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Abstract

Constraining the mechanisms controlling the riverine flux of major cations and their isotopes including that of Mg to the World Ocean is one of the challenges in Earth surface isotope geochemistry. In an attempt to identify the main factors affecting the Mg isotopic composition of large rivers including vegetation, climate and lithology of the watershed, we studied the largest, in terms of discharge, Siberian river, Yenisey, and 20 of its main tributaries, during spring flood, summer flow and winter. The working hypothesis was that the influence of bedrock composition is most pronounced in winter, when the soils are frozen and the rivers are fed by deep underground waters. Thus, we anticipated that the presence of permafrost will help to distinguish the impact of surface processes, linked to biological uptake and release, and deep soil/underground transport of Mg from mineral sources. In contrast to these expectations, no sizable differences in the Mg isotope composition of the river water (±0.1 ‰) for both the Yenisey tributaries and its main channel has been observed between the spring flood (May) and the winter (March) period. Those two periods are characterized by the differences of discharge and degree of lithological impact on element source in the river water. Regardless of the season, there was no straightforward control of lithology (relative abundance of carbonates, basalts, granites and sedimentary rocks) on δ^{26}Mg in the main tributaries of the Yenisey river. Our findings suggest that the use of riverine Mg isotope signature for tracing weathering mechanisms and dominant lithological impact is not straightforward at the scale of large rivers whose watersheds present multiple lithologies, variable climatic conditions and vegetation types.

1. Introduction

An extensive amount of work in the past has focused on estimating elemental river fluxes into the ocean, in order to budget short and long-term elemental cycles (e.g. Dürr et al., 2011; Huh et al., 1998a; 1998b; Huh and Edmond, 1999). More recently, advances in mass spectrometry allowed for high resolution analyses of a wide number of isotopic systems, including Ca, Mg and Si. The use of the isotopic signatures of these elements in riverine transport studies has provided new insights into the processes and mechanisms of isotope fractionation during weathering but also on the elemental cycles. For example, as it has been shown earlier by Tipper et al. (2006) the global isotopic signature of riverine runoff exhibits a lower average δ^{26}Mg value compared to that of ocean waters, allowing for a better constraint of the hydrological budget of Mg sources and sinks.

Magnesium isotopes are known to exhibit significant fractionation during weathering (Tipper et al., 2008, 2012; Wimpenny et al., 2010, 2014; Pogge von Strandmann et al., 2008; Brenot et al., 2008). River waters that drain silicate catchments generally appear to be enriched in the lighter Mg isotope (^{24}Mg) relative to bedrock (Huang et al., 2012; Liu et al., 2014; Opfergelt et al., 2012; 2014; Wimpenny et al., 2010; 2014; Tipper et al., 2012). This has been interpreted as the uptake of the heavier Mg isotope (^{26}Mg) in Si-bearing secondary phases. Other processes that can impact the Mg isotopic composition of riverine waters are the dissolution of carbonates, secondary silicate mineral formation in soils, and dissolution of particulate suspended matter in the river channel, as well as Mg uptake by plants and its release from litterfall (Black et al., 2008; Bolou-Bi et al., 2010; Shirokova et al., 2013; Kimmig et al., 2018).

The motivation of this study is to verify earlier observations suggesting that large rivers are relative insensitive to lithology, but small ones exhibit a distinct difference between carbonate and silicate watersheds, especially in the case of vegetation-free watersheds (Tipper

et al., 2012). The reasons of the uniformity met in the Mg isotope signatures of large rivers are unclear, but likely stem from 1) the δ^{26}Mg composition of parent silicate rocks such as granites, basalts and shales that dominate in the majority of large rivers, is rather homogeneous (i.e. -0.3±0.15‰; Teng, 2017) and 2) the main processes controlling Mg isotope fractionation in surface fluids are very similar, once Mg is released from the bedrocks. These processes include *i*) the removal of Mg from the aqueous phase in the form of formation of- or adsorption to secondary clays and *ii*) the uptake of Mg by vegetation and its release from plant litter.

In this study we continue our efforts on characterizing weathering processes in major Siberian rivers (Pokrovsky et al., 2013; Mavromatis et al., 2014b; 2016). Earlier we focused on the isotopic composition of major and minor tributaries of Yenisey during the spring flood. These earlier works demonstrated that parameters such as the degree of the permafrost coverage, the type of vegetation and the lithology exhibit a rather weak influence on the Mg isotope composition of river waters (Mavromatis et al., 2016). We have also shown that N. Tunguska, the largest tributary of Yenisey river exhibits inter-seasonal variations in its riverine Mg isotope composition as large as 0.5‰ that can be attributed to Mg uptake from vegetation and the intensity of carbonate mineral dissolution (Mavromatis et al., 2014b). In an effort to test the effect of seasonality on the Mg isotope composition of Yenisey and its tributaries, in this study we examine the Mg isotope composition of samples collected over the course of three hydrological periods (i.e. March, May and August of 2015) and we compare them with data of June 2012 (Mavromatis et al., 2016). These observations are coupled with radiogenic $^{87}Sr/^{86}Sr$ measurements that are used as a tracer of the bedrock lithology in the watersheds of the tributaries. The Yenisey River is the largest contributor of freshwater to the Arctic Ocean, providing 18% of the total annual river discharge (Holmes et al., 2013). Due to its highly variable lithology, forest, and wetland coverage, it is largely representative of the rivers draining to the Arctic Ocean (Gladyshev et al., 2015; Roth et al.,

2013; Fabre et al., 2019). The Yenisey river system allows for testing the mechanisms of Mg fractionation within its main channel and numerous tributaries which drain through rocks of highly variable lithology and exhibit contrasting permafrost, forest, wetland, and vegetation coverage thus allowing for distinguishing the effects of bedrock, weathering and vegetation uptake / release within this large subarctic watershed. In contrast to river systems located in tropical and the sub-tropical zones, the fresh water fluxes in boreal and permafrost-affected rivers exhibit strong seasonal variations. Actually, 45% of the annual water discharging into the Arctic Ocean occurs during the snowmelt (Holmes et al., 2013), together with the largest elemental fluxes from the watersheds. In monolithological catchments in Central Siberia (Pokrovsky et al., 2006; 2013; Bagard et al., 2011) the major source of river solutes is derived from chemical weathering of bedrock with an important contribution of element cycling through plants. The impact of the watershed's bedrock lithology (i.e. granites, basalts, carbonates or terrigenous rocks) to a river is mostly manifested during winter baseflow, when the soils are frozen and the river is fed by taliks (i.e. unfrozen water paths in continuous permafrost zone) from deep underground water reservoirs (Bagard et al., 2011; 2013; Pokrovsky et al., 2013). Additionally, the chemical composition of river waters may be also affected by the annual biomass turnover. This effect is especially pronounced during spring freshet, when sizeable leaching of organic topsoil and plant litter can supply sizable amount of base cations including Mg to the river (Pokrovsky et al., 2005). Therefore, it can be expected that Mg isotope signatures in Arctic rivers over the year will range from a shallow organic source controlled at high flow to a deep soil source controlled at low flow. Over the winter period, the main source of Mg is expected to be deep carbonate and silicate rocks, whose dissolution may create favorable conditions for precipitation of secondary Mg-bearing minerals. During the permafrost-free period, congruent dissolution of silicate suspended material, leaching from plant litter, and uptake of Mg by vegetation in soil fluids are the dominant processes (Mavromatis et al., 2016). The present study is designed to investigate the

116 role of the parameters such as landscape, climate and permafrost that are significantly variant
117 among the lithologically-contrasting small tributaries of Yenisey River across its sizeable
118 geographical gradient. The aims are to examine the major mechanisms controlling isotopic
119 composition in Yenisey and its tributaries over the hydrological cycle and constrain in detail
120 the Mg budget of isotopic fluxes into the Arctic Ocean.
121
122 **2. Sampling and analytical procedures**
123 *2.1 Sample collection*
124 In our previous study of Mg isotopes in Siberian rivers (i.e. Mavromatis et al., 2014b)
125 research focused on year-round survey of medium size river draining central Siberian basalts
126 and its catchment where we studied the impact of vegetation, soil and suspended load on the
127 Mg isotopic signature. In similar terms Hindshaw et al. (2019) presented recently δ^{26}Mg
128 values of Yenisey river at Igarka over the time period between April and November of 2015.
129 In the context of Mg isotopes in the Yenisey River and its tributaries at a single hydrological
130 event, the end of spring flood, work has been presented by Mavromatis et al. (2016). Here we
131 used higher temporal resolution for such a big riverine system, and we analyze the main stem
132 of Yenisey River and its tributaries over 3 hydrological periods of the year: winter baseflow,
133 peak of spring flood and summer flow.
134 The river samples at freshet (between 25th and 30th of May) and summer flow
135 (between the 3rd and the 9th of August) periods of 2015 were collected during cruises on a
136 tugboat. Winter river samples, representing winter base flow conditions, were collected under
137 ice conditions (March and April of 2015). The samples were collected from the main Yenisey
138 River channel and all of its significant tributaries, including the Angara, the Podkamennaya
139 Tunguska, and the Nizhnyaya Tunguska Rivers, that together provide more than 50% of the
140 annual Yenisey river discharge to the Arctic Ocean (Table 1, Figs. 1 and 2).

During ice-free period water samples were collected in the middle of the river channels at a depth of 10-20 cm below the surface. During ice coverage in winter, water samples were collected through boreholes of ~15 cm diameter. The main stem of the Yenisey river was sampled at 9 stations. A shipboard laboratory allowed immediate sample filtration (pre-combusted Whatman glass fiber filters (GFF), 0.7 μm nominal pore size) and preservation. Note here that filter pore size has been shown to have no impact on Mg concentration (i.e. < 5%) in organic-rich river waters of the left and the main right tributaries of Yenisey (Pokrovsky et al., 2016; Bagard et al., 2011) and Mg isotopes in organic rich lacustrine waters (Ilina et al., 2013). Water temperature, pH and specific conductivity were measured directly in the rivers using a portable pH/T/conductivity meter HI8734 (Hanna Instruments, USA).

2.2. Chemical and Isotopic Analyses

The concentrations of major cations in water samples were measured by ICP-MS (Agilent 7500ce) at the Observatoire Midi Pyrénées (OMP) facilities (GET laboratory, Toulouse, France). Indium and rhenium were used as internal standards to correct for instrument drift and potential matrix effects. The accuracy of the Si, Mg, Ca, and Sr analyses was assessed using the SLRS-5 river water reference material, with the difference between the certified values and the measured values to be less than 10%. In addition, Mg was analyzed by atomic absorption spectroscopy with an analytical uncertainty of 1% and a detection limit of 10 μg L^{-1}. The non-acidified filtered water samples were used for analyses of dissolved inorganic carbon (DIC). Elemental analyses were performed using total combustion at 800°C using a SHIMADZU Pt catalyser (TOC-VCSN) with a 5% analytical uncertainty and a detection limit of 0.1 mg L^{-1} (see Prokushkin et al., 2011). Chloride and sulfate were determined using liquid chromatography with a DIONEX ICS-2000 system with analytical uncertainty of 2% and a detection limit of 0.02 mg L^{-1}.

Water samples were purified from matrix elements prior to Mg isotopic analyses by cation exchange chromatography. Prior to analyses water samples were treated with 30% H_2O_2 to remove organics and evaporated to dryness. Separation of the Mg from the matrix elements was done by following the protocol described by Mavromatis et al. (2013) using the AG50W-X12 resin eluted with 1.0 M HNO_3. After Mg separation samples were evaporated to dryness and re-dissolved to 0.35M HNO_3. The recovery of Mg processed through cation-exchange chromatography was better than 99%. Impurities of about 5% were insignificant to cause isobaric interferences during mass spectrometer. Magnesium isotopic ratios were measured using a Thermo-Finnigan 'Neptune' Multi Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at the OMP facilities (GET laboratory, Toulouse, France). All samples were prepared in 0.35 M HNO_3 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 sample-standard-sample bracketing, and all results are presented in delta notation relative to the DSM3 reference material as: $[\delta^{x}Mg= (({}^{x}Mg/{}^{24}Mg)_{sample} / ({}^{x}Mg/{}^{24}Mg)_{DSM3} -1)\times1000)]$ where x refers to the Mg mass of interest. All results are consistent with mass-dependent fractionation (see Table 2). The reproducibility of the $\delta^{26}Mg$ analyses, assessed by replicate analyses of the mono-elemental DSM3, CAM-1 and OUMg Mg reference standards and was typically better than 0.08‰; these measurements were also in agreement with the previously published values from our lab (e.g., Mavromatis et al. 2012, 2014a, 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). 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 was better than 0.08‰ (Table 2)

The $^{87}Sr/^{86}Sr$ ratios of the water samples were measured using a Triton Plus thermal ionization mass spectrometer (TIMS) at OMP facilities (GET laboratory, Toulouse, France).

Water samples were evaporated, taken up in 3M HNO_3 and run through Sr-spec columns (Jones et al., 2012; 2014). The purified Sr was then loaded onto outgassed Ta filaments. The samples were run at ^{88}Sr beam potentials of 2V and 100 ratios were collected using a multi-dynamic peak jumping routine. Resulting $^{87}Sr/^{86}Sr$ ratios were normalized to an $^{86}Sr/^{88}Sr$ ratio of 0.1194. Eight analyses of the SRM987 (formerly NBS987) standard yielded an average $^{87}Sr/^{86}Sr$ of 0.710215±0.000012 (2SD). The certified value of NBS987 is 0.71034 ±0.00026. Individual analytical errors did not exceed ±0.000011 $^{87}Sr/^{86}Sr$. Total blanks for Sr were found to be negligible (<0.1%) compared to the Sr amounts from the samples.

3. Results

3.1 Chemical composition of Yenisey and its tributaries over the hydrological year

The chemical composition of major elements in all river water samples can be found in Table 2. Overall the maximum concentrations of Ca and Mg are lowest in May sampling (Spring period). During this sampling period, the maximum Ca concentration measured was 587 μM L^{-1} in Kem, a river whose bed rock lithology is dominated by sedimentary silicates (Table 1). The maximum measured Mg concentrations in samples collected during May 2015, was 189 μM L^{-1} in Angara, a river whose bedrock coverage includes granites and sedimentary silicates (Table 1). The concentrations of Ca and Mg over August (summer) and March (winter) campaigns are in the same order of magnitude. In detail the maximum concentration of Ca over summer and winter periods are 1382 (Kem) and 1500 (Sovinskaya) μM L^{-1}, respectively. Similarly, the maximum concentrations of Mg over summer and winter periods are 492 and 655 μM L^{-1}, respectively, and are observed in P. Tunguska a river draining through basalts, tuffs and carbonates. The contribution of major elements in the riverine water from silicate and/or carbonate sources (e.g., Gaillardet et al., 1999, 2003) was assessed using Mg vs. Ca concentrations plots of riverine waters normalized against the sum of Na and K. The obtained results exhibit a linear trend for all the three seasons (Fig. 2), in agreement with

the chemical composition of Yenisey river waters collected in June of 2012 (Mavromatis et al., 2016) and a number of other Siberian rivers (Pokrovsky et al., 2005).

The seasonal variations of dissolved Sr concentrations are similar to those of Mg and Ca. They ranged over an order of magnitude between spring and winter or summer, regardless of the bedrock lithology, exhibiting strong dilution in spring at high water discharge (see Table 2). For example, in the Garevka river that is a small tributary of Yenisey dominated by a granitic lithology (Mavromatis et al., 2016), Sr concentrations are low but different amongst seasons being equal to 0.18, 0.08 and 0.14 μM L^{-1}during August, May and March, respectively. Another example is P. Tunguska, which exhibited the highest Sr concentrations of all river samples collected in this study of 8.00, 0.68 and 16.21 μM L^{-1} during August, May and March, respectively.

3.2 Strontium isotope composition of Yenisey and its tributaries over the hydrological year

The $^{87}Sr/^{86}Sr$ ratios of Yenisey tributaries sampled during May and March campaigns plotted against the respective values of samples collected over the August campaign exhibited a linear trend (Fig. 3). The values of samples collected in August have been used here, because they reflect the maximum impact of vegetation on the chemical and isotopic composition of river waters. In addition it is worth noting that despite the large variations of Sr concentrations both amongst rivers and amongst seasons, the sample tributaries exhibit a range of $^{87}Sr/^{86}Sr$ ratios between 0.708 and 0.713. An exception is the $^{87}Sr/^{86}Sr$ ratios of Garevka and Tis, (0.728 and 0.718, respectively, Table 2). Those elevated values can likely be attributed to the predominance of granitic rocks in their watersheds. Similar values have been earlier documented for riverine water of the same tributaries over the late spring flood of 2012 (Mavromatis et al., 2016). Overall the $^{87}Sr/^{86}Sr$ ratios of Yenisey tributaries for all the three seasonal campaigns are within the same range for Eastern Siberian rivers (Huh et al., 1998a,b; Huh and Edmond, 1999) and Yenisey coastal sediments (0.712; Guo et al., 2004). Within

uncertainty they are also comparable to Canadian rivers (0.7111; Wadleigh et al., 1985), and the global river average which ranges from 0.7116 (Pearce et al., 2015) to 0.7119 (Palmer and Edmond, 1989).

3.3 Magnesium isotope composition of Yenisey and its tributaries over the hydrological year

The overall variation of $\delta^{26}Mg$ values measured in this study spans a 0.8‰ range and falls within the range of $\delta^{26}Mg$ values reported earlier for Yenisey tributaries in a post-flood period (June 2012; Mavromatis et al., 2016). The riverine water samples collected from the main channel of the Yenisey exhibit an increase in $\delta^{26}Mg$ northwards. However samples collected in the mouth of the river exhibit variations that do not exceed 0.2‰ over the hydrological seasons. In addition, the samples collected at ~66.5N during May and August of 2015, exhibit similar values to those reported recently by Hindshaw et al. (2019) for the Igarka station that were also sampled in 2015 (see Fig. 4). Similarly, most tributaries did not exhibit any sizable variation of $\delta^{26}Mg$ between seasons. Generally, there were three groups of tributaries depending on their value $\delta^{26}Mg_{spring/summer}$ - $\delta^{26}Mg_{winter}$: i) < 0.05‰ (Nizhnaya Tunguska, Podkamennaya Tunguska, Vorogovka, Kas); ii) 0.1 to 0.18‰ (Bolshoi Pit, Tis, Dubches, Garevka) and iii) 0.27 ‰ (Sym). We did not evidence any straightforward link between the value of this difference and the lithology, climate, size, or vegetative coverage of the river watershed. We note however that for all the tributaries plotted in Fig. 4, the Mg isotope composition is lower at the end of spring flood (2012) compared to the peak of spring flood (2015). The magnitude of this difference was not linked to lithology, size of the river, and permafrost coverage.

Moreover, the most ^{26}Mg enriched samples were those collected from N. Tunguska, that is draining the Central Siberian basalt province (see Fig. 4). Note here that the samples collected from N. Tunguska tributary exhibit similar seasonal variations to those reported

earlier for the same river 600 km upstream its confluence with Yenisey (Mavromatis et al., 2014b). The Mg isotope composition of the water samples collected in the spring campaign of 2015 (May) of this study are systematically enriched in ^{26}Mg compared to samples at the end of the post-flood period in 2012 (Mavromatis et al., 2016). Their difference range between <0.1‰ for Turukhan, to more than 0.5‰ for P. Tunguska (see Fig. 4). Note here that Turukhan drains through wetlands and peatlands of terrigenous terrain whereas P. Tunguska drains through a mixture of basalts, carbonates and terrigenous material. We attribute the observed differences to the different timing of sampling, which was at the peak of the spring flood in 2015 in this study (late May), whereas in 2012 it was the end of the spring flood (late June). Indeed, there are significant isotopic variations over the hydrological year, specially between winter, early and late spring that have been demonstrated in two rivers of Central Siberia plateau (see Mavromatis et al., 2014b)

In order to test the effect of multiple factors on the Mg isotopic composition, a multivariate principle component analysis (PCA) has been conducted using the whole set of parameters that may affect isotopic fractionation for each of the three seasons individually, using the statistical software Statistica (v. 11.2). For this analysis, we considered Mg and Sr isotopic composition, major cation and anion concentration of the river water and landscape and lithological parameters of the watersheds as listed in Tables 1, 2 and S1 (see Appendix). The PCA exhibited a rather weak capacity in explaining the variability of more than 20 parameters. The overall explanation by each of 2 factors was below 10%; the F1+F2 together explained less than 20% of overall variability. However, the PCA analysis demonstrated the following features: i) In winter, the $\delta^{26}Mg$ value is controlled by the 2nd factor and positively linked to Mg/Ca and Mg/(Na+K) ratios, pH and DIC (Tables S2-S5; Appendix). This can be interpreted as the effect of carbonate (notably dolomitic) rocks at the catchment, which is pronounced through underground contribution via taliks of large and medium sized rivers; ii)

295 in spring, $\delta^{26}Mg$ is positively linked to latitude and river suspended matter but negatively
296 linked to pH and DIC. During high water flow, this may reflect the importance of Mg
297 desorption/leaching from silicate suspended particles and dilution of underground waters
298 interacting with soluble carbonate rocks. Finally, in summer, $\delta^{26}Mg$ cannot be explained by
299 any factor. This is consistent with simultaneous action of counter-balancing processes the
300 secondary clay precipitation in soil fluids and the uptake of Mg by vegetation.

301

302 **4 Discussion**

303 *4.1 Mg isotope variations in riverine waters over the hydrological year*

304 As it has been argued earlier (Bochkarev, 1959; Alekin, 1970; Pokrovsky et al., 2006)
305 the chemical composition of river waters in Siberian Rivers is the result of the combination of
306 two major sources: *i*) leaching from the surface organic-rich soil layer including plant litter
307 and *ii*) dissolution of minerals in deep soils and in the base rock; the latter delivers the mineral
308 constituents to the river via taliks (Anisimova, 1981; Bagard et al., 2011, 2013). It has to be
309 noted that, due to the complexity of large river lithology, the impact of rock distribution as
310 derived from geological maps can be compromised by river feeding from both surface
311 (basalts) and deep (carbonates) reservoirs (Pokrovsky et al., 2005; Mavromatis et al., 2014b).
312 However, permafrost is present at the majority of the Yenisey basin. Its presence impacts the
313 chemical composition of river waters that are influenced by the surface bedrock layers (0-10
314 m) rather than the deep rock lithology. Indeed, the extent and duration of permafrost is likely
315 the main parameter controlling the relative contribution of each process over the hydrological
316 year. For example, the major contributions from the upper soil layer and plant litter occur
317 during the spring flood (Pokrovsky et al., 2013; Mavromatis et al., 2014b). Progressive
318 thickening of the thaw layer achieves its maximum value at the end of summer (i.e. August).
319 The corresponding active layer depth limits the contribution of the top layers to the lateral

export flux of cations to the river. The dissolved products of chemical weathering of thawed soils and leaching of plant litter are delivered to the river via so called suprapermafrost flow, a water flux travelling at the base of active layer, over the frozen horizons. The $^{87}Sr/^{86}Sr$ composition of water samples collected from the same tributaries during June of 2012 suggests a similar source of Sr in the riverine waters regardless of the season (Fig. 3), and this composition is not affected by secondary mineral precipitation reactions (Mavromatis et al., 2016). For example, the $^{87}Sr/^{86}Sr$ ratios of N. Tunguska river exhibit variations of 0.0002 among seasons and reflect the $^{87}Sr/^{86}Sr$ ratios of the draining rock, the Patom paleobasin dolostones (i.e. 0.7080-0.7085; Pokrovsky et al., 2011). We note here however that differences in the contributions of each source, evidenced from Sr isotope variations, do not necessarily result in variations in elemental ratio composition of riverine waters. Indeed, the linear trend presented in Fig. 2 suggests that the origin of Mg and Ca varies among three seasons. This elemental ratio reflects mixing of two or more sources such as Precambrian dolomite, basalts, granites and larch litter. Note that some impact of atmospheric dust on seasonal variation in radiogenic Sr cannot be ruled out given that particulate deposition of Sr is comparable with its dissolved form in atmospheric snow of central Siberia (Shevchenko et al., 2017). At the same time, a single slope of the dependences shown in Fig. 2 suggests similar Mg/Ca ratio in the different solute pools as it has been highlighted earlier for bedrocks, soil and plant litter of Central Siberian catchments (Pokrovsky et al., 2005).

Further, the dissolution of riverine suspended matter (RSM) within the main channel can represent sizeable source of dissolved elements to the riverine waters, thus providing important source of solutes to the aqueous phase. The increase in active layer thickness over the frost-free season leads to progressive decreasing of the depth of suprapermafrost flow, which traverses organic horizons in spring and mineral soil horizons towards the end of summer-autumn. The contribution of riverine suspended matter as element source in the fluid phase is expected to be at maximum during the spring flood, when the coastal abrasion and

346 flood zone sediment resuspension are the highest. As a result, the delivery of cations to the
347 river water is strongly controlled by the season, via organic versus mineral soil and bedrock
348 contributions, and related to river discharge or local storm events via mobilization of
349 suspended matter and plant debris. However, the isotopic signatures of Mg and Sr in the
350 whole Yenisey River watershed over the hydrological year do not follow a simple relationship
351 with season (discharge), unlike the cation concentrations. Three reasons may be responsible
352 for such a decoupling. First, the permafrost is not homogeneously distributed in the Yenisey
353 drainage area that spans over 2000 km in the S-N gradient from lake Baikal in the south to the
354 Arctic Ocean (Fig. 1). In fact, the watershed of some river basins such as Kem and Kas are
355 not affected at all by permafrost. As a result, there may be a possible effect on the δ^{26}Mg
356 value of riverine waters from the weathering of the organic rich layer and leaching of plant
357 litter that is generally depleted in ^{26}Mg compared to the host rock (Opfergelt et al., 2014;
358 Teng, 2017).
359 A second reason of Sr-Mg isotope decoupling is illustrated in Fig. 5 where a cross-plot
360 of the isotopic composition of riverine waters between the winter campaign in March 2015 vs.
361 the summer campaign during August 2015 suggests an enrichment of most summer samples
362 with ^{26}Mg over winter samples. Such an enrichment is more evident for samples retrieved
363 from Sym, Dubches and B. Pit rivers, draining terrigenous silicates and not affected by deep
364 carbonate rocks and permafrost whereas it is negligible for P. Tunguska, N. Tunguska and
365 Vorogovka rivers, draining through basalts or carbonates, and fed by deep underground taliks
366 in winter. We note here that the major effect on the isotopic composition of Yenisey river and
367 its tributaries can be anticipated to be strongly influenced by the bedrock composition occur
368 during winter baseflow, when the rivers are fed by taliks through unfrozen paths. The isotopic
369 signal of bedrock can be blurred during summer flow due to removal of isotopically light Mg
370 via i) plant uptake (Mavromatis et al., 2014b) and ii) secondary clay precipitation in the
371 interstitial soil solutions (soil porewaters) or shallow subsurface water reservoirs.

372 Finally, a third reason of isotope decoupling can be assessed by the δ^{26}Mg values of
373 riverine samples collected during open water period (May to October) and exhibit a good
374 correlation with the riverine suspended material ($R_{Pearson}$ = 0.44 at $p < 0.05$; Fig. 6). Indeed,
375 ^{26}Mg – enriched waters collected in spring (May) and summer (August) exhibit increasing
376 RSM concentrations. We attribute this isotopically light composition of spring and summer
377 waters to the extensive dissolution of RSM in the river channel. The RSM is composed of
378 silicates (clays) and organic debris such as plant litter (Pokrovsky et al., 2005; 2013). Both
379 have δ^{26}Mg close to zero (-0.2±0.2‰, Mavromatis et al., 2014b) which is released to aqueous
380 solution without substantial fractionation.

381

382 *4.2 Isotopic composition of Mg flux to the Arctic Ocean*

383 The Yenisey is the world's sixth largest river in terms of discharge and the largest
384 contributor of freshwater to the Arctic Ocean, providing 18% of the total annual river
385 discharge (Holmes et al., 2013). It drains through rocks of highly variable lithology and
386 exhibits contrasting permafrost, forest, and wetland coverage. The western tributaries of
387 Yenisey River drain through thawed and frozen peatlands of Western Siberian Lowland and
388 as such represent many other permafrost-affected Artic rivers of low runoff (e.g. Pechora, Ob,
389 Nadym, Pur and Taz). On the other hand the large eastern tributaries of Yenisey drain through
390 granites, basalts and carbonates of mountainous regions with high runoff thus representing
391 the other Central and Eastern Siberian rivers of the Lena basin. As such, the obtained results
392 can provide first-order estimates of isotopic composition of Mg flux from the largest Arctic
393 river. During the sampling campaigns of 2015, the riverine water samples have been collected
394 from the main channel of Yenisey as north as 66.5°N, representing ca. 98% of the total river
395 watershed, and their δ^{26}Mg values were -1.36±0.04 ‰, -1.13±0.02 ‰, -1.13±0.01 ‰ for
396 winter (March), spring (May) and summer (August) campaigns, respectively (Fig. 4). These

values suggest an 0.23‰ difference in the Yenisey water $\delta^{26}Mg$ value between winter and spring. Partially, this difference may be due to release of ^{26}Mg from the RSM given that the RSM concentration in winter is an order of magnitude lower than that during spring flood, as reported at the Yenisey gauging station (McClelland et al., 2016). At the same time, the rivers most likely to be affected by underground waters draining carbonate rocks and feeding the river during winter (Vorogovka, P. Tunguska, N. Tunguska), the $\delta^{26}Mg$ was virtually the same (i.e. 0.04‰ variation) in winter and summer. The difference between summer and winter values was not systematically different among tributaries. For N. Tunguska, Kas, P. Tunguska, Vorogovka, this difference was < 0.5‰, whereas Sym, B. Pit, Tis, Dubches and Garevka exhibited up to 0.27 ‰ lower isotopic composition in winter compared to summer. As such, we cannot attribute the observed differences to one single factor such as carbonate rocks (N. Tunguska, Vorogovka, but also B. Pit), permafrost (N. Tunguska, Garevka) or vegetation (all rivers).

Altogether, the Yenisey isotopic measurements of this and our previous study (Mavromatis et al., 2016), together with those reported by Tipper et al. (2006) for the Lena river suggest that Siberian rivers are characterized by an isotopic composition lower compared to that of seawater or the Arctic Ocean (i.e -0.82‰; Teng et al., 2017). It can reasonably be suggested that the parameters controlling the low isotopic composition of Yenisey and likely Lena is the weathering of the highly reactive Precambrian dolomites, which are abundant in the southern Siberian Platform and are characterized by Mg isotope compositions as low as -2.5‰ (Pokrovsky et al., 2011). Indeed, hydrochemical analyses of present day alkalinity (DIC) features in the Yenisey River demonstrate similar contributions of carbonate and silicate weathering (53 and 47%, respectively, Tank et al., 2012). As such, the Mg isotopic signal of the Yenisey River may be explained by the linear mixture of carbonate that span in the range -2.0 ‰ $\leq \delta^{26}Mg_{carbonate} \leq$ -2.5 ‰ and silicate (0.0‰ $\leq \delta^{26}Mg_{silicate} \leq$ -0.2‰) end members providing an average of ca. -1.2±0.1‰.

Although elemental fluxes in boreal and permafrost-affected rivers are known to exhibit strong seasonal variations similar to water discharge (Guo et al., 2004, 2012; Bagard et al., 2011; 2013), the magnesium isotope composition of Yenisey over the hydrological year exhibits rather small variability, ca. within ±0.2‰, whereas the Mg concentration at the Yenisey river gauging station ranges from 62 to 250 μM L^{-1} (Holmes et al., 2018). In order to provide a first-order estimation of the average annual isotope composition of Mg discharge flux by the Yenisey River to the Arctic Ocean, we can use discharge weighted fluxes as:

$$\delta^{26}Mg_{annual} = \delta^{26}Mg_{spring} \times 0.29 + \delta^{26}Mg_{summer} \times 0.265 + \delta^{26}Mg_{winter} \times 0.445 \quad (1)$$

where the subscripts ‘‘spring” (i.e. May to June), ‘‘summer” (i.e. July to September) and ‘‘winter” (i.e. October to April) denote the isotopic composition of Yenisey River water during the corresponding hydrological period, whereas the fractions of the annual fluxes for Mg have been calculated after Holmes et al. (2012) similar to Mavromatis et al. (2016). For the spring isotopic composition we use here the average of the measured Mg isotope composition of the post spring (June) and spring (May) sampling campaigns in years 2012 and 2015, respectively (i.e. -1.21±0.08‰). The resulting flux-averaged annual isotope signatures of Mg from the Yenisey River to the Arctic Ocean is thereby estimated to be $\delta^{26}Mg_{annual}$ = -1.25 ± 0.15‰. This value is within uncertainty similar to that estimated earlier by Mavromatis et al. (2016) and Hindshaw et al. (2019) as well as with the mean global runoff of -1.09‰ estimated earlier by Tipper et al. (2006), but about 0.4‰ lighter compared to the $\delta^{26}Mg$ of seawater (i.e -0.82‰; Teng et al., 2017).

Whether the 0.15‰ difference in $\delta^{26}Mg$ of global runoff and the Yenisey river is significant cannot be unequivocally resolved. However, it is possible that Siberian permafrost-bearing rivers such as Yenisey (this study) and Lena ($\delta^{26}Mg$ = -1.28±0.08 ‰; Tipper et al., 2006) are indeed enriched in lighter Mg isotopes compared to the world rivers, even though the discharge-weighted $\delta^{26}Mg$ for the world rivers is lacking. Because preferential removal of

heavier isotopes by vegetation would require strong non-stationary conditions which is not the case in Siberia, we argue that the dissolution of carbonate (dolomite) rocks in the watersheds of Central and Eastern Siberian rivers is the main cause of relatively negative δ^{26}Mg values of these rivers. In this regard, assessment of Mg isotope signature in large Siberian rivers not subjected to strong carbonate influence such as Ob, Pur and Taz of western Siberian lowland is essential for detailed constraining of the Mg isotopic budget of the Arctic Ocean.

Conclusions

The Yenisey river main channel, as well as it's large and medium tributaries were sampled over three hydrological periods, spring, summer and winter. This allowed to assess seasonal variations in Mg isotopic ratios and to relate δ^{26}Mg values to river discharge, landscape and lithological parameters of watersheds. Contrary to our expectations, the spring flood (May) and winter (March) period, two most different months in terms of discharge and degree of lithological impact on element source in the river water, did not show any measurable difference in δ^{26}Mg signature of the river water (±0.1‰) for both the Yenisey tributaries and its main channel. Moreover, the summer season which is characterized by maximum impact of vegetation and maximally thawed soils, was not significantly (> 0.2‰) different from the other seasons. Despite these relatively homogeneous isotopic compositions of the Yenisey basin in space and time, some fine features of Mg isotope fractionation were revealed.

Some impact of river suspended matter on δ^{26}Mg in the river water was observed via ca. 0.6‰ increase in δ^{26}Mg accompanied with 5 times RSM concentration increase. A 0.2‰ difference in δ^{26}Mg of Yenisey main channel between summer and spring (-1.36 and -1.13‰, respectively) could be attributed to removal of heavy isotope by biotic processes at the watershed and in the main stream. Direct lithological impact on Mg isotope composition is

not seen, or the effect of dominant silicate (isotopically heavy) rock dissolution is completely masked by the high reactivity of isotopically light dolomites and limestones. The average annual isotopic flux of Mg by the Yenisey River to the Arctic Ocean is equal to -1.25‰ which is ~0.15‰ lower than the world average. This value is likely within the natural variation of isotopic signature in rivers. Together with the low value of the Lena river reported by Tipper et al. (2008), this may signify a pronounced influence of isotopically light Precambrian dolomites and limestones for these two Siberian rivers.

The results of this study cast certain doubts on the usefulness of Mg isotope in rivers as tracers of weathering processes and assessing lithological impact on isotopic signature of riverine Mg flux, at least in the context of forested and permafrost-dominated watershed with highly variable lithology. Even minor proportion of isotopically light, highly reactive dolomites and limestones are capable to completely offset the impact of less reactive, isotopically heavy silicates. Further, because several drastically different processes such as formation of secondary clays, carbonate precipitation, or the biological uptake, are characterized by similar isotopic shift, the overall impact of these processes on Mg riverine isotopic signature may not be distinguishable.

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701 Table 1. List of riverine stations that are illustrated in Fig. 1 together with the basin area of each river as well as the abundances of major rocks in the
702 watershed.

Map ID	**River name**	**Basin Area (km^2)**	**Lithology (%)**								**MAAT (°C)**	**Permafrost**				
			basalts	basalts (50%), sedimentary silicates (50%)	granites	sedimentary silicates	sedimentary silicates (90%), carbonates (10%)	sedimentary silicates (50%), carbonates (50%)	carbonates	Other		Continuous C (%)	Discontinious D (%)	Isolated I (%)	Sporadic S (%)	Without permafrost (%)
1	Angara	1051424	2.6	1.9	19.9	27.5	6.2	7.8	4.6	29.5	-3.3	4	0	33	4	58
2	Kem'	9014	0.0	0.0	0.0	77.1	0.0	22.9	0.0	0.0	-1.0	0	0	0	0	100
3	Bolshoy Pit	21598	0.3	0.0	13.6	8.5	74.9	2.0	0.8	0.0	-4.3	0	0	97	0	3
4	Kiya	3373	0.0	0.0	18.2	8.8	64.6	0.0	4.1	4.3	-3.5					
5	Tis	2713	0.0	0.0	47.6	14.6	37.8	0.0	0.0	0.0	-3.6					
6	Kas	11775	0.0	0.0	0.0	84.1	0.0	15.9	0.0	0.0	-1.8	0	0	0	0	100
7	Garevka	927	0.0	0.0	99.4	0.6	0.0	0.0	0.0	0.0	-4.0	0	0	81	0	19
8	Sym	31849	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	-2.5	0	0	64	0	35
9	Nizhnyaya Surnikha	476366	0.0	0.0	75.3	0.0	23.1	0.0	1.6	0.0	-3.6					
10	Tugulan	1195	0.0	0.0	0.0	97.8	2.1	0.0	0.1	0.0	-2.7					
11	Vorogovka	3758	4.0	0.0	22.5	20.8	45.0	0.0	7.7	0.0	-4.3	0	0	98	0	2
12	Dubches	15376	0.0	0.0	0.0	99.9	0.1	0.0	0.0	0.0	-3.4	0	0	76	24	0
13	Podkamennaya Tunguska	238708	12.1	30.1	1.8	33.0	4.1	10.5	8.4	0.0	-6.5	10	16	37	36	0
14	Bakhta	36177	37.2	3.2	0.0	42.2	5.1	3.2	9.0	0.0	-6.6	0	10	10	79	0
15	Yeloguy	27143	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	-3.9	0	0	12	88	0
16	Komsa	1608	12.5	0.0	0.0	31.9	19.3	0.0	36.3	0.0	-4.9	0	0	0	100	0
17	Sukhaya Tunguska	7165	33.9	0.0	0.0	48.3	0.0	13.1	4.8	0.0	-6.6	0	46	0	54	0
18	Miroedikha	584	0.0	0.0	0.0	98.4	0.0	0.0	1.6	0.0	-6.5	0	0	0	100	0
19	Turukhan	35726	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	-6.3	0	85	0	15	0
20	Nizhnyaya Tunguska	476366	39.8	41.9	0.0	11.8	3.1	0.7	2.7	0.0	-9.2	76	12	2	10	0

703 Table 2: Sampling date, geographic coordination of the stations, stable Mg and radiogenic Sr composition of riverine waters together with concentrations of Ca,
704 K, Mg, Na, Sr, SO_4, Cl and DIC in µM L^{-1} and riverine suspended matter (RSM) for samples taken in the 2015 campaigns. The analytical uncertainty of the
705 $^{87}Sr/^{86}Sr$ analyses has been estimated as ±0.000011 based on replicate analyses of SRM987 reference material.

Sampling station		Sampling date	$\delta^{25}Mg$ (‰)	2σ	$\delta^{26}Mg$ (‰)	2σ	$^{87}Sr/^{86}Sr$	Ca	K	Mg	Na	Sr	SO_4	Cl	DIC	RSM (mg/L)	Latitude (°N)	Longtitude (°E)
Summer																		
E001	Tugulan	05/08/15	-0.43	0.01	-0.82	0.10	0.708727	469	18	189	176	0.86	24.79	1.76	305.70	4.13	60.79	89.78
E002	Kem'	03/08/15	-0.46	0.04	-0.90	0.02	0.709449	1382	33	411	360	3.05	9.87	15.23	477.77		58.52	92.08
E003	Turukhan	08/08/15	-0.45	0.04	-0.88	0.08	0.708872	213	6	125	88	0.31	6.68	6.73	231.85	4.58	65.9	87.58
E004	P. Tunguska	06/08/15	-0.64	0.03	-1.24	0.06	0.708998	891	26	492	816	8.01	582.91	255.99	397.94	1.73	61.62	90.18
E005	Kiya	04/08/15					0.713971	226	8	97	67	0.38	2.17	19.61	193.75	1.77	59.16	91.50
E006	Dubches	05/08/15	-0.52	0.05	-1.01	0.05	0.708880	408	11	258	148	0.57	3.48	10.60	279.52	12.75	60.99	89.61
E007	Sukhaya Tunguska	08/08/15					0.708670	301	5	164	155	0.55	82.88	35.39	203.44	1.43	65.16	88.00
E008	Miroedikha	08/08/15					0.708725	590	4	374	98	0.52	5.89	8.35	387.87	1.58	65.6	88.07
E009	Kas	04/08/15	-0.47	0.02	-0.91	0.01	0.709619	742	20	246	172	1.33	4.15	5.54	356.88	3.80	59.99	90.55
E010	Bakhta	06/08/15	-0.50	0.01	-0.98	0.02	0.708651	560	12	233	180	1.96	72.66	136.57	323.77	1.07	62.48	89.03
E011	Garevka	04/08/15	-0.48	0.02	-0.94	0.02	0.727949	96	10	39	61	0.18	2.64	10.70	119.33		59.85	90.79
E012	N. Tunguska	08/08/15	-0.45	0.04	-0.84	0.04	0.708540	553	14	173	898	1.94	1133.96	79.30	246.39	3.73	65.80	88.09
E013	Elogyi	07/08/15	-0.51	0.04	-0.98	0.02	0.708580	332	10	206	197	0.48	3.66	7.25	383.44	3.87	63.19	87.75
E014	Angara	03/08/15	-0.60	0.02	-1.17	0.01	0.709293	658	28	231	356	1.94	230.02	93.55	311.95	2.12	58.07	93.08
E015	N. Syrnikha	05/08/15					0.711289	461	7	266	42	0.60	3.39	98.57	299.57		60.41	90.13
E016	Sym	05/08/15	-0.39	0.02	-0.78	0.02	0.709603	244	14	106	107	0.50	3.56	7.63	191.29	9.02	60.25	90.05
E017	Bolshoi Pit	03/08/15	-0.63	0.01	-1.21	0.01	0.710689	311	10	135	65	1.36	10.57	57.67	230.11	4.18	59.03	91.73
E018	Vorogovka	05/08/15	-0.78	0.06	-1.49	0.04	0.709919	430	6	221	36	0.67	3.96	31.16	269.03		60.79	89.88
E019	Komsa	07/08/15	-0.61	0.03	-1.17	0.07	0.708735	221	8	147	90	0.51	23.75	62.48	391.51	2.36	63.26	87.72
E020	Tis	04/08/15	-0.72	0.01	-1.38	0.03	0.717517	214	9	133	60	0.32	4.03	24.63	186.49	1.42	59.55	90.92
E021	Yenisey 1	03/08/15					0.708354	482	17	111	111	1.07				2.35	58.02	93.20
E022	Yenisey 2	03/08/15	-0.66	0.03	-1.27	0.03	0.708841	623	24	195	286	1.81					59.00	91.71
E022*			-0.67	0.04	-1.31	0.05												
E023	Yenisey 3	05/08/15					0.708847	594	21	179	202	1.45				2.76	60.29	90.12
E024	Yenisey 5	06/08/15					0.708923	542	20	164	236	1.54				2.08	61.58	90.14
E025	Yenisey 6	06/08/15	-0.70	0.02	-1.31	0.02	0.708969	679	23	242	353	2.81				3.82	62.46	88.97
E026	Yenisey 7	07/08/15					0.708955	634	22	269	395	3.30				2.46	63.25	87.69
E027	Yenisey 8	07/08/15					0.708920	690	23	222	311	2.32				3.40	64.13	87.54
E028	Yenisey 9	05/08/15					0.708939	640	23	240	334	2.45				3.97	65.77	87.99
E029	Yenisey 10	09/08/15	-0.58	0.01	-1.13	0.01	0.709870	637	20	243	462	2.64				5.35	66.46	87.23
Spring																		
E030	Sym	27/05/15					0.711693	46	16	20	25	0.11	1.02	8.96	11.75	29.36	60.25	90.05
E031	Kas	26/05/15					0.709652	117	20	40	34	0.28	3.02	13.49	33.93	23.48	59.99	90.55
E032	Komsa	29/05/15					0.708730	85	5	51	23	0.16	2.94	8.59	40.49		63.26	87.72
E033	Kem'	25/05/15	-0.44	0.07	-0.88	0.04	0.709598	587	33	185	167	1.33	8.13	22.31	253.93		58.52	92.08

Sampling station		Sampling date	δ^{25}Mg (‰)	2σ	δ^{26}Mg (‰)	2σ	$^{87}Sr/^{86}Sr$	Ca	K	Mg	Na	Sr	SO_4	Cl	DIC	RSM (mg/L)	Latitude (°N)	Longtitude (°E)
E034	Garevka	26/05/15					0.726515	34	9	15	29	0.08	2.77	13.72	15.29		59.85	90.79
E035	Turukhan	30/05/15	-0.52	0.05	-1.01	0.03	0.709028	159	15	82	71	0.42	24.99	21.79	105.25	7.85	65.90	87.58
E036	Kiya	26/05/15					0.717154	71	7	27	28	0.13	1.56	15.29	50.82	7.21	59.16	91.50
E037	Angara	26/05/15	-0.58	0.02	-1.13	0.03	0.708962	461	26	189	348	1.59	217.29	91.86	191.31	6.83	58.07	93.08
E038	P. Tunguska	28/05/15	-0.52	0.03	-0.99	0.07	0.709117	147	15	74	55	0.68	22.72	27.23	77.38	9.65	61.62	90.18
E038*			-0.50	0.04	-1.00	0.05												
E039	N. Syrnikha	27/05/15						158	8	92	22	0.20	1.67	32.63	94.26		60.41	90.13
E040	Bolshoi Pit	26/05/15					0.713730	103	6	43	29	0.26	3.42	24.58	55.74	16.56	59.03	91.73
E041	Tis	26/05/15					0.720764	63	7	34	29	0.10	3.28	16.01	37.54	7.53	59.55	90.92
E042	Sukhaya Tunguska	30/05/15					0.708653	89	6	52	38	0.15	18.93	11.08	50.00		65.16	88.00
E043	Elogyi	29/05/15					0.708854	89	13	48	36	0.19	3.13	7.50	50.98	17.22	63.19	87.75
E044	Dubches	27/05/15					0.709093	83	14	47	33	0.15	1.95	8.64	39.51	34.65	60.99	89.61
E045	Vorogovka	27/05/15	-0.75	0.02	-1.42	0.06	0.710019	190	6	88	22	0.31	3.63	18.63	94.26		60.79	89.88
E046	N. Tunguska	30/05/15	-0.36	0.05	-0.70	0.12	0.708534	140	7	51	136	0.42	101.74	14.61	48.20	13.67	65.8	88.09
E047	Yenisey 1	25/05/15					0.708400	366	18	134	116	1.03				4.12	58.02	93.20
E048	Yenisey 2	26/05/15					0.709004	426	23	168	228	1.42					59.00	91.71
E049	Yenisey 3	27/05/15					0.713280	94	8	41	42	0.22				14.91	60.29	90.12
E050	Yenisey 4	27/05/15					0.708991	269	20	92	105	0.77				10.9	60.91	89.69
E051	Yenisey 6	28/05/15					0.709236	209	12	91	78	0.77					62.46	88.97
E052	Yenisey 7	29/05/15					0.709219	191	11	86	71	0.70				13.58	63.25	87.69
E053	Yenisey 8	29/05/15					0.709178	168	10	76	61	0.61				13.12	64.13	87.54
E054	Yenisey 10	30/05/15	-0.58	0.02	-1.13	0.02	0.709014	147	9	66	71	0.47					66.46	87.23
E054*			-0.55	0.04	-1.09	0.05												
Winter																		
Yenisey IGARKA	Yenisey Igarka	02/03/15					0.708947	233	12	97	128	0.79					67.42	86.52
J137	N. Tunguska	11/03/15	-0.44	0.01	-0.85	0.03	0.708722	411	14	170	119	0.76	762.43	2065.84	348.09		65.8	88.09
J138	Khoiba	10/03/15	-0.49	0.03	-0.95	0.05		213	14	108	131	0.47	1.39	3.76	70.01		60.91	89.51
J139	Devyatikha	11/03/15					0.710011	439	19	174	199	0.98	3.19	8.65	301.05		59.63	90.82
J140	Tankov	11/03/15					0.708671	305	12	123	47	0.56	2.43	6.59	93.55		60.70	89.97
J141	Chistoklet	12/03/15						624	17	185	166	1.14	3.46	9.37	342.16		59.39	91.11
J142	Turukhan	13/05/15					0.709781	970	25	349	329	2.16					65.9	87.58
J143	Isakova	11/03/15					0.713276	726	15	384	82	0.80	3.82	10.34	194.61		60.25	90.31
J144	Tugulan	05/03/15	-0.43	0.06	-0.84	0.08	0.719447	443	17	193	170	0.90	7.24	19.61	156.17		60.79	89.78
J145	Kas	28/01/15					0.709621	856	18	251	176	1.47					59.99	90.55
J146	Podbel	10/03/15					0.708880	421	10	179	108	0.67	1.23	3.34	135.25		61.18	89.46
J147	Kas	11/03/15	-0.47	0.02	-0.93	0.03	0.709612	859	18	253	169	1.49	4.28	11.60	220.13		59.99	90.55
J148	P. Tunguska	09/03/15	-0.63	0.03	-1.21	0.02	0.708969	1321	31	655	1159	16.22	459.71	1245.60	298.70		61.62	90.18
J149	Sym	28/01/15					0.709538	336	16	146	132	0.72					60.25	90.05
J150	Yenisey at Ust-Pit	13/03/15	-0.54	0.05	-1.05	0.06	0.708613	714	23	187	226	1.69					59.00	91.42

Sampling station		Sampling date	$\delta^{25}Mg$ (‰)	2σ	$\delta^{26}Mg$ (‰)	2σ	$^{87}Sr/^{86}Sr$	Ca	K	Mg	Na	Sr	SO_4	Cl	DIC	RSM (mg/L)	Latitude (°N)	Longtitude (°E)
J151	Kiya	13/03/15	-0.68	0.04	-1.31	0.04	0.713038	305	10	148	74	0.57	1.73	4.68	231.47		59.16	91.5
J152	Khakhalevka	09/03/15					0.708823	1081	16	638	265	1.39	2.36	6.40	336.55		61.35	89.57
J153	Verkhnayaya	11/03/15					0.708883	223	13	120	140	0.51	3.77	10.23	80.91		60.47	89.98
J154	Razvilki	10/03/15						48	12	26	49	0.14	1.35	3.66	9.44		60.85	89.44
J155	B. Pit	13/03/15	-0.70	0.01	-1.35	0.03	0.710101	611	12	257	79	3.71	8.59	23.27	202.73		59.03	91.73
J156	Sovinskaya	12/03/15					0.709359	1500	25	437	310	3.37	1.88	5.11	341.05		59.16	91.40
J157	Tis	12/03/15	-0.79	0.03	-1.51	0.08		271	12	188	71	0.48	4.74	12.85	92.71		59.55	90.92
J158	Yenisey at Zotino	07/03/15	-0.49	0.03	-0.95	0.03	0.708995	499	18	170	155	1.12					60.54	89.41
J159	Vorogovka	07/03/15	-0.79	0.02	-1.53	0.05	0.709774	719	13	424	52	1.23	3.13	8.49	239.04		60.79	89.88
J160	Dubches	10/03/15	-0.62	0.01	-1.19	0.05	0.708902	611	14	321	185	0.80	2.19	5.93	200.76		60.99	89.61
J161	Garevka	11/03/15	-0.55	0.02	-1.05	0.04		123	14	51	75	0.21	1.50	4.07	165.89		59.85	90.79
J162	Yenisey at Turukhnask	13/04/15	-0.70	0.04	-1.36	0.04	0.708914	846	26	323	475	4.84					65.36	88.04
J163	Sym	12/03/15	-0.55	0.06	-1.05	0.10	0.709551	401	18	173	148	0.87	2.48	6.73	132.97		60.25	90.05
J164	Turukhan	13/04/15	-0.61	0.03	-1.17	0.04	0.708835	944	32	186	1268	4.40	50.33	136.38	348.09		65.90	87.58
J165	Pucheglazikha	12/03/15					0.709713	1263	22	371	309	2.39	2.38	6.46	337.86		59.35	91.17
J166	N. Surnikha	11/03/15					0.710521	676	12	361	48	0.88	1.67	4.53	172.76		60.41	90.13
Reference materials**																		
DSM3 (70)			0.00	0.05	0.00	0.08												
CAM-1 (15)			-1.35	0.04	-2.65	0.07												
OUMg (15)			-1.43	0.08	-2.82	0.06												
IAPSO (6)			-0.42	0.04	-0.82	0.06												
JDo-1 (6)			-1.22	0.05	-2.39	0.08												

*Denotes full procedural analyses of duplicate samples

** The number in parenthesis denotes number of replicates of each reference material.