



# Lithological controls of the Mg isotope composition of the Lena River across seasons and its impact on the annual isotope flux to the Arctic Ocean

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## ABSTRACT

Given the importance of permafrost regions in providing the major elements to the Arctic Ocean, and the vulnerability of these regions to ongoing climate change due to permafrost thaw and landscape modifications, assessing the magnitude and characterizing the factors governing isotope compositions in river waters across seasons and space is of high priority.

Towards identifying possible environmental controlling factors (climate, vegetation, rock lithology) and quantifying annual fluxes of dissolved Mg isotopic signatures in large Arctic rivers located in the continuous permafrost zone, here we measured hydrochemical and Mg isotope compositions of the Lena River main channel and its various tributaries over different seasons of the year. In general, we did not find evidence of any statistically significant ( $p < 0.05$ ) correlation between  $\delta^{26}\text{Mg}$  and main physico-geographical parameters of the river watersheds (temperature, permafrost, type of vegetation). The exception is the decrease in riverine  $\delta^{26}\text{Mg}$  values that was accompanied by an increase in the carbonate rock proportion in the watershed, whereas an opposite trend was observed for the abundance of terrigenous and silicate rocks. An incontestable control of dolomite rocks on Mg isotope signature in the Lena River was also supported by decreasing  $\delta^{26}\text{Mg}$  values with increasing Dissolved Inorganic Carbon (DIC) concentration, as also observed for other Arctic River basins. This relationship was mostly pronounced during the high-flow period, when secondary Mg silicate formation in soils and underground waters and so the terrestrial uptake of Mg were the lowest. In the Lena River main channel, the lowest  $\delta^{26}\text{Mg}$  values ( $-1.5 \pm 0.05$  ‰) were observed during autumn-winter (September to March), probably reflecting a dominant role of underground reservoirs and subsurface soil weathering of isotopically light Precambrian dolomites.

The mean  $\delta^{26}\text{Mg}$  values of the Lena River during two months of spring ( $-1.02$  to  $-1.28$  ‰), 4 months of summer baseflow ( $-1.30$  ‰) and 6 months of winter yields a mean discharge-weighted annual value of  $-1.26 \pm 0.05$  ‰. This number coincides with the value of summer baseflow reported in earlier works. Therefore, like in the recently studied Yenisey River basin, the Mg isotope signature of the Lena River water likely stems from a mixture of carbonate ( $-2.0 \geq \delta^{26}\text{Mg} \geq -2.5$  ‰) and silicate ( $0 \geq \delta^{26}\text{Mg} \geq -0.2$  ‰) rocks in its watershed. We also argue that the discharge-weighted mean annual isotopic signature of an element in the Arctic rivers can be reasonably approximated by a single sampling campaign during summer baseflow. This allows cost-effective assessment of mean riverine isotopic signatures of other elements in both small and large rivers to the Arctic Ocean.

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## 1. Introduction

High latitude permafrost regions are the dominant source of major elements such as Mg to the Arctic Ocean. The vulnerability of these regions to ongoing climate change due to modifications in permafrost thawing, hydrological regime, vegetation and soil reactivity requires assessment of the magnitude and characterization of the factors governing macro-chemical compositions in river waters across seasons and space. This is even more important for isotope compositions of these rivers, because stable isotopes can be used as valuable tracers of weathering regimes and sources of elements in the river water (Pogge von Strandmann et al., 2006; Tipper et al., 2012; Mavromatis et al., 2014; Murphy et al., 2019). Furthermore, the mean isotopic ratio of riverine inputs to the ocean is crucially needed for constraining the isotope balance of the ocean (e.g. Tipper et al., 2006, 2010), interpreting paleo-reconstructions and assessing the sinks of element in the ocean such as biotic uptake or authigenic mineral formation (e.g. Huh et al., 1998b).

In the present study, we characterized the Mg isotope compositions of the Lena River and its main tributaries, which represent a catchment area with a wide variety in lithology. Among all the great Arctic rivers (Yenisey, Ob, Mackenzie) the Lena River is the most affected by

permafrost, with ~80% of its watershed territory being characterized by continuous permafrost (Brown et al., 1997). This feature of continuous permafrost coverage has been the motivation for exploring chemical and isotopic composition and weathering inputs of the Lena River in a suite of recent studies (Kutscher et al., 2017; Sun et al., 2018; Hirst et al., 2020, 2023). Owing to this difference in permafrost coverage and the controls it exerts on the annual distribution of water discharge that typically exhibits variations of two orders of magnitude between late spring flood season and summer/winter baseflow, it could be expected that permafrost would affect the distribution of  $\delta^{26}\text{Mg}$  compositions of the Lena River and its tributaries over the year. In contrast to this assumption, however, a recent work on the Yenisey River and its major tributaries argued that permafrost coverage of the catchment *per se* has no visible impact on the Mg isotope composition of river water (Mavromatis et al., 2020). In that study, it was demonstrated that, at the scale of a large watershed such as the Yenisey River, the Mg isotope signature cannot be used as a robust tool for tracing weathering mechanisms and dominant lithological impact. The present work aims to verify whether this assumption also holds true for another large Arctic river, the Lena River, which exhibits similar geomorphological but different lithological characteristics to the Yenisey River. The Lena River catchment is characterized by an extensive area ( $\sim 2.5 \times 10^6 \text{ km}^2$ ) and exhibits highly

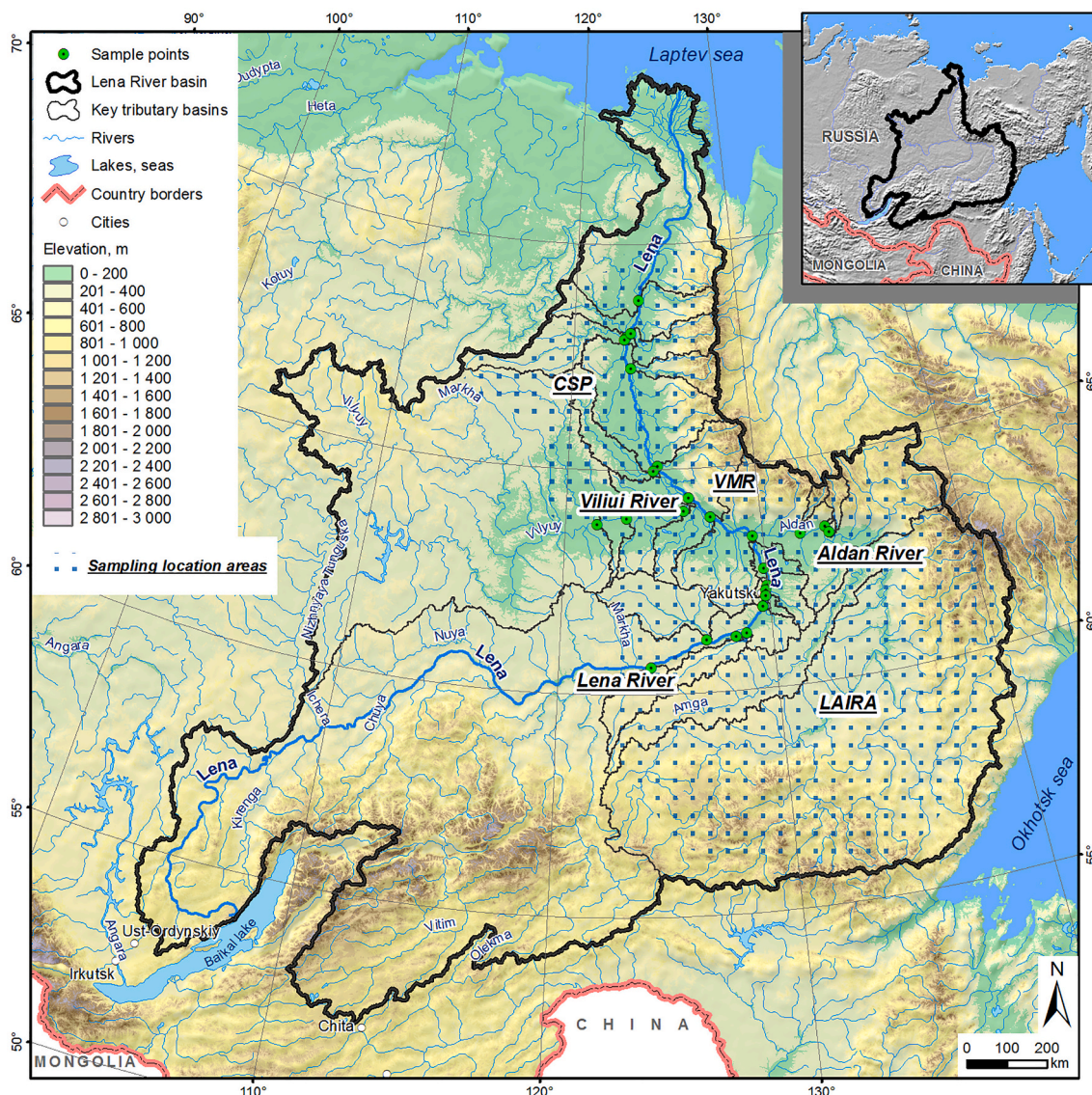


Fig. 1. Map of the area and sampling stations along the Lena River.

variable lithology, climatic conditions and vegetation types.

The only available data on the Lena River Mg isotope signature are those of [Tipper et al. \(2006\)](#), who provided a  $\delta^{26}\text{Mg}$  value of  $-1.28 \pm 0.08$  ‰ for the summer baseflow. Specific objectives in this study were to: *i*) assess the variations of Mg isotope composition between the main channel and the tributaries, *ii*) evaluate the impact of hydrochemical parameters, lithology, landscape, vegetation, permafrost and climate factors on the riverine  $\delta^{26}\text{Mg}$  composition of selected tributaries; and *iii*) provide Mg isotope compositions of Lena River during previously unknown winter baseflow and spring period and thus calculate the mean annual export flux of Mg isotopes by the Lena River to the Arctic Ocean.

## 2. Study site description

The Lena River basin is located in eastern Siberia ([Fig. 1](#)) and is one of the three great Siberian rivers, draining a watershed area of  $2.46 \times 10^6$  km<sup>2</sup>. The headwaters of the Lena River originate in the Baikal Mountains and flow northwards entering the Arctic Ocean in the Laptev Sea. The annual freshwater contribution of the Lena River to the Arctic Ocean is ~18% of the total riverine Eurasian input and it follows a pattern similar to that observed in other permafrost-affected Siberian rivers. About 30–40% of the annual water flux is provided by the spring

flood that occurs in late May and June ([Ye et al., 2003](#)). The watershed of the Lena River is characterized by continuous permafrost in all the regions north of 60°N, with thicknesses that vary between 50 and 1500 m ([Brown et al., 1997](#); [Chevychev and Bosikov, 2010](#)). The active layer thaws seasonally with a depth that varies from a few centimeters to several meters ([Huh et al., 1998a](#)). A detailed geological description of the Lena Basin is provided by [Huh et al. \(1998a\)](#) and [Huh and Edmond \(1999\)](#). Briefly, the Lena River flows over the Central Siberian Plateau (CSP), which is underlain by Proterozoic crystalline and metamorphic basement of the stable Siberian Platform. The CSP is characterized by extensive flood basalts and various sediments consisting of Precambrian to Quaternary marine carbonates and evaporites, along with terrigenous sandstone, shale, red beds, and coal beds.

The total watershed area of the rivers sampled in this work represents 95% of the entire Lena River basin. The mean annual air temperatures (MAAT) range from  $-5.2$  °C in the southern part of the basin to  $-9.0$  °C in the central part of the basin. The range of MAAT for 20 tributaries is from  $-7.2$  to  $-17.0$  °C. The mean annual precipitation (MAP) ranges from 350 to 500 mm y<sup>-1</sup> in the southern and southwestern part of the basin to 200–250 mm y<sup>-1</sup> in the central and northern parts ([Chevychev and Bosikov, 2010](#)). For the entire Lena basin, the mean MAAT is  $-9.7 \pm 3.2$  °C and the MAP is  $383 \pm 83$  mm y<sup>-1</sup>.

**Table 1**

Sampling stations, Mg, Ca and alkalinity concentrations and Mg isotope compositions of samples reported in this study.

Sample		Sampling date	Latitude	Longitude	Mg (μM)	Ca (μM)	Alk (μEq)	$\delta^{26}\text{Mg}$	2σ	$\delta^{26}\text{Mg}$	2σ
LR2012-01	Lena	12/07/2012	62.2626	130.0172	108	225	440	-0.70	0.02	-1.36	0.03
LR2013-49	Lena	16/06/2013	67.9291	123.0021	157	222	295	-0.65	0.00	-1.23	0.04
LR2015-122	Lena	28/05/2015			154	352	600	-0.69	0.02	-1.30	0.05
LR2015-86	Lena	06/05/2015			502	856	1700	-0.68	0.05	-1.31	0.07
LR2015-93	Lena	08/05/2015			180	369	1500	-0.64	0.01	-1.26	0.05
LR2015-96	Lena	14/05/2015			185	379	700	-0.65	0.03	-1.24	0.02
LR2012-02	Lena	12/07/2012	63.3879	129.5393	97	207	418	-0.67	0.07	-1.30	0.05
LR2012-04	Lena	14/07/2012	62.1577	129.9080	111	222	453	-0.55	0.03	-1.08	0.05
LR2012-25	Lena	22/07/2012	62.6492	129.9074	110	229	484	-0.71	0.02	-1.33	0.02
LR2013-45	Lena	15/06/2013	68.7433	123.9966	177	211	660	-0.66	0.01	-1.26	0.01
LR2013-57	Lena	21/06/2013	65.0511	124.8055	160	259	696	-0.75	0.00	-1.45	0.02
LR2013-71	Lena	27/06/2013	63.8859	127.5421	147	236	705	-0.72	0.01	-1.41	0.04
LR2013-79	Lena	16/09/2012			261	577	1180	-0.77	0.06	-1.50	0.06
LR2013-80	Lena	19/10/2012			289	652	1167	-0.79	0.03	-1.52	0.07
LR2013-81	Lena	21/11/2012			358	822	1692	-0.78	0.01	-1.50	0.07
LR2013-82	Lena	21/12/2012			464	1011	2107	-0.77	0.05	-1.50	0.08
LR2013-83	Lena	20/01/2013			248	547	1042	-0.80	0.03	-1.51	0.05
LR2013-84	Lena	28/02/2013			653	1381	2995	-0.80	0.07	-1.53	0.08
LR2013-85	Lena	21/03/2013			606	1319	3292	-0.83	0.01	-1.60	0.02
LR2013-40	Viliui	13/06/2013	64.3280	126.3720	207	316	875	-0.53	0.02	-1.03	0.03
LR2013-60	Viliui	23/06/2013	63.9089	123.1457	161	252	718	-0.51	0.01	-0.97	0.02
LR2013-62	Viliui	23/06/2013	63.7582	121.5983	167	222	708	-0.52	0.05	-0.99	0.04
LR2013-66	Viliui	24/06/2013	64.0530	126.0691	163	205	717	-0.47	0.01	-0.90	0.03
LR2012-36	CSP	28/07/2012	61.1680	126.8677	295	537	1638	-0.46	0.06	-0.86	0.10
LR2013-50	CSP	16/06/2013	67.8763	123.0364	156	308	728	-0.72	0.08	-1.38	0.02
LR2013-55	CSP	21/06/2013	64.9520	124.5963	98	166	463	-0.54	0.08	-1.04	0.01
LR2012-11	Aldan	18/07/2012	62.7106	134.6952	179	310	740	-0.75	0.04	-1.46	0.04
LR2012-06	VER	16/07/2012	63.3209	131.9309	178	737	808	-0.72	0.03	-1.38	0.03
LR2012-07	VER	17/07/2012	63.2044	133.2340	192	531	657	-0.66	0.02	-1.26	0.09
LR2012-19	VER	20/07/2012	63.3859	133.1369	57	149	246	-0.48	0.04	-0.92	0.10
LR2013-47	VER	16/06/2013	68.0216	123.4151	238	254	604	-0.45	0.01	-0.86	0.01
LR2013-51	VER	17/06/2013	67.2521	123.4084	222	407	698	-0.60	0.01	-1.18	0.04
LR2012-12	LAIRA	19/07/2012	62.6147	134.9229	834	823	2834	-0.81	0.02	-1.53	0.09
LR2012-27	LAIRA	24/07/2012	61.2510	128.7695	780	915	3387	-0.85	0.03	-1.67	0.05
LR2012-33	LAIRA	27/07/2012	60.5937	124.2726	588	866	2732	-0.79	0.02	-1.50	0.08
LR2012-37	LAIRA	29/07/2012	61.1946	128.2840	994	801	3548	-0.68	0.01	-1.29	0.03
DSM3								-0.01	0.03	0.02	0.04
CAM-1								-1.33	0.04	-2.62	0.08
OUMg								-1.42	0.05	-2.81	0.07
IAPSO								-0.42	0.02	-0.82	0.04
JD0-1								-1.24	0.06	-2.42	0.06

Further description of the Lena River basin landscapes, vegetation and lithology can be found elsewhere (Rachold et al., 1996; Huh and Edmond, 1999; Pipko et al., 2010; Semiletov et al., 2012; Kutscher et al., 2017; Juhls et al., 2020). The annual water discharge exhibits peaks that are latitude dependent and occurs in May in the south (Ust-Kut) and in June in the middle and low reaches of the Lena River (Yakutsk, Kuysyr). At the Kuysyr station the peak of discharge is 140,000–160,000 m<sup>3</sup>/s, the winter baseflow discharge is 2000–3000 m<sup>3</sup>/s, and the summer baseflow discharge is 20,000–40,000 m<sup>3</sup>/s (Yang et al., 2002; Ye et al., 2003, 2009; Berezovskaya et al., 2005; Smith and Pavelksky, 2008; Gelfan et al., 2017; Gautier et al., 2018; Suzuki et al., 2018; Ahmed et al., 2020).

### 3. Methodology

#### 3.1. Field sampling

The samples used in this study and the methods utilized during sampling are described in detail by Hirst et al. (2017) and Kutscher et al. (2017). River water samples were collected over three campaigns (July 2012, June 2013 and May 2015), across the Lena River and Yakutsk, as detailed in Table 1. Water samples were collected in acid-washed 10 L low density polyethylene (LDPE) bottles and filtered within a few hours through 0.22 µm nitrocellulose filters (pre-washed with 5% HCl and ultrapure Milli-Q water). At each sampling locality, pH, temperature and electrical conductivity were measured in-situ.

In this study, the geographical subdivision of rivers follows the same group categories presented earlier by Kutscher et al. (2017) and Murphy et al. (2019): (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

Filtered solutions for cations and trace element analyses were acidified (pH = 2) with ultrapure double-distilled HNO<sub>3</sub> and stored in HDPE bottles previously washed with 1 M HCl and rinsed with deionized water. Filtered water samples for anions were not acidified and stored without headspace in air-tight HDPE hermetic bottles previously washed according to the above-described procedure for cations. The major anion concentrations (Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were analyzed by ion chromatography (Dionex 2000i), with an uncertainty of 2%. The Dissolved Organic Carbon (DOC) and Dissolved Inorganic Carbon (DIC) were determined by a Shimadzu TOC-VSCN Analyzer with an uncertainty of 3% and a detection limit of 0.1 mg/L. The major and trace elements were measured by quadrupole ICP-MS (7500ce, Agilent Technologies).

#### 3.3. Magnesium isotope analyses

The separation of the Mg from the matrix elements in the water samples followed the protocol described by Mavromatis et al. (2014) using AG50W-X12 resin. After Mg separation, samples were evaporated to dryness and re-dissolved in 0.35 M HNO<sub>3</sub>. The recovery of Mg processed through cation-exchange chromatography was better than 99%. Magnesium isotope ratios were measured using a Thermo-Finnigan 'Neptune' Multi Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at the Observatoire Midi Pyrenees (OMP) facilities (Geosciences Environment Toulouse - GET laboratory, Toulouse, France). All samples were prepared in 0.35 M HNO<sub>3</sub> and introduced into the Ar plasma with a large stable introduction system spray chamber (double Scott Cyclonic spray chamber). Instrumental mass fractionation effects were corrected by standard-sample-standard bracketing, and all results are presented in delta notation relative to the DSM3 reference

material as  $\delta^x\text{Mg} = ((^x\text{Mg}/^{24}\text{Mg})_{\text{sample}} / (^x\text{Mg}/^{24}\text{Mg})_{\text{DSM3-1}}) \times 1000$  where x refers to either the mass 25 or 26. Only mass 26 is considered hereafter, but  $\delta^{25}\text{Mg}$  values are reported in Table 1 for quality control. All results are consistent with mass-dependent fractionation, exhibiting a slope of 0.514 in a  $\delta^{25}\text{Mg}$  vs.  $\delta^{26}\text{Mg}$  plot. The reproducibility of the Mg isotope analyses, assessed by replicate analyses of the mono-elemental DSM3, CAM-1 and OUMg Mg reference standards and was typically better than 0.08‰ (Table 1). The Mg isotope composition of mono-elemental reference materials were in agreement with values previously published from this laboratory (e.g., Mavromatis et al., 2012, 2013; Beinlich et al., 2014, 2018) as well as from other laboratories (Geske et al., 2015; Riechelmann et al., 2016, 2018; Mavromatis et al., 2017; Bolou-Bi et al., 2009; Wombacher et al., 2009). Finally, the reproducibility of chromatographic separation was assessed by repeated analyses of selected samples and the total procedural process of JDo-1 (dolomite) and IAPSO seawater (see Table 1). For the  $\delta^{26}\text{Mg}$  value the reproducibility was better than 0.08‰ (2σ).

#### 3.4. Landscape parameters and water surface area of the Lena basin

The physico-geographical characteristics of the Lena main channel and tributaries were obtained from an available digital elevation model (DEM GMTED2010), as well as soil, vegetation, lithological, and geo-cryological maps. The landscape parameters were assigned using TerraNorte Database of Land Cover of Russia (Bartalev et al., 2011). This included various type of forest (evergreen, deciduous, needleleaf/broadleaf), grassland, tundra, wetlands, water bodies and other area. The climate and permafrost parameters of the watershed were obtained from CRU grid data (1950–2016) (Harris et al., 2014) and NCSCD data (Hugelius et al., 2013; Bolin Centre for Climate Research, Stockholm University, 2018), respectively, whereas the biomass and soil OC content were obtained from BIOMASAR2 (Santoro et al., 2010) and NCSCD databases. The lithology of the catchments was retrieved from a GIS version of the Geological map of the Russian Federation (scale 1:5,000,000, <http://www.geolokarta.ru/>). This provided quantitative coverage of the river catchment by different type of rocks. To test the effect of main rocks on dissolved C parameters, we distinguished between acidic crystalline, terrigenous silicate rocks and dolostones and limestones of upper Proterozoic, Cambrian and Ordovician age.

The Pearson rank order correlation coefficients ( $R_p$ ,  $p < 0.05$ ) and linear regressions ( $p < 0.05$ ) were used to determine the relationships between  $\delta^{26}\text{Mg}$  composition and climatic, lithological and landscape parameters of the Lena River main stem and tributaries.

## 4. Results and discussion

#### 4.1. Magnesium geochemistry in the river water

Sampling location and date, together with Mg concentration and Mg isotope composition of each sample can be found in Table 1. Other major elemental data (i.e. Ca, K, Na, Si, Sr) are provided in Table S1 of the Supplementary Material. The Mg concentrations in riverine samples from the Lena River and its tributaries range between 54 and 653 µmol L<sup>-1</sup>. A similar range of concentrations has been observed in the Yenisey River, which also partially drains the CSP (e.g. Mavromatis et al., 2020). The contribution of major elements in the Lena River waters and tributaries from carbonate and/or silicate rock sources (e.g. Gaillardet et al., 1999) was assessed with the aid of Mg vs. Ca concentration plots of riverine waters normalized against the sum of Na and K. The obtained results exhibit a linear trend for all samples (except for two tributaries) as can be seen in Fig. 2. This linear trend is consistent with mixing of two or more end-members. A similar model of two end-member mixing has been proposed earlier to explain the chemical composition of other Siberian rivers (e.g. Bochkarev, 1959; Alekin, 1970; Pokrovsky et al., 2006). According to this model, two major processes contribute solutes in riverine waters in catchments that are affected partially or in total by

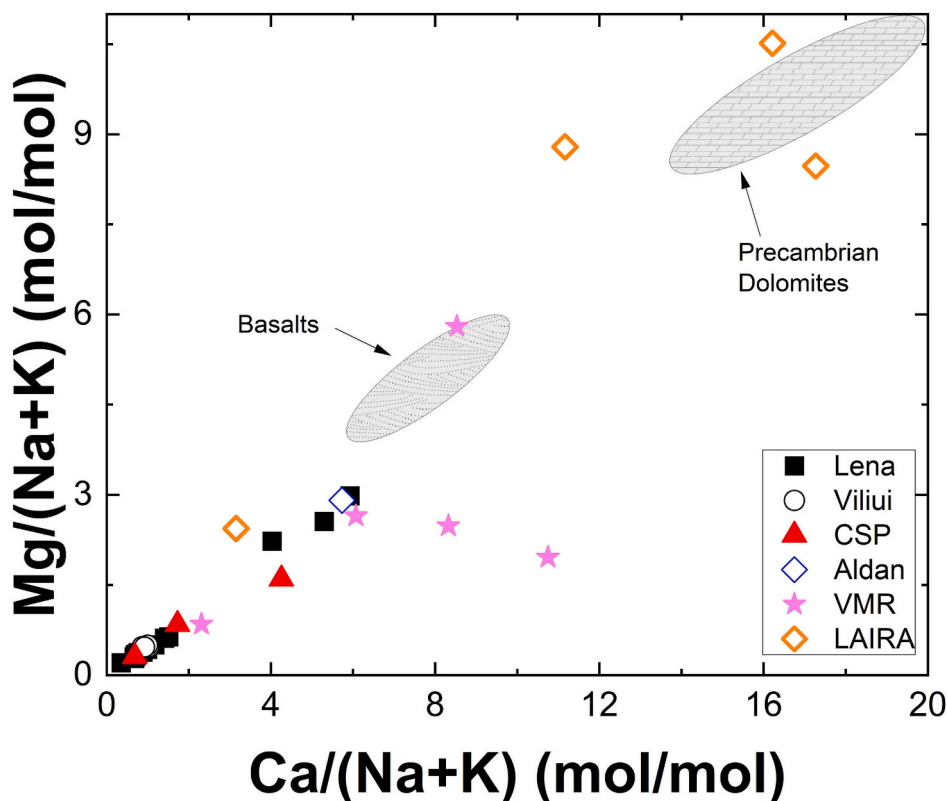


Fig. 2. Diagram of Mg. Vs. Ca normalized to Na + K concentrations in river water samples of this study.

permafrost. These are 1) leaching of the surface organic-rich soil layer, including plant litter, and 2) the dissolution of minerals and rocks (e.g. Precambrian dolomites, marine evaporitic carbonates and basalts) that occurs in unfrozen water reservoirs in depths that are not affected by permafrost and are fed to the rivers via taliks (Anisimova, 1981; Bagard et al., 2011, 2013). The partial contribution of those two reservoirs varies over the year, being controlled by the connectivity between groundwater reservoirs and surface waters. In general, it is expected that topsoil and plant litter leaching dominates during the early spring, whereas the underlying mineral soil horizons are more reactive at the end of the summer when the thickness of the thaw layer is at its maximum; the weathering of the rock basement is most pronounced during winter baseflow.

#### 4.2. Isotopic signatures and their correlation with physico-geographical and hydrochemical parameters

The Mg isotope composition of riverine samples span a range of  $\sim 0.8\text{‰}$ , with the lower measured value of  $-1.67\text{‰}$  recorded in Buotama, a LAIRA tributary whose geology is dominated by  $>97\%$  carbonate rocks. The higher  $\delta^{26}\text{Mg}$  signal of  $-0.86\text{‰}$  was recorded in the Menkere River, a tributary of VMR whose geology is mainly terrigenous. Notably, all four LAIRA tributaries analyzed in this study for their  $\delta^{26}\text{Mg}$  composition exhibited generally  $^{24}\text{Mg}$ -enriched values consistent with the predominance of carbonate rock dissolution in the catchment. The  $\delta^{26}\text{Mg}$  values did not exhibit statistically significant (at  $p < 0.05$ ) correlations with most of watershed physico-geographic parameters, including the basin area, MAAT, % of forest, wetland and tundra on the watershed (Table S2). The same observation holds true for most lithological compositions with the exception of watersheds draining carbonate-dominated rocks and terrigenous rocks. Indeed, a decrease in riverine  $\delta^{26}\text{Mg}$  value is accompanied by an increase in the carbonate rock proportion in the watershed (Fig. 3A), whereas an opposite trend was observed for the relative abundance of terrigenous rocks (Fig. 3B).

The other chemical and isotopic parameters of the river water that are known to be useful for tracing specific weathering processes, the sources of dissolved solutes, and secondary mineral precipitation in soil or sedimentary fluids, such as Si concentrations, Ca/Si ratios, radiogenic Sr or stable Li isotopic compositions, did not exhibit statistically significant associations with  $\delta^{26}\text{Mg}$  values in the Lena River main channel and its tributaries, as illustrated in Figs. S1 – S4, likely because more and/or different sources of Li and Sr affect the chemical and isotopic composition of these elements in the waters of Lena river (e.g. Murphy et al., 2019).

#### 4.3. Lithological and permafrost control of river water Mg isotopic signatures

In contrast to the main working hypothesis of the present study, the similarity of mechanisms controlling  $\delta^{26}\text{Mg}$  in the Yenisey and Lena rivers, the measured  $\delta^{26}\text{Mg}$  values of the Lena River and tributaries exhibited a good correlation ( $R_p = 0.7$   $p < 0.05$ ) with the lithological occurrences of carbonate and terrigenous rocks within the river watersheds (Fig. 3 A, B). This effect can be assigned to the presence of Mg-bearing carbonates (i.e. magnesite and dolomite) of Precambrian age that are abundant in the upper reaches and middle course of the Lena River, and much less present in the Yenisey basin. These carbonate rocks exhibit  $\delta^{26}\text{Mg}$  values ranging from  $-1.5$  to  $-2.2\text{‰}$  (Pokrovsky et al., 2011) and are capable of directly affecting the Mg isotope compositions of rivers of the SW part of the basin and the LAIRA region which obtained  $\delta^{26}\text{Mg}$  compositions of  $-1.3 \geq \delta^{26}\text{Mg} \geq -1.7\text{‰}$ . In contrast, the terrigenous rocks are typically depleted in  $^{24}\text{Mg}$ , having Mg isotope compositions of  $-0.3 \pm 0.1\text{‰}$ . It thus can be argued that similar to the recently studied Yenisey River basin, the Mg isotope signature of the Lena River water likely stems from a mixture of carbonate ( $-2.0 \geq \delta^{26}\text{Mg} \geq -2.5\text{‰}$ ) and silicate ( $0 \geq \delta^{26}\text{Mg} \geq -0.2\text{‰}$ ) rocks in its watershed. Generally, the predominant control of carbonate rock lithology on riverine Mg isotopic ratio has been shown to be present in

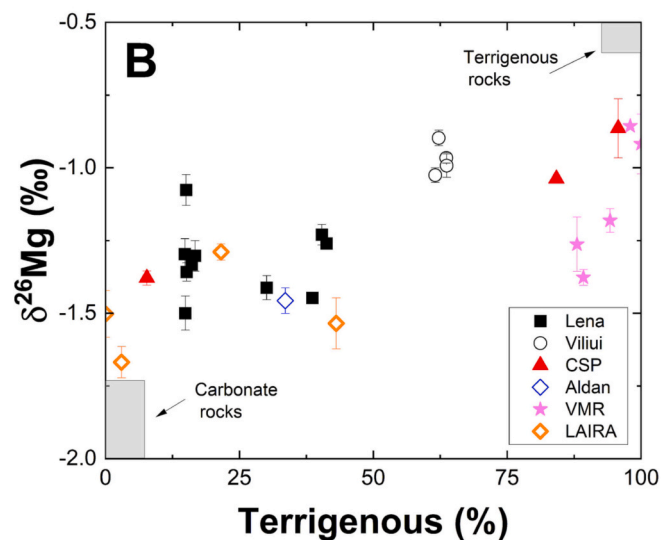
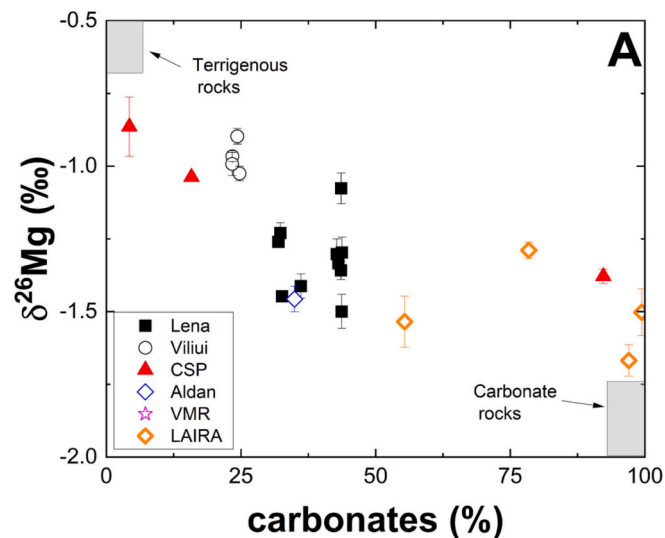


Fig. 3. Riverine  $\delta^{26}\text{Mg}$  compositions versus the percentage of watershed covered with A) carbonates (Pokrovsky et al., 2011) and B) terrigenous rocks (Mavromatis et al., 2014).

major riverine systems (i.e., Xu et al., 2022; Zhao et al., 2022).

Towards the presence of two reservoirs mainly affecting the Mg isotope compositions of the Lena River and its tributaries points also the good correlation of riverine  $\delta^{26}\text{Mg}$  values against the inverse of Mg concentration (Fig. 4A). Such a trend can be indicative of at least two sources with distinctively different  $\delta^{26}\text{Mg}$  compositions as it is demonstrated for Mg and/or  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in other riverine systems (see Zhang et al., 2021; Ruan and Galy, 2021). Note however, that the observed binary mixing does not necessarily exclude the mixing of several endmembers, as previously suggested for the Mackenzie Basin (Tipper et al., 2012). On the other hand, the  $\delta^{26}\text{Mg}$  compositions of basalts (i.e.  $-0.25\text{‰}$ ), granites (i.e.  $-0.3\text{‰}$ ) and plant litter (i.e.  $-0.25 \geq \delta^{26}\text{Mg} \geq -0.7\text{‰}$ ) are very similar (see Mavromatis et al., 2014). Although based solely on trends shown in Fig. 4A, one cannot quantitatively discriminate the major Mg sources in riverine waters, the dominating effect of lithology can be assessed with the aid of correlation ( $R^2 = 0.41$ ,  $p < 0.05$ ) between  $\delta^{26}\text{Mg}$  values of riverine waters and alkalinity (DIC) concentrations (Fig. 4B). It can be seen from this figure that the samples exhibiting the highest alkalinity are those with the highest  $^{24}\text{Mg}$  enrichment. Although silicate rock weathering and plant

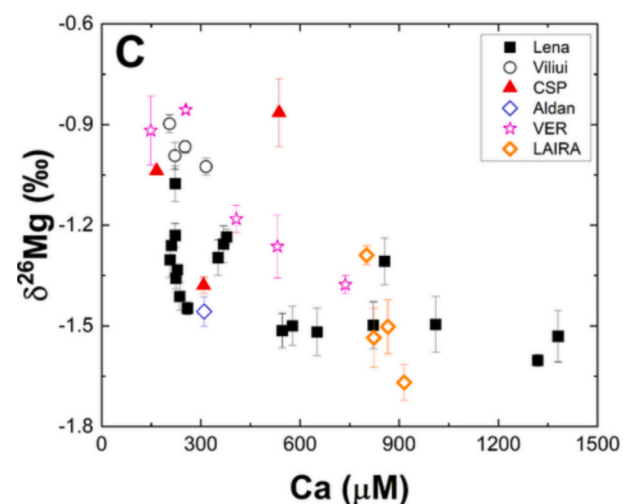
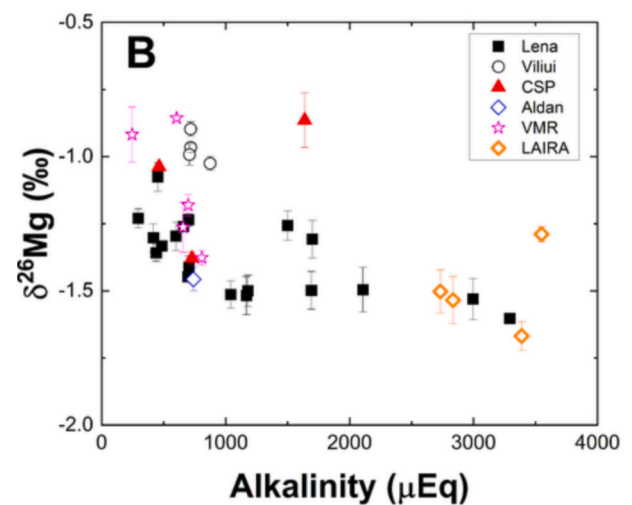
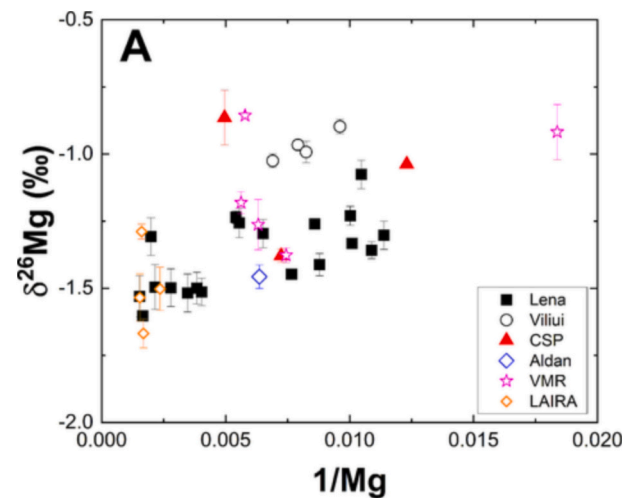


Fig. 4. Riverine  $\delta^{26}\text{Mg}$  compositions versus A) the inverse of dissolved Mg concentrations for rivers in the Lena River watershed, B) the alkalinity concentration and C) the dissolved Ca concentrations.

litter degradation are equally capable of delivering Mg to the river water (Pokrovsky et al., 2006), these processes add relatively little DIC to the river compared to Precambrian carbonate rock dissolution (Mavromatis et al., 2014). The waters originating from the latter source are likely to exhibit  $\delta^{26}\text{Mg}$  ranging from  $-1.5$  to  $-2.2\text{‰}$  (Pokrovsky et al., 2011). Calcium delivery to the Lena River water is primarily controlled by dissolution of both limestones and dolomites (Vorobyev et al., 2021a, 2021b), whereas it is essentially dolomites that control the Mg isotope composition of riverine water. Indeed,  $\delta^{26}\text{Mg}$  values decrease with an increase in Ca concentration (Fig. 4 C), although this dependence is much less pronounced ( $R^2 = 0.3$ ,  $p < 0.05$ ) compared to that between  $\delta^{26}\text{Mg}$  and DIC.

A general negative correlation between  $\delta^{26}\text{Mg}$  values and increasing water alkalinity in river water up to  $2000 \mu\text{Eq}$  during high flow period is illustrated for the Mackenzie River, Yenisey and its tributaries (Fig. 5). It is important to note that the trend is most pronounced during high water season, whereas the samples of winter and summer baseflow did not demonstrate significant (at  $p < 0.05$ ) dependence (not shown). We interpret this signal as a seasonal effect occurring only at high flow period. These conditions allow both carbonate and silicate sources to be pronounced, without the effect of secondary Mg-bearing mineral precipitation (Pokrovsky et al., 2005; Bagard et al., 2011; Mavromatis et al., 2020). The latter can occur either in soils, during silicate weathering and secondary smectite or amorphous Mg silicate formation, as it is known in basalt settings (e.g., Pokrovsky et al., 2005 and references therein), or within the groundwater reservoirs, when they mostly feed the river during winter baseflow.

A recent study (Cai et al., 2022) demonstrated a buffering effect of the exchangeable fraction in regolith (soil and saprolite) on riverine Mg isotope signatures in a temperate forested watershed underlain by paragneiss. Although there is no regolith in the Lena basin, due to relatively weak weathering of felsic rocks in harsh and rather dry climate, a potential buffering effect of other secondary phases cannot be excluded. This process can partially contribute to the decrease of the magnitude of Mg isotope variations across seasons compared to pure end member primary silicate – carbonate weathering signals.

The precipitation of secondary Mg-bearing carbonate minerals is known to significantly enrich the solid phase in lighter Mg isotopes relative to remaining fluid ( $-1.0 < \Delta^{26}\text{Mg}_{\text{solid-liquid}} < -3.2\text{‰}$ ; see e.g. Mavromatis et al., 2013; Harrison et al., 2021). In contrast, Mg-bearing silicates exhibit a smaller enrichment or depletion in  $^{24}\text{Mg}$  compared to

forming fluid (i.e.,  $\leq 0.3\text{‰}$ ; Opfergelt et al., 2012; Tipper et al., 2012; Wimpenny et al., 2014; Oskierski et al., 2019; Hindshaw et al., 2020). Furthermore, some uptake of Mg by growing vegetation (during summer) also leads to relative enrichment of the biomass in heavier Mg isotopes (e.g. Bolou-Bi et al., 2010; Kimmig et al., 2018; Uhlig et al., 2022). Therefore, rivers draining variable lithology, when sampled during baseflow seasons, are likely to show very complex Mg isotope pattern, reflecting, on the one hand, a mixture of isotopically heavy silicates and isotopically light carbonates, and, on the other hand, various processes of abiotic (and, partially, biotic) uptake of lighter Mg isotopes and enrichment of remaining fluid in heavier isotopes. In contrast, during high flow when the ratio of fluid to solid at the river catchment is at its maximum, the surface waters are strongly undersaturated with respect to secondary Mg-bearing minerals (e.g. Pokrovsky et al., 2015; Mavromatis et al., 2014). During this season there is no Mg precipitation during weathering and biological uptake into the biomass of growing vegetation (i.e., Mavromatis et al., 2014) is also negligible. During this period, the river water reflects a mixture of two main endmembers – carbonate and silicate rocks considering that, similar to other regions in permafrost dominated areas, during high-flow periods the influence of deep underground waters is minimal.

#### 4.4. Mean annual flux of Mg isotopes in the Arctic Ocean

For assessing mean annual values of discharge-weighted isotopic flux, we can use an approach elaborated for other Arctic rivers (i.e., Mavromatis et al., 2016) which approximates the annual value by a sum of discharge-normalized spring flood, summer baseflow and winter period. In the Lena River, the 2 months of spring (May–June), 4 months of summer (July–October) and 6 months of winter (November to April) provided  $216$ ,  $306$  and  $59 \text{ m}^3/\text{s}$  of total annual discharge of  $581 \text{ m}^3/\text{s}$  (Holmes et al., 2012). Considering the mean values of  $\delta^{26}\text{Mg}$  during spring, summer and winter ( $-1.28 \pm 0.03$ ,  $-1.31 \pm 0.26$  and  $-1.52 \pm 0.04\text{‰}$ ) measured in this study, the mean annual discharge-weighted  $\delta^{26}\text{Mg}$  value amounts to  $-1.31 \pm 0.05\text{‰}$ . Given that the spring time the mean  $\delta^{26}\text{Mg}$  value in the tributaries is somewhat lower than that in the main channel ( $-1.02 \pm 0.17\text{‰}$ ), we prefer our annual value of  $\delta^{26}\text{Mg} = -1.26 \pm 0.05\text{‰}$ .

A noticeable result is that, despite the great importance of the Lena River in covering a permafrost region, and contrary to initial expectations, the  $\delta^{26}\text{Mg}$  value is not sensitive to most environmental factors. Indeed, our new Mg isotope dataset that includes  $\delta^{26}\text{Mg}$  measurements of the Lena river main channel and its major tributaries during summer and winter base flow and spring flood does not demonstrate significant variations across highly contrasting hydrological seasons. In fact, the mean annual discharge-weighted  $\delta^{26}\text{Mg}$  value in the Lena River coincides with the summer-period  $\delta^{26}\text{Mg}$  ( $-1.28 \pm 0.08\text{‰}$ ) presented by Tipper et al. (2006). This corroborates the previous estimations for the  $\delta^{26}\text{Mg}$  in the Yenisey River ( $-1.13 \pm 0.02\text{‰}$  in summer (August) and  $-1.25 \pm 0.15\text{‰}$  mean annual; Mavromatis et al., 2020). Therefore, a suitability of single-month approach for assessing the annual isotopic fluxes agrees with recent results on concentration and fluxes of major and trace elements in other Arctic Rivers (Pechora, Taz, Severnaya Dvina): mean August-period values can reasonably ( $\pm 20\%$ ) approximated by a single, summer baseflow campaign (Chupakov et al., 2023; Pokrovsky et al., 2022).

Together with a few available values for other large Arctic rivers such as Yenisey ( $-1.25 \pm 0.15\text{‰}$ ), Mackenzie ( $-1.4 \pm 0.1\text{‰}$ ) and smaller ones of N. America ( $-1.35\text{‰}$  for the Red River;  $-1.15 \pm 0.10\text{‰}$  for the Liard River; Tipper et al., 2012), we argue that the mean Mg isotope riverine discharge to the Arctic Ocean is between  $-1.0$  and  $-1.5\text{‰}$  which is slightly lower than that of the mean global river runoff ( $-1.09\text{‰}$ , Tipper et al., 2006). Missing in these estimations, however, are mid-size Eastern Siberian, European Arctic rivers and the Ob River, which provide as much as 35% of annual Eurasian freshwater discharge to the Arctic Ocean. To provide a first-order estimation of these rivers,

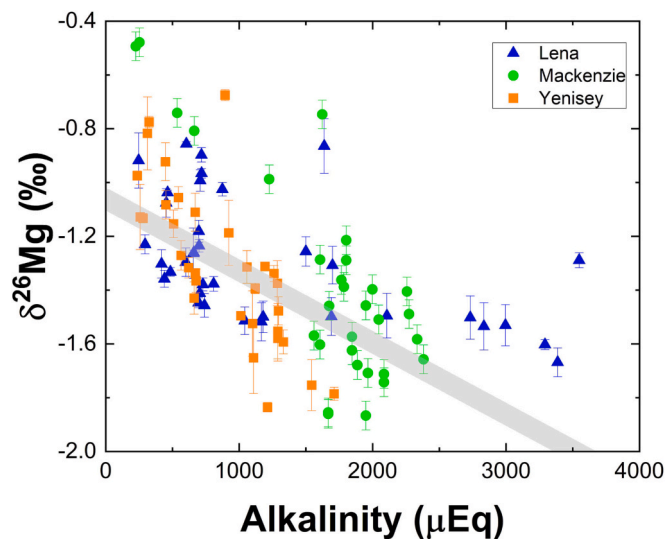


Fig. 5. Riverine  $\delta^{26}\text{Mg}$  compositions versus alkalinity for major Arctic rivers, Lena (This study), Yenisey (Mavromatis et al., 2016) and Mackenzie (Tipper et al., 2012; Millot et al., 2003) during the late spring-early summer flood period. The linear regression line has been constructed using Eq. (1).

we used mean multi-annual values of  $\text{HCO}_3^-$  concentrations (Gordeev et al., 1996) and a linear regression with  $\delta^{26}\text{Mg}$  values for Yenisey and Lena rivers (Fig. 5) that can be described as:

$$\delta^{26}\text{Mg}_{\text{river}} = -0.0002 \times [\text{HCO}_3^-] - 1.096; R^2 = 0.35 \quad (1)$$

The estimated  $\delta^{26}\text{Mg}$  values based on the  $\text{HCO}_3^-$  concentrations from Gordeev et al. (1996) are listed in Table 2. Considering the discharge of each river, the mean discharge-weighted  $\delta^{26}\text{Mg}$  value to Ob, Yenisey, Lena and 9 mid-sized Eurasian Arctic rivers is  $-1.66 \pm 0.15 \text{‰}$ . Addition of the Mackenzie River increases this value  $-1.63 \text{‰}$  which is within the uncertainty.

## 5. Conclusions

New data of Mg isotope composition in the Lena River, obtained for previously uncharacterized winter baseflow and spring flood periods, and the Lena River tributaries during summer period. The data allowed testing the impact of watershed rock lithology, permafrost and vegetation parameters on the Mg isotopic signature of river waters and providing the mean annual  $\delta^{26}\text{Mg}$  value of the export flux to the Arctic Ocean.

The main physico-geographical (vegetation, runoff) and climatic (including permafrost) parameters of the watersheds did not correlate with the Mg isotope composition in the rivers and therefore they cannot serve as proxies for riverine  $\delta^{26}\text{Mg}$  values. At the same time, an increase in river water carbonate alkalinity (DIC) led to sizable decreases of  $\delta^{26}\text{Mg}$  values, which marked the dominant role of Precambrian dolomites in providing isotopically-light Mg to the Lena River and its tributaries. Strong lithological control (carbonate vs. silicate rocks) was demonstrated by a negative correlation between  $\delta^{26}\text{Mg}$  and the percentage of carbonate rock. These relationships were mostly pronounced during periods of high flow, when secondary Mg mineral formation and Mg removal via adsorption or biotic uptake could not interfere with water isotope signatures. At high water to solid ratio, the  $\delta^{26}\text{Mg}$  in the river stemmed from a linear combination of two sources capable to deliver Mg to the river water: isotopically light ( $-1.75 \geq \delta^{26}\text{Mg} \geq -2.0 \text{‰}$ ) carbonate rocks and isotopically heavy ( $-0.1 \geq \delta^{26}\text{Mg} \geq -0.6 \text{‰}$ ) silicate rocks, plant litter and organic soil horizons. The mean discharge-weighted  $\delta^{26}\text{Mg}$  of 12 large and mid-size Eurasian Arctic rivers, with a total discharge of  $2173 \text{ km}^3$  which is 73% of the entire Eurasian Arctic, is  $-1.66 \pm 0.15 \text{‰}$ .

Given the similarity (within  $\pm 0.05 \text{‰}$ ) of discharged-weighted mean annual isotopic flux value and that of the summer baseflow period previously assessed by Tipper et al. (2006) and measured in this study, and based on former time series on major and trace solutes in other Arctic rivers, we argue that single month sampling campaign is sufficient for assessing the mean annual discharge-weighted isotopic ratios. This opens a possibility of extensive measurements of isotopic fluxes of other elements from the land to the Arctic Ocean.

## CRedit authorship contribution statement

**Vasileios Mavromatis:** Writing – review & editing, Writing – original draft, Methodology, Funding acquisition. **Don Porcelli:** Writing – review & editing, Resources, Funding acquisition, Conceptualization. **Per S. Andersson:** Writing – review & editing, Resources, Methodology, Investigation, Funding acquisition, Conceptualization. **Mikhail A. Korets:** Software, Formal analysis, Data curation. **Oleg S. Pokrovsky:** Writing – review & editing, Writing – original draft, Resources, Methodology, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

**Table 2**

Estimated  $\delta^{26}\text{Mg}$  values of mid-size Eastern Siberian, European Arctic rivers and the Ob River based on Eq. (1) and the  $\text{HCO}_3^-$  values reported by Gordeev et al. (1996). Annual discharges of Eurasian rivers are from Gordeev et al. (1996). The isotopic signature of the Yenisey and Lena Rivers was measured by Mavromatis et al. (2020) and this study, respectively.

River	Discharge, $\text{km}^3 \text{ y}^{-1}$	Alkalinity ( $\mu\text{Eq}$ )	$\delta^{26}\text{Mg}$ (‰)
Sev. Dvina	110	8833	-2.86
Pechora	131	3292	-1.75
Taz	44	5408	-2.18
Pur	34	2133	-1.52
Ob	429	6358	-2.37
Anabar	17	2842	-1.66
Olenek	36	6625	-2.42
Kolyma	132	2375	-1.57
Yana	34	1700	-1.44
Indigirka	61	2608	-1.62
Yenisey	620		-1.25
Lena	525		-1.26

the work reported in this paper.

## Data availability

All data used in this study are included in the tables of the manuscript

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2024.121957>.

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