}_{\text{diss}}$ are plotted against Li/Na ratios in Fig. 5, where a broad negative correlation between these two parameters is evident and similar to that observed in other river systems (Millot et al., 2010; Bagard et al., 2015; Liu et al., 2015; Wang et al., 2015).

The relationship between Li removal into secondary minerals and associated Li isotope fractionation was investigated using a modelling approach found in other studies (Pogge von Strandmann et al., 2010; Bouchez et al., 2013; Dellinger et al., 2014; Bagard et al., 2015; Pogge von Strandmann et al., 2017). The model considers water within a watershed (i.e. groundwaters and surface waters) that initially has Li/Na and $\delta^7\text{Li}$ values equal to those of weathering rocks. It is assumed that Li and Na are released together and that Li isotopes are not fractionated by dissolution processes. Lithium then is only progressively depleted in the water by incremental loss of Li (while the Li remaining in the water is well-mixed). This loss results in fractionation of Li isotopes, since Li adsorbed on, or incorporated into,

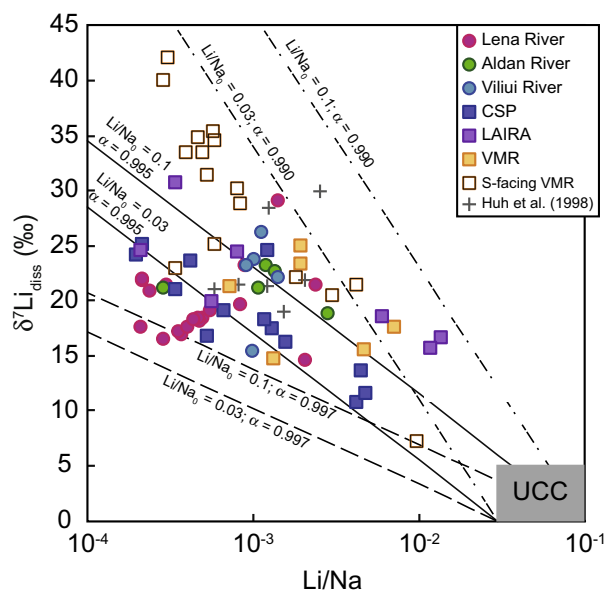


Fig. 5. Relationship between measured $\delta^7\text{Li}_{\text{diss}}$ and Li/Na molar ratios for the Lena River. Shown for comparison are Lena River data from Huh et al. (1998a). The lines represent the evolution of $\delta^7\text{Li}$ and Li/Na following a Rayleigh distillation model, in which Li is supplied to waters by dissolution of primary silicate minerals, followed by the progressive removal of Li into secondary minerals. Curves are shown for different starting values and different fractionation factors for Li removal. The grey field represents the range of values that are generally expected for dissolution of silicate rocks, with Li/Na molar ratios between the highest measured in the Lena River watershed and the composition of upper continental crust (UCC), and $\delta^7\text{Li}$ values for UCC and typical shales (Taylor and McLennan, 1995; Teng et al., 2004; Dellinger et al., 2014; Sauzéat et al., 2015). CSP = Central Siberian Plateau; LAIRA = Lena-Amginsky inter-river area; VMR = Verkhoyansk Mountain Range. Open symbols represent VMR rivers draining south-facing catchments.

secondary minerals has a lower $^7\text{Li}/^6\text{Li}$ than that of Li in the water. In this case, the value of $\delta^7\text{Li}$ of Li in the water will increase as Li/Na decreases according to a Rayleigh distillation relationship that is controlled by the fractionation factor (α) that reflects the preferential removal of ^6Li .

$$\delta^7\text{Li}_{\text{diss}} = \delta^7\text{Li}_0 + 1000(\alpha - 1)\ln(f_{\text{diss}}^{\text{Li}}) \quad (1)$$

where $\delta^7\text{Li}_{\text{diss}}$ is the Li isotope composition of the dissolved phase and $\delta^7\text{Li}_0$ is the value for Li released into the water, equal to the mean $\delta^7\text{Li}_{\text{rock}}$ of the weathered rocks. The term $f_{\text{diss}}^{\text{Li}}$ is the fraction of Li remaining in solution, calculated using the equation:

$$f_{\text{diss}}^{\text{Li}} = \frac{\text{Li}/\text{Na}_{\text{diss}}}{\text{Li}/\text{Na}_0} \quad (2)$$

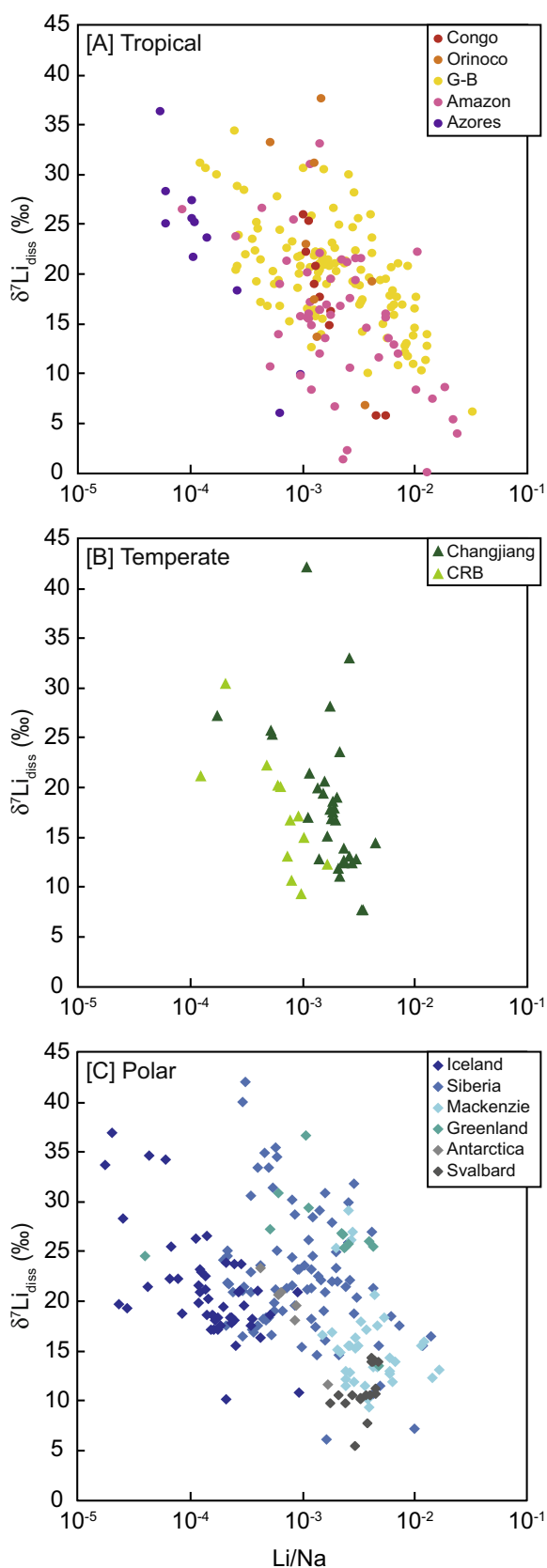
The fractionation lines represent the calculated compositions of waters subjected to different degrees of Li removal from a single starting Li/Na and $\delta^7\text{Li}$ composition. A starting isotopic composition ($\delta^7\text{Li}_0$) of 0‰ is used, which is a representative value for the average upper continental crust. Changing $\delta^7\text{Li}_0$ to values of -2 to $+5$ ‰ observed in river-

ine suspended sediments, shales and upper continental crustal rocks and basalts will result in small shifts in the model curves (not shown), although this will not substantially affect the range of fractionation factors needed to explain the range of measured compositions. The bedrock Li/Na ratio (and hence the initial ratio of Li/Na released into waters), is difficult to constrain for such a large, multi-lithological catchment and undoubtedly varies between sub-catchments and across the watershed. To account for a range of possible end-member values, a Li/Na₀ molar ratio of 0.03, equal to the highest dissolved value found in the Lena catchment area, and a value of 0.1, which is that of the upper continental crust (Taylor and McLennan, 1995) have been adopted in the model calculations. This range of initial Li/Na₀ are depicted by the grey box in Fig. 5.

The range of data within the Lena River catchment cannot be explained by a single isotopic fractionation factor. The majority of data fall within the curves for α values ranging from ~ 0.997 to 0.990 ($\Delta^7\text{Li} = -3$ ‰ and -10 ‰). However, a number of outliers (particularly for rivers draining south-facing slopes within the VMR) fall outside these α values, requiring a wider range of fractionation factors. The range of isotopic fractionation factors in Fig. 5 are consistent with experimentally determined values for various secondary minerals, including those predicted to be oversaturated within the Lena River (see Section 5.2), with $\alpha_{\text{vermiculite}} = 0.971$, $\alpha_{\text{kaolinite}} = 0.979$, $\alpha_{\text{gibbsite}} = 0.984$ – 0.993 , $\alpha_{\text{ferrihydrite}} \approx 0.998$, and $\alpha_{\text{smectite}} = 0.984$ (Zhang et al. 1998; Pistiner and Henderson, 2003; Millot and Girard, 2007; Vigier et al. 2008; Wimpenny et al. 2015). The range of α is also comparable to that those observed in other global rivers (e.g., Amazon (Dellinger et al., 2015); Ganges (Bagard et al., 2015; Pogge von Strandmann et al., 2017)). Overall, the range of fractionation factors required to explain the data reflects the complex behavior of Li in such a vast catchment. Other processes such as adsorption, precipitation in other phases, or interaction with organics, may also result in a wider variation in fractionation factors. It is likely that there are also other processes within each watershed that have caused variations in the relationship between Li/Na and $\delta^7\text{Li}$ values. For example, mixing occurs amongst different sub-surface and surface waters with different evolutionary histories and so different Li characteristics. In addition, variability may be caused by the uptake of Na into some secondary minerals (such as clays or zeolites), and/or desorption of Na from mineral surfaces in soils, thus decoupling Li/Na from $\delta^7\text{Li}$. It is not possible to distinguish whether these processes occur within the river, or is controlled by sub-surface residence time.

5.6. Comparison with global rivers

Huh et al. (1998a) also measured dissolved $\delta^7\text{Li}$ in the Lena River catchment, and several other Siberian rivers. They observed a wide range in $\delta^7\text{Li}$ values (~ 6 to 30 ‰), similar to the values observed in this study. The dissolved $\delta^7\text{Li}$ observed in the Lena River catchment (from this study and Huh et al. 1998a) overlap with those of other polar,



cold climate rivers that are underlain by continuous, discontinuous, sporadic or isolated permafrost (e.g., the Mackenzie River basin (~ 9 to 29% ; Millot et al. 2010)), Svalbard (~ 8 to 14% ; Hindshaw et al. (2018)) and Antarctic rivers (~ 12 to 23% ; Witherow et al. (2010)). They also overlap with values from glaciated and non-glaciated rivers in west Greenland that are underlain by permafrost (~ 14 to 36% ; Wimpenny et al. (2010b)), and those of rivers in Iceland that are unaffected by permafrost (Pogge von Strandmann et al. (2006); Vigier et al. (2009)).

Interestingly, the overall range in $\delta^7\text{Li}$ and Li/Na values in these cold climate, polar regions (including regions impacted by permafrost and glacial weathering processes) are similar to those found in temperate and tropical rivers (Fig. 6). It has been proposed that weathering rates are strongly controlled by temperature and hence climate (precipitation and runoff) (e.g. West et al., 2005; Gislason et al., 2009). Warmer, wetter watersheds are expected to have greater chemical weathering rates than watersheds in high latitude permafrost-dominated regions, where the cold climate and restricted water-rock and water-soil interactions are predicted to reduce the rate of chemical weathering (Huh and Edmond, 1999). Whilst Li isotopes cannot constrain the rates of silicate weathering (for a discussion, see Pogge von Strandmann et al., 2017), the magnitude of Li isotope fractionation, and hence intensity of weathering (i.e., the rate of secondary mineral formation relative to the rate of primary mineral dissolution) observed in such cold climate, polar regions is partly due to the increased availability of Li in primary minerals due to enhanced physical erosion facilitating greater chemical weathering. The unique role of cryogenic weathering processes such as repeat freeze-thaw cycles, frost shattering and salt weathering continually expose fresh primary minerals and prevents the accumulation of weathered products and development of thick soil profiles. The high degree of physical erosion,

Fig. 6. A compilation of dissolved Li isotope values versus molar Li/Na for rivers in [A] tropical, [B] temperate and [C] polar regions. Despite vastly different climatic and weathering regimes, the same range of riverine $\delta^7\text{Li}$ values globally suggests that cryogenic weathering features typical of permafrost-dominated regions and climate (temperature and runoff), are not a dominant control on $\delta^7\text{Li}$ fractionation. Data include the Lena River and other Siberian rivers (this study; Huh et al., 1998a); the Mackenzie River (Millot et al., 2003; Millot et al., 2010); Antarctic rivers (Witherow et al., 2010); Greenland (Wimpenny et al., 2010b); Svalbard (Hindshaw et al., 2016; Hindshaw et al., 2018); the High Himalayas (Huh et al., 1998a; Kısakürek et al., 2005); the Ganges-Brahmaputra (Huh et al., 1998a; Kısakürek et al., 2005; Bagard et al., 2015; Frings et al., 2015; Manaka et al., 2017; Pogge von Strandmann et al., 2017); the Amazon (Huh et al., 1998a; Dellinger et al., 2015); the Orinoco (Stallard et al., 1995, 1996; Huh et al., 1998a); the Congo (Henchiri et al., 2016); Changjiang (Yangtze) River (Huh et al., 1998a; Liu et al., 2011; Wang et al., 2015); and basalts from Iceland, the Azores and the Columbia River Basalts (Pogge von Strandmann et al., 2006; Vigier et al., 2009; Pogge von Strandmann et al., 2010; Liu et al., 2015).

together with chemical weathering in the presence of organic acids is sufficient to overcome the temperature inhibition on the mineral reaction kinetics (Huh et al., 1998c; Huh et al., 1998b; Huh and Edmond, 1999).

Global rivers are further compared in Fig. 7, which shows the frequency of dissolved Li isotope data for some of the large global rivers and rivers draining basaltic terrains. Typically, the Ganges, Lena and basalts all have similar frequency peaks, clustering around the global riverine mean of $\sim 23\text{‰}$ (Huh et al., 1998a). Rivers draining the high Himalayas have a slightly lower average value (~ 14 to 16‰), consistent with greater exposure rates of fresh rock driving the Li isotopic compositions towards crustal rock values. Interestingly, the Amazon and Mackenzie Rivers have the lightest mean values of these large datasets, of $\sim 16\text{‰}$. Hence, the mean values of these different catchments are quite similar relative to the overall variability in $\delta^7\text{Li}$ observed in rivers. This, in combination with the trends with Li/Na, further supports the conclusion that climatic controls (e.g., temperature and runoff) are weak secondary controls on Li isotopes and hence silicate weathering processes of primary rock dissolution relative to secondary mineral formation. The data therefore suggest that similar processes control global Li geochemistry in rivers from cold, temperate and tropical regions.

This has implications for the use of $\delta^7\text{Li}$ as a palaeo-weathering tracer, because it implies that the global riverine mean of 23‰ is not the result of mixing Li with a wide range of $\delta^7\text{Li}$ values in different rivers (as it is, for example, for $^{87}\text{Sr}/^{86}\text{Sr}$; Palmer and Edmond, 1989), but rather that many major rivers share a value of $\sim 23\text{‰}$, irrespective of

climate and weathering regime. This therefore suggests that in order to explain the $\delta^7\text{Li}_{\text{seawater}} \sim 9\text{‰}$ increase observed during the early Cenozoic (Hathorne and James, 2006; Misra and Froelich, 2012), the global weathering conditions would have to have significantly changed from low weathering intensity conditions imparting low riverine $\delta^7\text{Li}_{\text{diss}}$ input to the oceans, to the present day weathering conditions imparting a mean riverine $\delta^7\text{Li}_{\text{diss}}$ of 23‰ . Hence, if the global riverine $\delta^7\text{Li}$ is not principally controlled by climate, this may suggest that the Cenozoic Li curve may be more significantly controlled by changing riverine fluxes (Wanner et al., 2014), rather than isotope ratios, possibly coupled with changes associated with the removal of Li from the oceans (Li and West, 2014; Coogan et al., 2017).

6. CONCLUSIONS

In this study, we report Li data for over 70 river waters and 11 suspended sediments from the Lena River Basin, a large, complex, multi-lithological catchment underlain by continuous permafrost discharging into the Arctic Ocean. A fractionation factor (α) during weathering of between ~ 0.997 and 0.990 can explain the data for the Lena River, comparable to previously published experimental and field based values from highly disparate climates and weathering regimes. Contrary to reports from other studies from rivers in non-permafrost terrains, there are no systematic trends observed between riverine $\delta^7\text{Li}_{\text{diss}}$ and watershed mean slope angle (a proxy for erosion rate), and so between values for rivers draining the Verkhnyansk Mountain Range (VMR) when compared to those for low-lying rivers of the Central Siberian Plateau. South-facing catchments from the VMR exhibit more $\delta^7\text{Li}$ variation than other areas, likely due to the higher insolation affecting the thickness of the active layer. Cryogenic weathering processes found in permafrost-dominated regions may obscure any topographical controls on Li isotope fractionation observed in rivers draining non-permafrost.

At the basin scale, the Lena River has a remarkably similar range in $\delta^7\text{Li}$ values to global rivers from contrasting climate and weathering regimes from polar, temperate and tropical regions. Overall, temperature, the presence of permafrost, and indeed climate are weak controls on riverine Li isotope compositions, and similar processes (that is, the balance between primary silicate mineral dissolution and the preferential incorporation or adsorption of ^6Li during formation of secondary minerals) that operate in different climates control global riverine Li geochemistry. This suggests that climate changes likely will little affect the isotope composition of Li delivered to the ocean, and changing riverine flux must be considered when using sedimentary records of Li isotopes to understand changes in past weathering regimes.

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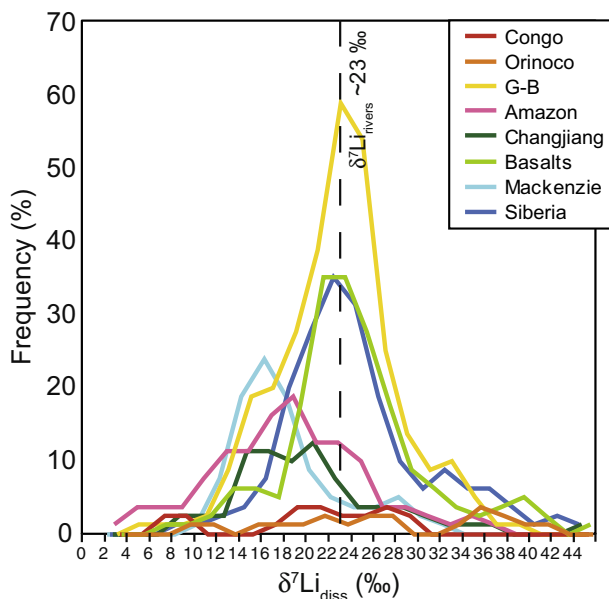


Fig. 7. A two point moving average frequency histogram (2 permil bin width) summarising dissolved $\delta^7\text{Li}$ compositions from large global rivers, and rivers draining basaltic terrains. A large peak can be seen clustering around the global median value of 23‰ (Huh et al., 1998b), with a smaller peak around ~ 14 to 16‰ . Data from same sources as Fig. 6.

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APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gca.2018.10.024>.

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