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1 **Weak impact of landscape parameters and rock lithology on Mg isotope**
2 **composition of the Yenisey River and its tributaries**

3

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16

17 **Abstract**

18 Constraining the mechanisms controlling the riverine flux of major cations and their isotopes
19 including that of Mg to the World Ocean is one of the challenges in Earth surface isotope
20 geochemistry. In an attempt to identify the main factors affecting the Mg isotopic composition
21 of large rivers including vegetation, climate and lithology of the watershed, we studied the
22 largest, in terms of discharge, Siberian river, Yenisey, and 20 of its main tributaries, during
23 spring flood, summer flow and winter. The working hypothesis was that the influence of
24 bedrock composition is most pronounced in winter, when the soils are frozen and the rivers
25 are fed by deep underground waters. Thus, we anticipated that the presence of permafrost will
26 help to distinguish the impact of surface processes, linked to biological uptake and release,
27 and deep soil/underground transport of Mg from mineral sources. In contrast to these
28 expectations, no sizable differences in the Mg isotope composition of the river water (± 0.1
29 ‰) for both the Yenisey tributaries and its main channel has been observed between the
30 spring flood (May) and the winter (March) period. Those two periods are characterized by the
31 differences of discharge and degree of lithological impact on element source in the river
32 water. Regardless of the season, there was no straightforward control of lithology (relative
33 abundance of carbonates, basalts, granites and sedimentary rocks) on $\delta^{26}\text{Mg}$ in the main
34 tributaries of the Yenisey river. Our findings suggest that the use of riverine Mg isotope
35 signature for tracing weathering mechanisms and dominant lithological impact is not
36 straightforward at the scale of large rivers whose watersheds present multiple lithologies,
37 variable climatic conditions and vegetation types.

38

39 **1. Introduction**

40 An extensive amount of work in the past has focused on estimating elemental river
41 fluxes into the ocean, in order to budget short and long-term elemental cycles (e.g. Dürr et al.,
42 2011; Huh et al., 1998a; 1998b; Huh and Edmond, 1999). More recently, advances in mass
43 spectrometry allowed for high resolution analyses of a wide number of isotopic systems,
44 including Ca, Mg and Si. The use of the isotopic signatures of these elements in riverine
45 transport studies has provided new insights into the processes and mechanisms of isotope
46 fractionation during weathering but also on the elemental cycles. For example, as it has been
47 shown earlier by Tipper et al. (2006) the global isotopic signature of riverine runoff exhibits a
48 lower average $\delta^{26}\text{Mg}$ value compared to that of ocean waters, allowing for a better constraint
49 of the hydrological budget of Mg sources and sinks.

50 Magnesium isotopes are known to exhibit significant fractionation during weathering
51 (Tipper et al., 2008, 2012; Wimpenny et al., 2010, 2014; Pogge von Strandmann et al., 2008;
52 Brenot et al., 2008). River waters that drain silicate catchments generally appear to be
53 enriched in the lighter Mg isotope (^{24}Mg) relative to bedrock (Huang et al., 2012; Liu et al.,
54 2014; Opfergelt et al., 2012; 2014; Wimpenny et al., 2010; 2014; Tipper et al., 2012). This
55 has been interpreted as the uptake of the heavier Mg isotope (^{26}Mg) in Si-bearing secondary
56 phases. Other processes that can impact the Mg isotopic composition of riverine waters are
57 the dissolution of carbonates, secondary silicate mineral formation in soils, and dissolution of
58 particulate suspended matter in the river channel, as well as Mg uptake by plants and its
59 release from litterfall (Black et al., 2008; Bolou-Bi et al., 2010; Shirokova et al., 2013;
60 Kimmig et al., 2018).

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

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

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

90 2013; Fabre et al., 2019). The Yenisey river system allows for testing the mechanisms of Mg
91 fractionation within its main channel and numerous tributaries which drain through rocks of
92 highly variable lithology and exhibit contrasting permafrost, forest, wetland, and vegetation
93 coverage thus allowing for distinguishing the effects of bedrock, weathering and vegetation
94 uptake / release within this large subarctic watershed. In contrast to river systems located in
95 tropical and the sub-tropical zones, the fresh water fluxes in boreal and permafrost-affected
96 rivers exhibit strong seasonal variations. Actually, 45% of the annual water discharging into
97 the Arctic Ocean occurs during the snowmelt (Holmes et al., 2013), together with the largest
98 elemental fluxes from the watersheds. In monolithological catchments in Central Siberia
99 (Pokrovsky et al., 2006; 2013; Bagard et al., 2011) the major source of river solutes is derived
100 from chemical weathering of bedrock with an important contribution of element cycling
101 through plants. The impact of the watershed's bedrock lithology (i.e. granites, basalts,
102 carbonates or terrigenous rocks) to a river is mostly manifested during winter baseflow, when
103 the soils are frozen and the river is fed by taliks (i.e. unfrozen water paths in continuous
104 permafrost zone) from deep underground water reservoirs (Bagard et al., 2011; 2013;
105 Pokrovsky et al., 2013). Additionally, the chemical composition of river waters may be also
106 affected by the annual biomass turnover. This effect is especially pronounced during spring
107 freshet, when sizeable leaching of organic topsoil and plant litter can supply sizable amount of
108 base cations including Mg to the river (Pokrovsky et al., 2005). Therefore, it can be expected
109 that Mg isotope signatures in Arctic rivers over the year will range from a shallow organic
110 source controlled at high flow to a deep soil source controlled at low flow. Over the winter
111 period, the main source of Mg is expected to be deep carbonate and silicate rocks, whose
112 dissolution may create favorable conditions for precipitation of secondary Mg-bearing
113 minerals. During the permafrost-free period, congruent dissolution of silicate suspended
114 material, leaching from plant litter, and uptake of Mg by vegetation in soil fluids are the
115 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 $\delta^{26}\text{Mg}$
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).

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

152

153 *2.2. Chemical and Isotopic Analyses*

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

167 Water samples were purified from matrix elements prior to Mg isotopic analyses by
168 cation exchange chromatography. Prior to analyses water samples were treated with 30%
169 H₂O₂ to remove organics and evaporated to dryness. Separation of the Mg from the matrix
170 elements was done by following the protocol described by Mavromatis et al. (2013) using the
171 AG50W-X12 resin eluted with 1.0 M HNO₃. After Mg separation samples were evaporated to
172 dryness and re-dissolved to 0.35M HNO₃. The recovery of Mg processed through cation-
173 exchange chromatography was better than 99%. Impurities of about 5% were insignificant to
174 cause isobaric interferences during mass spectrometer. Magnesium isotopic ratios were
175 measured using a Thermo-Finnigan ‘Neptune’ Multi Collector Inductively Coupled Plasma
176 Mass Spectrometer (MC-ICP-MS) at the OMP facilities (GET laboratory, Toulouse, France).
177 All samples were prepared in 0.35 M HNO₃ and introduced into the Ar plasma with a large
178 Stable Introduction System spray chamber (double Scott Cyclonic spray chamber).
179 Instrumental mass fractionation effects were corrected by sample-standard-sample bracketing,
180 and all results are presented in delta notation relative to the DSM3 reference material as:
181 $[\delta^x\text{Mg} = ((^x\text{Mg}/^{24}\text{Mg})_{\text{sample}} / (^x\text{Mg}/^{24}\text{Mg})_{\text{DSM3}} - 1) \times 1000]$ where x refers to the Mg mass of
182 interest. All results are consistent with mass-dependent fractionation (see Table 2). The
183 reproducibility of the $\delta^{26}\text{Mg}$ analyses, assessed by replicate analyses of the mono-elemental
184 DSM3, CAM-1 and OUMg Mg reference standards and was typically better than 0.08‰;
185 these measurements were also in agreement with the previously published values from our lab
186 (e.g., Mavromatis et al. 2012, 2014a, Beinlich et al., 2014; 2018) as well as from other
187 laboratories (Geske et al., 2015; Riechelmann et al. 2016; 2018; Mavromatis et al., 2017;
188 Bolou-Bi et al., 2009, Wombacher et al. 2009). The reproducibility of chromatographic
189 separation was assessed by repeated analyses of selected samples and the total procedural
190 process of JDo-1 (dolomite) and IAPSO seawater was better than 0.08‰ (Table 2)

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

193 Water samples were evaporated, taken up in 3M HNO₃ and run through Sr-spec columns
194 (Jones et al., 2012; 2014). The purified Sr was then loaded onto outgassed Ta filaments. The
195 samples were run at ⁸⁸Sr beam potentials of 2V and 100 ratios were collected using a multi-
196 dynamic peak jumping routine. Resulting ⁸⁷Sr/⁸⁶Sr ratios were normalized to an ⁸⁶Sr/⁸⁸Sr ratio
197 of 0.1194. Eight analyses of the SRM987 (formerly NBS987) standard yielded an average
198 ⁸⁷Sr/⁸⁶Sr of 0.710215±0.000012 (2SD). The certified value of NBS987 is 0.71034 ±0.00026.
199 Individual analytical errors did not exceed ±0.000011 ⁸⁷Sr/⁸⁶Sr. Total blanks for Sr were
200 found to be negligible (<0.1%) compared to the Sr amounts from the samples.

201

202 **3. Results**

203 *3.1 Chemical composition of Yenisey and its tributaries over the hydrological year*

204 The chemical composition of major elements in all river water samples can be found
205 in Table 2. Overall the maximum concentrations of Ca and Mg are lowest in May sampling
206 (Spring period). During this sampling period, the maximum Ca concentration measured was
207 587 μM L⁻¹ in Kem, a river whose bed rock lithology is dominated by sedimentary silicates
208 (Table 1). The maximum measured Mg concentrations in samples collected during May 2015,
209 was 189 μM L⁻¹ in Angara, a river whose bedrock coverage includes granites and sedimentary
210 silicates (Table 1). The concentrations of Ca and Mg over August (summer) and March
211 (winter) campaigns are in the same order of magnitude. In detail the maximum concentration
212 of Ca over summer and winter periods are 1382 (Kem) and 1500 (Sovinskaya) μM L⁻¹,
213 respectively. Similarly, the maximum concentrations of Mg over summer and winter periods
214 are 492 and 655 μM L⁻¹, respectively, and are observed in P. Tunguska a river draining
215 through basalts, tuffs and carbonates. The contribution of major elements in the riverine water
216 from silicate and/or carbonate sources (e.g., Gaillardet et al., 1999, 2003) was assessed using
217 Mg vs. Ca concentrations plots of riverine waters normalized against the sum of Na and K.
218 The obtained results exhibit a linear trend for all the three seasons (Fig. 2), in agreement with

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

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

230

231 *3.2 Strontium isotope composition of Yenisey and its tributaries over the hydrological year*

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

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

248

249 *3.3 Magnesium isotope composition of Yenisey and its tributaries over the hydrological year*

250 The overall variation of $\delta^{26}\text{Mg}$ values measured in this study spans a 0.8‰ range and
251 falls within the range of $\delta^{26}\text{Mg}$ values reported earlier for Yenisey tributaries in a post-flood
252 period (June 2012; Mavromatis et al., 2016). The riverine water samples collected from the
253 main channel of the Yenisey exhibit an increase in $\delta^{26}\text{Mg}$ northwards. However samples
254 collected in the mouth of the river exhibit variations that do not exceed 0.2‰ over the
255 hydrological seasons. In addition, the samples collected at ~66.5N during May and August of
256 2015, exhibit similar values to those reported recently by Hindshaw et al. (2019) for the
257 Igarka station that were also sampled in 2015 (see Fig. 4). Similarly, most tributaries did not
258 exhibit any sizable variation of $\delta^{26}\text{Mg}$ between seasons. Generally, there were three groups of
259 tributaries depending on their value $\delta^{26}\text{Mg}_{\text{spring/summer}} - \delta^{26}\text{Mg}_{\text{winter}}$: i) $< 0.05\text{‰}$ (Nizhnaya
260 Tunguska, Podkamennaya Tunguska, Vorogovka, Kas); ii) 0.1 to 0.18‰ (Bolshoi Pit, Tis,
261 Dubches, Garevka) and iii) 0.27 ‰ (Sym). We did not evidence any straightforward link
262 between the value of this difference and the lithology, climate, size, or vegetative coverage of
263 the river watershed. We note however that for all the tributaries plotted in Fig. 4, the Mg
264 isotope composition is lower at the end of spring flood (2012) compared to the peak of spring
265 flood (2015). The magnitude of this difference was not linked to lithology, size of the river,
266 and permafrost coverage.

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

270 earlier for the same river 600 km upstream its confluence with Yenisey (Mavromatis et al.,
271 2014b). The Mg isotope composition of the water samples collected in the spring campaign of
272 2015 (May) of this study are systematically enriched in ^{26}Mg compared to samples at the end
273 of the post-flood period in 2012 (Mavromatis et al., 2016). Their difference range between
274 $<0.1\text{‰}$ for Turukhan, to more than 0.5‰ for P. Tunguska (see Fig. 4). Note here that
275 Turukhan drains through wetlands and peatlands of terrigenous terrain whereas P. Tunguska
276 drains through a mixture of basalts, carbonates and terrigenous material. We attribute the
277 observed differences to the different timing of sampling, which was at the peak of the spring
278 flood in 2015 in this study (late May), whereas in 2012 it was the end of the spring flood (late
279 June). Indeed, there are significant isotopic variations over the hydrological year, specially
280 between winter, early and late spring that have been demonstrated in two rivers of Central
281 Siberia plateau (see Mavromatis et al., 2014b)

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

295 in spring, $\delta^{26}\text{Mg}$ 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, $\delta^{26}\text{Mg}$ 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

320 export flux of cations to the river. The dissolved products of chemical weathering of thawed
321 soils and leaching of plant litter are delivered to the river via so called suprapermafrost flow, a
322 water flux travelling at the base of active layer, over the frozen horizons. The $^{87}\text{Sr}/^{86}\text{Sr}$
323 composition of water samples collected from the same tributaries during June of 2012
324 suggests a similar source of Sr in the riverine waters regardless of the season (Fig. 3), and this
325 composition is not affected by secondary mineral precipitation reactions (Mavromatis et al.,
326 2016). For example, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of N. Tunguska river exhibit variations of 0.0002
327 among seasons and reflect the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the draining rock, the Patom paleobasin
328 dolostones (i.e. 0.7080-0.7085; Pokrovsky et al., 2011). We note here however that
329 differences in the contributions of each source, evidenced from Sr isotope variations, do not
330 necessarily result in variations in elemental ratio composition of riverine waters. Indeed, the
331 linear trend presented in Fig. 2 suggests that the origin of Mg and Ca varies among three
332 seasons. This elemental ratio reflects mixing of two or more sources such as Precambrian
333 dolomite, basalts, granites and larch litter. Note that some impact of atmospheric dust on
334 seasonal variation in radiogenic Sr cannot be ruled out given that particulate deposition of Sr
335 is comparable with its dissolved form in atmospheric snow of central Siberia (Shevchenko et
336 al., 2017). At the same time, a single slope of the dependences shown in Fig. 2 suggests
337 similar Mg/Ca ratio in the different solute pools as it has been highlighted earlier for
338 bedrocks, soil and plant litter of Central Siberian catchments (Pokrovsky et al., 2005).

339 Further, the dissolution of riverine suspended matter (RSM) within the main channel
340 can represent sizeable source of dissolved elements to the riverine waters, thus providing
341 important source of solutes to the aqueous phase. The increase in active layer thickness over
342 the frost-free season leads to progressive decreasing of the depth of suprapermafrost flow,
343 which traverses organic horizons in spring and mineral soil horizons towards the end of
344 summer-autumn. The contribution of riverine suspended matter as element source in the fluid
345 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 $\delta^{26}\text{Mg}$
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 $\delta^{26}\text{Mg}$ values of
373 riverine samples collected during open water period (May to October) and exhibit a good
374 correlation with the riverine suspended material ($R_{\text{Pearson}} = 0.44$ 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 $\delta^{26}\text{Mg}$ close to zero ($-0.2 \pm 0.2\text{‰}$, 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 Arctic 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 $\delta^{26}\text{Mg}$ values were $-1.36 \pm 0.04 \text{‰}$, $-1.13 \pm 0.02 \text{‰}$, $-1.13 \pm 0.01 \text{‰}$ for
396 winter (March), spring (May) and summer (August) campaigns, respectively (Fig. 4). These

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

410 Altogether, the Yenisey isotopic measurements of this and our previous study
411 (Mavromatis et al., 2016), together with those reported by Tipper et al. (2006) for the Lena
412 river suggest that Siberian rivers are characterized by an isotopic composition lower
413 compared to that of seawater or the Arctic Ocean (i.e -0.82‰ ; Teng et al., 2017). It can
414 reasonably be suggested that the parameters controlling the low isotopic composition of
415 Yenisey and likely Lena is the weathering of the highly reactive Precambrian dolomites,
416 which are abundant in the southern Siberian Platform and are characterized by Mg isotope
417 compositions as low as -2.5‰ (Pokrovsky et al., 2011). Indeed, hydrochemical analyses of
418 present day alkalinity (DIC) features in the Yenisey River demonstrate similar contributions
419 of carbonate and silicate weathering (53 and 47%, respectively, Tank et al., 2012). As such,
420 the Mg isotopic signal of the Yenisey River may be explained by the linear mixture of
421 carbonate that span in the range $-2.0\text{‰} \leq \delta^{26}\text{Mg}_{\text{carbonate}} \leq -2.5\text{‰}$ and silicate ($0.0\text{‰} \leq$
422 $\delta^{26}\text{Mg}_{\text{silicate}} \leq -0.2\text{‰}$) end members providing an average of ca. $-1.2 \pm 0.1\text{‰}$.

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

$$430 \delta^{26}\text{Mg}_{\text{annual}} = \delta^{26}\text{Mg}_{\text{spring}} \times 0.29 + \delta^{26}\text{Mg}_{\text{summer}} \times 0.265 + \delta^{26}\text{Mg}_{\text{winter}} \times 0.445 \quad (1)$$

431 where the subscripts “spring” (i.e. May to June), “summer” (i.e. July to September) and
432 “winter” (i.e. October to April) denote the isotopic composition of Yenisey River water
433 during the corresponding hydrological period, whereas the fractions of the annual fluxes for
434 Mg have been calculated after Holmes et al. (2012) similar to Mavromatis et al. (2016). For
435 the spring isotopic composition we use here the average of the measured Mg isotope
436 composition of the post spring (June) and spring (May) sampling campaigns in years 2012
437 and 2015, respectively (i.e. $-1.21 \pm 0.08\text{‰}$). The resulting flux-averaged annual isotope
438 signatures of Mg from the Yenisey River to the Arctic Ocean is thereby estimated to be
439 $\delta^{26}\text{Mg}_{\text{annual}} = -1.25 \pm 0.15\text{‰}$. This value is within uncertainty similar to that estimated earlier
440 by Mavromatis et al. (2016) and Hindshaw et al. (2019) as well as with the mean global
441 runoff of -1.09‰ estimated earlier by Tipper et al. (2006), but about 0.4‰ lighter compared
442 to the $\delta^{26}\text{Mg}$ of seawater (i.e. -0.82‰ ; Teng et al., 2017).

443 Whether the 0.15‰ difference in $\delta^{26}\text{Mg}$ of global runoff and the Yenisey river is
444 significant cannot be unequivocally resolved. However, it is possible that Siberian permafrost-
445 bearing rivers such as Yenisey (this study) and Lena ($\delta^{26}\text{Mg} = -1.28 \pm 0.08 \text{‰}$; Tipper et al.,
446 2006) are indeed enriched in lighter Mg isotopes compared to the world rivers, even though
447 the discharge-weighted $\delta^{26}\text{Mg}$ for the world rivers is lacking. Because preferential removal of

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

454

455 **Conclusions**

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

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

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

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

489

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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 (%)	Discontinuous 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	Nizhnaya 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	Nizhnaya 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, SO₄, 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 ⁸⁷Sr/⁸⁶Sr analyses has been estimated as ±0.000011 based on replicate analyses of SRM987 reference material.

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)	Longitude (°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	$\delta^{25}\text{Mg}$ (‰)	2σ	$\delta^{26}\text{Mg}$ (‰)	2σ	$^{87}\text{Sr}/^{86}\text{Sr}$	Ca	K	Mg	Na	Sr	SO_4	Cl	DIC	RSM (mg/L)	Latitude (°N)	Longitude (°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	$\delta^{25}\text{Mg}$ (‰)	2 σ	$\delta^{26}\text{Mg}$ (‰)	2 σ	$^{87}\text{Sr}/^{86}\text{Sr}$	Ca	K	Mg	Na	Sr	SO ₄	Cl	DIC	RSM (mg/L)	Latitude (°N)	Longitude (°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												

706 *Denotes full procedural analyses of duplicate samples

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